

# 7 Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; Mn, Tc, Re

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## 1 Introduction

This survey of the chemistry of the early transition metals follows the pattern of previous years in starting with binary compounds and then proceeding through coordination chemistry, where the running order is determined by the number of metal atoms involved and then the denticity of the ligand, and ending with a consideration of aspects of organometallic chemistry.

A review of ligand additivity rules in metal carbonyl derivatives has been made.<sup>1</sup> Examples from vibrational spectroscopy, electrochemistry, and photoelectron spectroscopy are discussed. The early transition metals provide many of the best examples of agostic behaviour, where for instance the hydrogen of a  $-\text{C}-\text{H}$  bond is attracted so strongly towards the metal that the hydrogen may be considered as being bonded to both the carbon and the metal centre. A review of this area includes nearly 250 references.<sup>2</sup>

Early transition metals form the major examples in reviews on redox stability in  $\sigma$ -organyl complexes<sup>3</sup> and nitrosyl complexes.<sup>4</sup>

## 2 Titanium, Zirconium, and Hafnium

There have been reviews on metal-metal bonded dinuclear compounds<sup>5</sup> and complexes of oxo-compounds<sup>6</sup> with the elements of Groups 4 and 5. A short discussion has been published<sup>7</sup> on the essential features of two-carbon fragments bonded to a single Group 4 metal centre. The geometry of the ion  $\text{TiH}_6^{2-}$  has been discussed from a molecular orbital viewpoint.<sup>8</sup> A thoughtful paper<sup>9</sup> comparing phase transitions in  $\text{Ti}_3\text{O}_5$  with those in  $\text{V}_3\text{O}_5$  shows that minor bonding differences in the fundamentally similar structures are responsible for the observed change to different space groups.

The basic sulphate  $\text{Zr}(\text{OH})_2\text{SO}_4$  adopts<sup>10</sup> a structure with infinite chains of  $[\text{ZrO}_4(\text{OH})_2]_n$  joined by sulphate groups. The surface acidity in Group 4 layered

<sup>1</sup> B. E. Bursten and M. R. Green, *Prog. Inorg. Chem.*, 1988, **36**, 393.

<sup>2</sup> M. Brookhart, M. L. H. Green, and L.-L. Wong, *Prog. Inorg. Chem.*, 1988, **36**, 1.

<sup>3</sup> R. Taube, D. Steinborn, H. Dreys, P. N. Chuong, N. Stransky, and J. Langlotz, *Z. Chem.*, 1988, 381.

<sup>4</sup> G. B. Richter-Addo and P. Legzdins, *Chem. Rev.*, 1988, **88**, 991.

<sup>5</sup> L. Messerle, *Chem. Rev.*, 1988, **88**, 1229.

<sup>6</sup> S. O. Gepasimova and Yu. Ya. Xharitonov, *Koord. Khim.*, 1988, **14**, 1443.

<sup>7</sup> S. L. Buchwald and R. B. Nielsen, *Chem. Rev.*, 1988, **88**, 1047.

<sup>8</sup> A. D. Cameron, G. Fitzgerald, and M. C. Zerner, *Inorg. Chem.*, 1988, **27**, 3437.

<sup>9</sup> S. Asbrink, *Chem. Scr.*, 1988, **28A**, 61.

<sup>10</sup> M. El Brahimi, J. Durand, and L. Cot, *Eur. J. Solid State Inorg. Chem.*, 1988, **25**, 185.

pyrophosphates has been assessed by measuring the OH stretching frequency and the spectra of adsorbed molecules by f.t.-i.r. The trend of Brønsted surface acidity was found to follow the electronegativities,  $\text{Ge} > \text{Sn} > \text{Ti} > \text{Zr}$ , whilst the opposite trend was found for Lewis acidities.<sup>11</sup> Pillaring is a process whereby material such as  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$  or  $\text{Zr}_4(\text{OH})_8^{8+}$  is used to expand the interlayer spacing of materials that do not swell in water. Alkylamines have been incorporated by this process into both titanium and zirconium phosphates.<sup>12</sup>

Solid-state n.m.r. was used<sup>13</sup> to characterize interstitial hydrogen in the metallic cluster  $\text{Zr}_6\text{Cl}_{12}\text{H}$ . New phases have been characterized in  $\text{LiM}'\text{M}_5\text{F}_{22}$ ,<sup>14</sup> where  $\text{M} = \text{Zr}$  or  $\text{Hf}$  and  $\text{M}' = \text{K}$ ,  $\text{Rb}$ ,  $\text{Tl}$ , or  $\text{NH}_4$ , and in  $\text{Zr}_6\text{I}_{14}\text{M}'$ ,<sup>15</sup> where  $\text{M}' = \text{Si}$ ,  $\text{Ge}$ , or  $\text{P}$ . Reaction between  $\text{Zr}$ ,  $\text{ZrI}_4$ , and  $\text{MI}_2$  at  $800^\circ\text{C}$  in a tantalum tube gives rise<sup>16</sup> to products such as  $\text{Zr}_n\text{I}_n\text{M}$ , where  $n = 12$  or  $14$  and  $\text{M} = \text{Cr}$ ,  $\text{Mn}$ ,  $\text{Fe}$ , or  $\text{Co}$ .

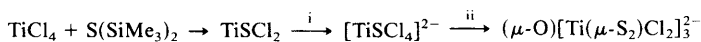
Calculations<sup>17</sup> using a non-local density method have shown that the bond strength for a wide range of ligands in  $\text{Cl}_3\text{M}-\text{L}$  increases in the order  $\text{Ti} < \text{Zr} < \text{Ta}$ . A considerable degree of polarity was found for  $\text{L} = \text{OH}$ ,  $\text{OMe}$ , and  $\text{NH}_2$ .

Electron diffraction methods indicate<sup>18</sup> that less than  $5^\circ$  deviation from ideal  $T_d$  symmetry occurs for  $\text{Zr}(\text{NMe}_2)_4$ .

The complex  $\text{TiF}_4(\text{MeCN})_2$  was identified<sup>19</sup> in acetonitrile solutions of  $\text{TiF}_4$  by the use of  $^{19}\text{F}$  n.m.r. spectroscopy. There were also indications of the presence of  $[\text{TiF}_4\text{MeCN}]_n$ . The single-crystal X-ray diffraction analysis of the complex  $[\text{Ti}_2(\text{MeCN})_4]\text{I}_3$  shows<sup>20</sup> square bipyramidal cations and linear symmetric anions.

Evidence for the transient existence of  $\text{L}_2\text{Zr}=\text{NR}$  compounds has been obtained from kinetic analysis and other trapping experiments.<sup>21,22</sup> Species with formulae  $\text{TiCl}_4\text{L}_2$ , where  $\text{L}$  is a Schiff base formed from amino-piperidines and aryl aldehydes, have been described.<sup>23</sup> Some interesting papers on alkoxides of titanium<sup>24</sup> and zirconium<sup>25,26</sup> have appeared.

The reactions shown in Scheme 1 lead to the formation of the  $\mu_3$ -oxo bridged species,<sup>27</sup> where the oxygen is believed to have been picked up from the gaseous atmosphere. A cluster-like structure with no metal-metal bonds is adopted.



Reagents: i,  $\text{Cl}^-$ ; ii,  $\text{CCl}_4$

Scheme 1

<sup>11</sup> G. Ramis, G. Busca, V. Lorenzelli, A. LaGinestra, P. Galli, and M. A. Massucci, *J. Chem. Soc., Dalton Trans.*, 1988, 881.

<sup>12</sup> A. Clearfield and B. D. Roberts, *Inorg. Chem.*, 1988, **27**, 3237.

<sup>13</sup> P. J. Chu, R. P. Ziebarth, J. D. Corbett, and B. C. Gerstein, *J. Am. Chem. Soc.*, 1988, **110**, 5324.

<sup>14</sup> D. Avignant, E. Caignol, J. C. Cousseins, and I. Mansouri, *Eur. J. Solid State Inorg. Chem.*, 1988, **25**, 65.

<sup>15</sup> G. Rosenthal and J. D. Corbett, *Inorg. Chem.*, 1988, **27**, 53.

<sup>16</sup> T. Hughbanks, G. Rosenthal, and J. D. Corbett, *J. Am. Chem. Soc.*, 1988, **110**, 1511.

<sup>17</sup> T. Ziegler, V. Tschinke, L. Versluis, E. J. Baerends, and W. Ravenek, *Polyhedron*, 1988, **7**, 1625.

<sup>18</sup> K. Hagen, C. J. Holwill, D. A. Rice, and J. D. Runnacles, *Inorg. Chem.*, 1988, **27**, 2032.

<sup>19</sup> J. Pauli, W. Storek, and L. Riesel, *Z. Chem.*, 1988, 226.

<sup>20</sup> S. I. Troyanov and G. N. Mao, *Zh. Neorg. Khim.*, 1988, **33**, 889.

<sup>21</sup> P. J. Walsh, F. J. Hollander, and R. G. Bergman, *J. Am. Chem. Soc.*, 1988, **110**, 8729.

<sup>22</sup> C. C. Cummins, S. M. Baxter, and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1988, **110**, 8731.

<sup>23</sup> A. Rodriguez, A. Macias, R. Bastida, C. Parrado, and A. Sousa, *An. Quim.*, 1988, **84**, 57.

<sup>24</sup> L. D. Durfee, P. E. Fanwick, and I. P. Rothwell, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1181.

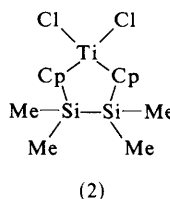
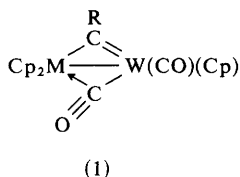
<sup>25</sup> (a) T. G. Hughes, C. Meredith, and H. Sutcliffe, *Inorg. Chim. Acta*, 1988, **143**, 209; (b) M. A. Atherton and H. Sutcliffe, *Inorg. Chim. Acta*, 1988, **143**, 213.

<sup>26</sup> R. K. Dubey, A. Singh, and R. C. Mehrotra, *Inorg. Chim. Acta*, 1988, **143**, 169.

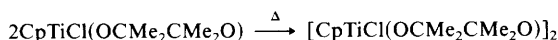
<sup>27</sup> U. Müller and V. Krug, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 293.

Structures of a number of zirconium phosphine complexes have been established.<sup>28</sup> These were formulated  $Zr_2Cl_6(phos)_4$ , where phos represents  $PR_3$  or  $\frac{1}{2}$ (diphos), and were shown to be edge-sharing bioctahedra with *cis*-phosphines in the same plane as the bridging chlorides.

The triphosphine ligand  $MeC(CH_2PMe_2)_3$  forms complexes  $M(CO)_4(triphos)$  ( $M = Ti, Zr$ , or  $Hf$ ) that adopt a 3:4 piano-stool configuration.<sup>29</sup> A sideways-on bonded carbonyl (1) is formed when  $MCl_2(Cp)_2$ , where  $M = Ti$  or  $Zr$ , is reacted<sup>30</sup> with  $W(=CR)(CO)_2(Cp)$ .



The thermochemistry of titanium dicyclopentadienyls has been reviewed.<sup>31</sup> A 'one-pot' synthesis of compound (2) has been described.<sup>32</sup> The reaction of  $Ph_2SnCl_2$  with  $Cp_2TiCl_2$  produces<sup>33</sup>  $Cp_2Ti(SnPh_3)Cl$ , where the titanium has been shown to take up a near tetrahedral configuration with a Ti—Sn distance of 2.84 Å that is longer than the sum of the covalent radii. Other papers concerning titanium cyclopentadienyl compounds discuss Ti—S bond enthalpies,<sup>34</sup> the use of  $^{77}Se$  n.m.r. spectroscopy in SeR adduct formation,<sup>35</sup> the structure of sulphur and selenium bridged species,<sup>36</sup> and an ascorbate complex.<sup>37</sup>



Scheme 2

The monomer and dimer shown in Scheme 2 have identical n.m.r. shifts in solution,<sup>38</sup> but the dimensions (such as the Ti—O—Cl angle and the Ti—O and Ti—Cl distances) are quite distinct in the solid state. The dimer has a near linear 10-membered ring. It is likely that the driving force for the dimerization results from non-bonded repulsions between the Cp rings and *syn* methyl groups.

<sup>28</sup> F. A. Cotton, M. P. Diebold, and P. A. Kibala, *Inorg. Chem.*, 1988, **27**, 799.

<sup>29</sup> D. W. Blackburn, K. M. Chi, S. R. Frerichs, M. L. Tinkham, and J. E. Ellis, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 437.

<sup>30</sup> A. F. Hill, H. D. Hönl, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 3031.

<sup>31</sup> A. R. Dias and J. A. Martinho Simoes, *Polyhedron*, 1988, **7**, 1531.

<sup>32</sup> Y. Wang, S.-S. Xu, X.-Z. Zhou, R.-J. Wang, X.-K. Yao, *Acta Chim., Sinica*, 1988, **46**, 674.

<sup>33</sup> W. Zheng and D. W. Stephan, *Inorg. Chem.*, 1988, **27**, 2386.

<sup>34</sup> M. J. Calhorda, M. A. A. F. de C. T. Carrondo, A. R. Dias, C. F. Frazão, M. B. Hursthouse, J. A. Martinho Simoes, and C. Teixeira, *Inorg. Chem.*, 1988, **27**, 2513.

<sup>35</sup> T. Klopötke, H. Köpf, and P. Gowik, *J. Chem., Soc., Dalton Trans.*, 1988, 1529.

<sup>36</sup> P. G. Maué and D. Fenske, *Z. Naturforsch., Teil B*, 1988, **43**, 1213.

<sup>37</sup> W. Jabs, W. Gaube, and R. Lukowski, *Z. Chem.*, 1988, 412.

<sup>38</sup> J. C. Huffman, K. C. Moloy, and K. G. Caulton, *Inorg. Chem.*, 1988, **27**, 2190.

The compound  $(\text{Cp}^*)_2\text{Zr}(\text{Fc})\text{Cl}$ , where  $\text{Cp}^*$  is per-methyl Cp and (Fc) represents the ferrocenyl group, is formed<sup>39</sup> by the reaction of  $(\text{Fc})\text{Li}$  with  $(\text{Cp}^*)_2\text{ZrCl}_2$ . It adopts a grossly distorted tetrahedral structure as a result of the steric demands of the  $\text{Cp}^*$  groups.

Proton ENDOR was used to show<sup>40</sup> that the geometry of the parent neutral molecule is preserved in the electrochemically-generated radical anion  $[(\eta^5\text{-Cp})\text{Ti}(\eta^7\text{-C}_7\text{H}_7)]^-$ .

### 3 Vanadium, Niobium, and Tantalum

Pathways involved in the thermal decomposition of ammonium metavanadate under atmospheric pressure, high pressure, and various hydrothermal conditions have been investigated.<sup>41</sup> The final product in the presence of air is always  $\text{V}_2\text{O}_5$ , but other species predominate under certain restricted conditions. Vibrational spectroscopy was used to assist in the identification of the complex ions  $\text{V}_2\text{F}_9^{3-}$ ,  $\text{V}_2\text{O}_2\text{F}_7^{3-}$ , and  $\text{V}_2\text{O}_4\text{F}_5^{3-}$ ,<sup>42</sup> and for  $\text{MV}_3\text{O}_{11}^{4-}$ ,<sup>43</sup> where M is one of the lanthanide elements. The synthesis and structure of  $\text{Na}_3\text{Ca}_2(\text{VO}_4)(\text{V}_2\text{O}_7)$  has been described.<sup>44</sup> Single crystals of  $\text{Mg}_4\text{Ta}_2\text{O}_9$  and  $\text{Mg}_2\text{NiTa}_2\text{O}_9$  have been grown from  $\text{CO}_2$ -laser heated melts and their structures shown to be related to that of corund.<sup>45</sup>

The structure of the mixed-valence pyrophosphate  $\text{V}_2(\text{VO})(\text{P}_2\text{O}_7)_2$  indicates<sup>46</sup> the presence of linear vanadium trimers with two octahedral  $\text{V}^{3+}$  ions edge-joined to a central  $\text{V}^{4+}$  square pyramid. The formulation  $(\text{NbO})_2(\text{HPO}_4)_3 \cdot 6\text{H}_2\text{O}$  has been proposed<sup>47</sup> for the ion-exchange material  $\text{Nb}^{\text{V}}$  phosphate. An exchange capacity for potassium ions of  $4.6 \text{ meq g}^{-1}$  was found, compared to a theoretical value of  $4.88 \text{ meq g}^{-1}$ . Mixed phosphates between vanadium and niobium were shown<sup>48</sup> to be solid solutions with up to 21% (molar) vanadium.

The ion  $\text{VW}_5\text{O}_{19}^{3-}$  has been studied<sup>49</sup> by  $^{51}\text{V}$  n.m.r. spectroscopy. The free molybdovanadophosphoric acids  $\text{P}_2\text{Mo}_{18-n}\text{V}_n\text{O}_{62}^{-(6+n)}$  for  $n = 1$  to 3 and  $\text{P}_2\text{Mo}_{18-n}\text{V}_n\text{O}_{62}\text{H}_2^{-(4+n)}$  for  $n = 4$  or 5, have been prepared and some thermal and solution properties investigated.<sup>50</sup>

It is claimed<sup>51</sup> that ENDOR procedures to investigate the solvation structures of vanadyl ions,  $\text{VO}^{2+}$ , in frozen water-methanol solutions have accuracies approaching that attainable for X-ray crystallography. The principal hyperfine coupling components of both  $^1\text{H}$  and  $^{13}\text{C}$  nuclei in solvent molecules bound to vanadyl ions were measured. These indicated that there are only slight deviations from axial symmetry.

<sup>39</sup> M. Wedler, H. W. Roesky, and F. T. Edelmann, *Z. Naturforsch., Teil B*, 1988, **43**, 1461.

<sup>40</sup> D. Gouri r and E. Samuel, *Inorg. Chem.*, 1988, **27**, 3018.

<sup>41</sup> K.-J. Range, R. Zintl, and A. M. Heyns, *Z. Naturforsch., Teil B*, 1988, **43**, 309.

<sup>42</sup> N. Bucholz, M. Leimk hler, L. Kiriazis, and R. Mattes, *Inorg. Chem.*, 1988, **27**, 2035.

<sup>43</sup> L. V. Kristallov, M. Ya. Khodes, L. A. Perelyaeva, and B. D. Zhuravlev, *Zh. Neorg. Khim.*, 1988, **33**, 1989.

<sup>44</sup> E. V. Murashova, Yu. A. Velikodny, and B. K. Trunov, *Zh. Neorg. Khim.*, 1988, **33**, 2818.

<sup>45</sup> G. Halle and Hk. M ller-Buschbaum, *Z. Anorg. Allgm. Chem.*, 1988, **562**, 87.

<sup>46</sup> J. W. Johnson, D. C. Johnston, H. E. King, Jr., T. R. Halbert, J. F. Brody, and D. P. Goshorn, *Inorg. Chem.*, 1988, **27**, 1646.

<sup>47</sup> M. Quershi, J. P. Gupta, H. Khan, and A. Ahmad, *Bull. Soc. Chim. Jpn.*, 1988, **61**, 2181.

<sup>48</sup> A. L. Garcia-Ponce, L. Moreno-Real, and A. Jimenez-Lopez, *Inorg. Chem.*, 1988, **27**, 3372.

<sup>49</sup> L. V. Derkach, A. M. Rios, and R. I. Maksimovskaya, *Zh. Neorg. Khim.*, 1988, **33**, 103.

<sup>50</sup> E.-B. Wang, L.-H. Gao, J. F. Liu, Z.-X. Liu, and D.-H. Yan, *Acta Chim. Sinica*, 1988, **46**, 757.

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Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; Mn, Tc, Re

Line-broadening of  $^{51}\text{V}$  n.m.r. signals in mixtures of  $\text{VO}_2^+$  and  $\text{VO}^{2+}$  in perchloric acid has been attributed<sup>52</sup> to an exchange reaction between  $\text{VO}_2^+$  and the mixed-valence complex  $\text{VO}_2^+ - \text{VO}^{2+}$ . A rate-law has been proposed. The kinetics of the outer-sphere electron-transfer-induced formation of *cis*- $\text{VO}_2^+$  from  $\text{VO}^{2+}$  have also been investigated.<sup>53</sup>

**Biologically Significant Complexes.**—A large part of the effort in the complex chemistry of the vanadium sub-group seems to be directed towards species which are either found in organisms or are of potential significance in developing an understanding of the biological role of vanadium. N.m.r. spectroscopy has particular importance as a non-destructive probe. The influence of factors such as the number of ligands, strain, and electronegativity on  $^{51}\text{V}$  chemical shifts in a range of vanadium(v) complexes has been noted,<sup>54</sup> and used<sup>55</sup> to measure formation constants of vanadate–glycoside complexes. Dipeptide complexes, formed at physiological pH conditions with  $\text{H}_2\text{VO}_4^-$ , employ not only the peptide function and the N-terminal amino group but also have likely involvement of side-chains.<sup>56</sup> Similar studies have pointed out potential sources of error in that vanadate has been shown to form complexes with both ‘tris’<sup>57</sup> and with various tri- and tetra-dentate ethanolamine derivatives<sup>58</sup> commonly used as buffers.

Controversy continues<sup>59</sup> over the assertion that vanadocytes in *Ascidia ceratodes* experience a pH of around 1.8. As well as the original evidence from e.s.r. spectroscopy, results from both X.A.S. and  $^1\text{H}$  n.m.r. are used to develop the argument. It is suggested that other investigators have used inappropriate methodologies and, for example, have failed to notice that incorrect settings in n.m.r. spectroscopy can lead to suppression of broad signals when working at high chemical shifts. Strong e.s.r. signals have been obtained from  $\text{VO}^{2+}$  in the branchial basket of *A. ahodori*.<sup>60</sup>

Formation constants of oxovanadium(IV) complexes in aqueous solution have been determined for acetate, glycolate, glycinate,<sup>61</sup>  $\beta$ -alaninate,<sup>62</sup> and malate, succinate, and mercaptosuccinate<sup>63</sup> ligands. Amongst the methods used were electronic absorbance spectroscopy, e.s.r. spectroscopy, and potentiometry.

Vanadium complexes with cysteine,<sup>64</sup> chiral imines of amino acids,<sup>65</sup> and guanine<sup>66</sup> have been synthesized.

**Other Complex Chemistry.**—The electrochemical behaviour in MeCN of  $\text{TaX}_5$  and  $\text{TaX}_6^-$ , where X is Cl or Br, has been studied by cyclic voltammetry and constant

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<sup>54</sup> D. Rehder, C. Weidemann, A. Duch, and W. Pribsch, *Inorg. Chem.*, 1988, **27**, 584.

<sup>55</sup> A. S. Tracey and M. J. Gresser, *Inorg. Chem.*, 1988, **27**, 2695.

<sup>56</sup> D. Rehder, *Inorg. Chem.*, 1988, **27**, 4312.

<sup>57</sup> A. S. Tracey and M. J. Gresser, *Inorg. Chem.*, 1988, **27**, 1269.

<sup>58</sup> D. C. Crans and P. K. Ahin, *Inorg. Chem.*, 1988, **27**, 1797.

<sup>59</sup> P. Frank, R. M. K. Carlson, and K. O. Hodgson, *Inorg. Chem.*, 1988, **27**, 118.

<sup>60</sup> H. Sakurai, J. Hirata, and H. Michibata, *Inorg. Chim. Acta*, 1988, **152**, 177.

<sup>61</sup> P. DiBernardo, G. Tomat, P. Zanonato, R. Portanova, and M. Tolazzi, *Inorg. Chim. Acta*, 1988, **145**, 285.

<sup>62</sup> J. Costa Pessoa, L. F. Vilas Boas, R. D. Gillard, and R. J. Lancashire, *Polyhedron*, 1988, **7**, 1245.

<sup>63</sup> G. Micera and J. Dessi, *J. Inorg. Biochem.*, 1988, **33**, 99.

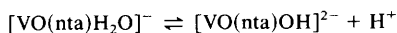
<sup>64</sup> M. D. Sifri and T. L. Riechel, *Inorg. Chim. Acta*, 1988, **142**, 229.

<sup>65</sup> L. Casella, M. Gulloti, A. Pintar, S. Colonna, and A. Manfredi, *Inorg. Chim. Acta*, 1988, **144**, 89.

<sup>66</sup> C. Floriani, M. Mazzanti, A. Chiesi-Villa, and C. Guastini, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 576.

potential electrolysis.<sup>67</sup> On a related theme, Hückel calculations have been performed<sup>68</sup> on all ten possible species  $\text{VCl}_x(\text{MeCN})_{6-x}^{3-x}$ . The occupancy of the *trans* site in  $\text{VCl}_3(\text{MeCN})_3$  was shown to be very important in terms of the bonding of a MeCN ligand. Treatment of  $\text{VCl}_2\text{py}_4$  with lithium formate was intended<sup>69</sup> to produce a V—V triple bond. However, the product was found to be the distorted octahedral species  $\text{V}(\text{form})_2\text{py}_2$  with axial pyridines.

Vanadium is in a distorted trigonal bipyramidal configuration<sup>70</sup> in  $\text{LVCl}_2$ , where L is the terdentate ligand  $-\text{N}(\text{CH}_2\text{CH}_2\text{NEt}_2)_2$ . The chlorines are in the equatorial position (Cl—V—Cl of  $123.1^\circ$ ) with the axial nitrogens making an angle of  $160.5^\circ$  at the vanadium. Treatment of  $\text{VBr}_3(\text{thf})_3$  with magnesium and the bulky chelating phosphine 1,2-bis-(di-isopropylphosphino)ethane gives<sup>71</sup> the coordinatively unsaturated vanadium(II) complex  $\text{VBr}_2(\text{diphos}) \cdot 1\frac{1}{2}\text{thf}$ . The corresponding chromium complex is a dimer with weak halide bridges, but the vanadium species was too insoluble for n.m.r. and crystals suitable for X-ray diffraction studies could not be obtained.



Scheme 3

The protolytic equilibrium shown in Scheme 3 has been followed<sup>72</sup> by e.s.r. spectroscopy. The intensity of the resonance lines shows considerable change with pH. Formation constants of vanadate-methanol complexes have been measured<sup>73</sup> by  $^{51}\text{V}$  n.m.r. spectroscopy, and the same technique has been used<sup>74</sup> to study alkyl vanadates. Characteristic shifts were obtained but it was not possible to determine from the equilibrium constants whether the hydroxyl group of the alcohol was primary, secondary, or tertiary. The infrared and mass spectra of  $\text{VO}(\text{OR})_3$ , where  $\text{R} = \text{Me}$ ,  $\text{Et}$ , or  $\text{Pr}^i$ , have been measured<sup>75</sup>. Complexes of niobium and tantalum with 2,6-diphenylphenoxide ( $-\text{OAr}$ ) have been studied.<sup>76,77</sup> For example, the distorted trigonal bipyramidal species  $\text{M}(\text{OAr})_3(\text{NMe}_2)(\text{HNMe}_2)$  was produced by reacting together  $\text{HOAr}$  and  $\text{M}(\text{NMe}_2)_5$  in toluene solution.

Treatment of  $\text{M}(\text{OTeF}_5)_5$ , where M is Nb or Ta, with  $(\text{OTeF}_5)^-$  gives rise to the complex ion  $[\text{M}(\text{OTeF}_5)_6]^-$ . This was isolated<sup>78</sup> as a number of different salts and studied by vibrational spectroscopy in the solid state, and by cyclic voltammetry in acetonitrile solution. Reaction between vanadium trichloride, sulphur, and sodium ethanedithiolate in acetonitrile leads<sup>79</sup> to the formation of a much wider range of products than previously envisaged. The product depends on the vanadium/sulphur

<sup>67</sup> D. E. Lightner, Jr., J. R. Kirk, and V. Katovic, *J. Coord. Chem.*, 1988, **19**, 223.

<sup>68</sup> J. O'Brien, *Inorg. Chim. Acta*, 1988, **149**, 285.

<sup>69</sup> F. A. Cotton and R. Poli, *Inorg. Chim. Acta*, 1988, **141**, 91.

<sup>70</sup> A. R. Wills, P. G. Edwards, R. L. Short, and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, 1988, 115.

<sup>71</sup> A. R. Hermes and G. S. Girolami, *Inorg. Chem.*, 1988, **27**, 1775.

<sup>72</sup> R. Meier, G. Werner, J. Stach, R. Kirmse, and L. Dunsch, *Z. Chem.*, 1988, **370**.

<sup>73</sup> A. S. Tracey, M. J. Gresser, and B. Galeffi, *Inorg. Chem.*, 1988, **27**, 157.

<sup>74</sup> A. S. Tracey and M. J. Gresser, *Can. J. Chem.*, 1988, **66**, 2570.

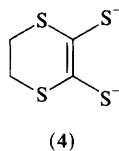
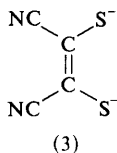
<sup>75</sup> E. P. Turevskaya, N. I. Kozlova, N. Ya. Turova, and B. G. Kessler, *Koord. Khim.*, 1986, **14**, 926.

<sup>76</sup> R. W. Chesnut, P. E. Fanwick, and I. P. Rothwell, *Inorg. Chem.*, 1988, **27**, 752.

<sup>77</sup> R. W. Chesnut, B. D. Steffrey, I. P. Rothwell, and J. C. Huffman, *Polyhedron*, 1988, **7**, 753.

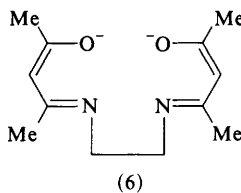
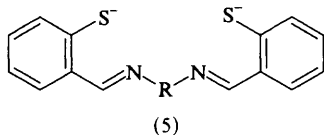
<sup>78</sup> K. Moock and K. Seppelt, *Z. Anorg. Allg. Chem.*, 1988, **561**, 132.

<sup>79</sup> J. K. Money, J. C. Huffman, and G. Christou, *Inorg. Chem.*, 1988, **27**, 507.



ratio. The dithiolate ligands L shown in (3) and L' in (4) have been used to produce  $[\text{VOL}_2]^{2-80}$  and  $[\text{VL}'_3]^{-81}$ . The formation of a N—O donor template ligand (L'') through the reaction of benzoylhydrazine with  $\text{VO}(\text{acac})_2$  to form  $\text{VL}''_2$  has been known for some time. An unusual feature of this reaction is the loss of vanadyl oxygen. A crystallographic study<sup>82</sup> shows that none of the donor oxygens is as close to the metal as was the oxo group.

Some vanadium Schiff base complexes have been examined.<sup>83,84</sup> A series of ligands (L), as shown in (5) where  $\text{R} = (\text{CH}_2)_{2 \text{ or } 3}$ , *o*-C<sub>6</sub>H<sub>4</sub>, or *o*-4,5-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>, have been used<sup>85</sup> to produce complexes formulated VOL. The object was to assess how electrochemical properties of a complex with a ligand donor set of S<sub>2</sub>N<sub>2</sub> differ from those with a donor set O<sub>2</sub>N<sub>2</sub>. The complexes proved to be harder to oxidize but easier to reduce.



The ligand (6) forms a compound  $\text{NbLCl}_2$  that has *trans* chloro groups.<sup>86</sup>

Reacting phthalodinitrile with  $\text{TaCl}_5$  produces<sup>87</sup> a phthalocyanine,  $\text{TaCl}_3(\text{pc})$ , which has the chloro atoms arranged as a trigonal cap to the tantalum which in turn is sited above a square base of nitrogens. Work on vanadium porphyrin species includes an investigation on the effect of substituent effects on redox properties,<sup>88</sup> and solvent effects on the vanadyl oxygen stretching frequency as measured by resonance Raman spectroscopy.<sup>89</sup>

**Cluster Species.**—The complex ion  $[\text{V}_2(\mu\text{-Br})_3\text{L}_6]^{-}$ , where L is thf or 3-Me(thf), contains octahedrally coordinated metal atoms with a long V—V distance of

<sup>80</sup> D. Colligon, F. E. Mabbs, J. Temperley, G. Christou, and J. C. Huffman, *J. Chem. Soc., Dalton Trans.*, 1988, 309.

<sup>81</sup> J. H. Welch, R. D. Bereman, and P. Singh, *Inorg. Chem.*, 1988, **27**, 2862.

<sup>82</sup> A. A. Diamantis, M. Manikas, M. A. Salam, M. R. Snow, and E. R. T. Tiekink, *Aust. J. Chem.*, 1988, **41**, 453.

<sup>83</sup> M. Rahaman, M. Athar, and N. Ahmad, *Synth. React. Inorg. Met.-Org. Chem.*, 1988, **18**, 179.

<sup>84</sup> X. Li, M. S. Lah, and V. L. Pecoraro, *Inorg. Chem.*, 1988, **27**, 4657.

<sup>85</sup> J. C. Dutton, G. D. Fallon, and K. S. Murray, *Inorg. Chem.*, 1988, **27**, 34.

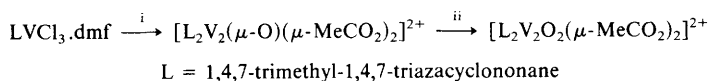
<sup>86</sup> C. Floriani, M. Mazzanti, S. Ciurli, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1988, 1361.

<sup>87</sup> F. Gingl and J. Strähle, *Z. Naturforsch. Teil B*, 1988, **43**, 445.

<sup>88</sup> K. M. Kadish, D. Sazou, C. Araullo, Y. M. Liu, A. Saoiabi, M. Ferhat, and R. Guillard, *Inorg. Chem.*, 1988, **27**, 2313.

<sup>89</sup> Y. O. Su, R. S. Czernuszewicz, L. A. Miller, and T. G. Spiro, *J. Am. Chem. Soc.*, 1988, **110**, 4150.

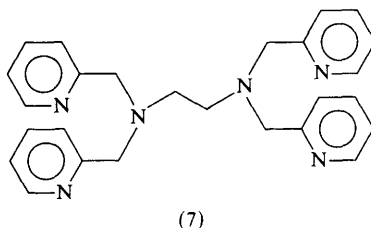
3.146 Å.<sup>90</sup> The initial hydrolysis in Scheme 4 gives<sup>91</sup> a green product in which the metal atoms are ferromagnetically spin-exchange coupled, whereas the final blue product has anti-ferromagnetic spin-exchange coupling.



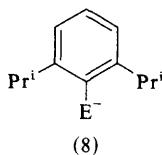
Reagents: i, anaerobic hydrolysis in aqueous sodium acetate; ii, air

#### Scheme 4

The ligand **L** shown in (7) affords  $\text{V}_2\text{Cl}_6\text{L}$  when treated<sup>92</sup> with  $\text{VCl}_3$  in acetonitrile, and on further reaction in water with oxygen followed by addition of sodium iodide, the salt  $[\{\text{VO}(\mu\text{-OH})\}_2\text{L}]\text{I}_2$  was isolated. The ligand wraps itself around the two metals making a distorted *fac* approach at each centre.



The chloro atoms in  $[\text{TaCl}_3\text{thf}_2]_2(\mu\text{-N}_2)$  can be replaced by the ligand shown in (8) ( $\text{E} = \text{O}$  or  $\text{S}$ ), to give  $[\text{TaL}_3\text{thf}]_2(\mu\text{-N}_2)$ .<sup>93</sup> Each has trigonal bipyramidal metals linked by the dinitrogen, but in the oxygen-containing compound the nitrogen is in an equatorial position, whereas when  $\text{E} = \text{S}$  it is axial.



Treatment of  $\text{NbCl}_5$  with magnesium in methanol gives  $\text{Nb}_2(\text{OMe})_9^-$ ,<sup>94</sup> which has a confacial bioctahedral configuration with near  $D_{3h}$  symmetry and a short Nb—Nb distance of 2.640 Å. Trinuclear and tetranuclear niobium clusters have also been investigated.<sup>95–97</sup> A species formulated as  $\{\text{NbOCl}_3, \text{OC}_3\text{Cl}_2\}_4$  contains a cyclopropene unit, with an eight membered Nb—O ring of alternate long and short Nb—O bonds as the central core.

<sup>90</sup> J. A. M. Canich, F. A. Cotton, W. J. Roth, and S. A. Duraj, *Polyhedron*, 1988, 7, 737.

<sup>91</sup> M. Köppen, G. Fresen, K. Wiegardt, R. M. Llugar, B. Nuber, and J. Weiss, *Inorg. Chem.*, 1988, 27, 721.

<sup>92</sup> A. Neves, K. Wiegardt, B. Nuber, and J. Weiss, *Inorg. Chim. Acta*, 1988, 150, 183.

<sup>93</sup> R. R. Schrock, M. Wesolek, A. H. Liu, K. C. Wallace, and J. C. Dewan, *Inorg. Chem.*, 1988, 27, 2050.

<sup>94</sup> F. A. Cotton, M. P. Diebold, and W. J. Roth, *Inorg. Chem.*, 1988, 27, 3596.

<sup>95</sup> F. A. Cotton, M. P. Diebold, X. Feng, and W. J. Roth, *Inorg. Chem.*, 1988, 27, 3413.

<sup>96</sup> F. A. Cotton and M. Shang, *J. Am. Chem. Soc.*, 1988, 110, 7719.

<sup>97</sup> U. Patt-Siebel, H. Thullen, U. Müller, and K. Dehnicke, *Z. Naturforsch., Teil B*, 1988, 43, 795.

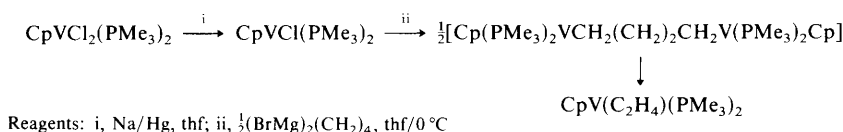


**Organometallics.**—A review with over 300 references has been made of the carbonyls of vanadium, niobium, and tantalum.<sup>98</sup>

Tetrahydrothiophene (tht) displaces a carbonyl from  $\text{CpV}(\text{CO})_4$  in a photochemical process to form  $\text{CpV}(\text{CO})_3(\text{tht})$ , which has been shown<sup>99</sup> to adopt a square pyramidal shape with an apical Cp.

The adsorption of vanadocene on to silica of differing levels of surface hydroxyls has been studied.<sup>100</sup> Exposure of the adsorbed species to carbon monoxide leads to the formation of  $\text{V}(\text{Cp})_2\text{CO}$ . Under the conditions used  $\text{CpV}(\text{CO})_4$  did not bind to the support.

The  $^{93}\text{Nb}$  n.m.r. spectrum of  $\text{Nb}(\text{CO})_6^-$  shows<sup>101</sup> temperature-dependence and is also affected by the isotopic composition of the carbonyls. A force field analysis was performed on data acquired by Raman and infrared spectroscopy.



Scheme 5

The reaction in Scheme 5 is notable for the formation of an ethene complex from the postulated 1,4-dimetallabutane intermediate species. The product has a simple piano stool configuration with eclipsed phosphines.<sup>102</sup>

The compound  $\text{Nb}(\eta\text{-C}_6\text{H}_5\text{Me})_2$  undergoes both one-electron reversible reduction and oxidation steps. Chemical oxidation in the presence of a phosphine<sup>103</sup> gave  $[\text{Nb}(\eta\text{-C}_6\text{H}_5\text{Me})_2\text{PR}_3]^+$ , which adopts a distorted trigonal structure.

Treatment of  $\text{NbCpCl}_4$  with potassium 2,4-dimethylpentadienyl gives an intermediate which by a process of intramolecular coupling gives  $\text{NbCp}(\eta^8\text{-C}_{14}\text{H}_{22})$ .<sup>104</sup> One of the diene units is *cis* and the other *trans*. Some niobium clusters compounds have been formed by the hydrolysis of various substituted cyclopentadienyl species.<sup>105–106</sup>

#### 4 Chromium, Molybdenum, and Tungsten

A review has been made<sup>107</sup> of mixed molybdenum–tungsten clusters with 2-, 3-, 4-, and 5-valent metals.

A paper<sup>108</sup> on chromium hydroxide stresses the importance of ageing when discussing speciation of aqueous solutions. It is also necessary to use methods that

<sup>98</sup> S. C. Srivastava and A. K. Shrima, *Polyhedron*, 1988, 7, 1639.

<sup>99</sup> S. Gambarotta, A. Chiesi-Villa, and C. Guastini, *Inorg. Chem.*, 1988, 27, 99.

<sup>100</sup> B. Jonson, B. Rebenstorf, and R. Larsson, *Acta Chem. Scand.*, 1988, A42, 156.

<sup>101</sup> C. J. Jameson, D. Rehder, and M. Hoch, *Inorg. Chem.*, 1988, 27, 3490.

<sup>102</sup> B. Hessen, A. Meetsma, and J. H. Teuben, *J. Am. Chem. Soc.*, 1988, 110, 4860.

<sup>103</sup> J. A. Bandy, K. Prout, F. G. N. Cloke, H. C. deLemos, and J. M. Wallis, *J. Chem. Soc., Dalton Trans.*, 1988, 1475.

<sup>104</sup> B. Melendez, A. M. Arif, A. L. Rheingold, and R. D. Ernst, *J. Am. Chem. Soc.*, 1988, 110, 8703.

<sup>105</sup> A. M. Andreu, F. A. Jalon, and A. Otero, *J. Organomet. Chem.*, 1988, 353, 185.

<sup>106</sup> M. D. Curtis and J. Real, *Inorg. Chem.*, 1988, 27, 3176.

<sup>107</sup> B. Wang, Y. Sasaki, A. Nagasawa, and T. Ito, *J. Coord. Chem.*, 1988, 18, 45.

<sup>108</sup> L. Spiccia, *Inorg. Chem.*, 1988, 27, 432.

are responsive to nuclearity rather than charge. An electron diffraction study<sup>109</sup> of  $\text{CrF}_4$  is consistent with  $T_d$  symmetry with  $\text{Cr}-\text{F}$  of 1.706 Å.

The oft-quoted analogy between chemistry and cookery became a step closer with the reported use of a commercial microwave cooker to synthesize  $\text{BaWO}_4$  from  $\text{BaO}$  and  $\text{WO}_3$ .<sup>110</sup> The method has the same short reaction time (30 min) as common in the more usual applications of such ovens, but is only applicable to the few oxides that absorb energy in the 2450 MHz region. In contrast,<sup>111</sup> the synthesis of  $\text{LiMoO}_2$  took 21 days 900 °C from  $\text{Mo/Li}_2\text{MoO}_4$ .

The minor product  $\text{Mo}_2\text{Cl}_8\text{O}$ , from the reaction of molybdic acid and thionyl chloride, has been shown<sup>112</sup> by single-crystal X-ray diffraction to be the singly chlorine-bridged cation  $\text{Mo}_2\text{Cl}_9^+$  linked into chains by weak bonding to the triply chlorine-bridged anion  $\text{Mo}_2\text{Cl}_7\text{O}_2^-$ .

The preparation of a series of salts of the ion  $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$  has been described.<sup>113</sup>

Oxymolybdates involving lanthanide metals have been reported,<sup>114,115</sup> and diazenido and hydrazido adducts of molybdates studied by X-ray diffraction and <sup>95</sup>Mo n.m.r. spectroscopy.<sup>116,117</sup> The ion  $\text{Mo}_7\text{O}_{24}^{6-}$  has been shown<sup>118</sup> to be a potent antitumour agent against certain strains of sarcoma and adenocarcinoma, and  $\text{W}_{10}\text{O}_{32}^{4-}$  promotes<sup>119</sup> the photochemical dimerization of olefins.

The HPLC retention behaviour of a series of heteropoly anions on ODS-silica<sup>120</sup> and the diamagnetic susceptibility of a series of anions and their two-electron reduction products<sup>121</sup> have been measured. The reduced product was more diamagnetic than the parent ion in each case examined. Multinuclear n.m.r. spectroscopy has been used to show that a large heteropoly ion is frequently constructed from smaller fragments.<sup>122,123</sup> The species  $\text{P}_4\text{W}_{14}\text{O}_{58}^{12-}$  has two  $\text{PW}_2\text{O}_9$  units, and  $\text{P}_2\text{W}_{19}\text{O}_{69}(\text{OH})_2^{14-}$  from two  $\alpha\text{-PW}_9\text{O}_{34}^{9-}$  ions linked through a  $\text{WO}(\text{OH})_2^{4+}$  unit.

A detailed analysis of the Mo—Mo bonding in  $\text{Mo}_{18}\text{O}_{26}^{7-}$  has been reported.<sup>124</sup>

**Coordination Chemistry.**—Infrared spectra and <sup>15</sup>N n.m.r. positions of a series of tungsten nitrido complexes have been measured.<sup>125</sup> A range of products have been noted from the treatment of  $\text{M}(\text{N}_2)_2(\text{L}-\text{L})_2$ , where  $\text{M} = \text{Mo}$  or  $\text{W}$  and  $\text{L}-\text{L}$  represents a range of diphosphine ligands, with  $\alpha,\omega$ -dibromoalkanes<sup>126</sup> or hydrohalic

<sup>109</sup> L. Hedberg, K. Hedberg, G. L. Gard, and J. O. Udeaja, *Acta Chem. Scand.*, 1988, **A42**, 318.

<sup>110</sup> D. R. Baghurst and D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1988, 829.

<sup>111</sup> L. E. Aleandri and R. E. McCarley, *Inorg. Chem.*, 1988, **27**, 1041.

<sup>112</sup> A. J. Edwards and D. R. Slim, *J. Chem. Soc., Dalton Trans.*, 1988, 485.

<sup>113</sup> A. M. Mitukov, B. B. Elentsov, N. A. Subbotina, P. E. Kazin, A. I. Zhironov, and M. G. Felin, *Zh. Neorg. Khim.*, 1988, **33**, 623.

<sup>114</sup> B. A. Efremov, N. N. Davidova, L. E. Goxhman, A. A. Ebdokimov, and V. K. Trunov, *Zh. Neorg. Khim.*, 1988, **33**, 3005.

<sup>115</sup> S. J. Hibble, A. K. Cheetham, A. R. L. Bogle, H. R. Wakerley, and D. E. Cox, *J. Am. Chem. Soc.*, 1988, **110**, 3295.

<sup>116</sup> S. Bank, S. Liu, S. N. Shaikh, X. Sun, J. Zubietta, and P. D. Ellis, *Inorg. Chem.*, 1988, **27**, 3535.

<sup>117</sup> S. Liu and J. Zubietta, *Polyhedron*, 1988, **7**, 401.

<sup>118</sup> T. Yamase, H. Fujita, and K. Fukushima, *Inorg. Chim. Acta*, 1988, **151**, 15.

<sup>119</sup> T. Yamase and T. Usami, *J. Chem. Soc., Dalton Trans.*, 1988, 183.

<sup>120</sup> Q.-D. Zeng, M.-H. Zhu, and Y.-D. Xu, *Acta Chim. Sinica*, 1988, **46**, 537.

<sup>121</sup> M. Kozik, N. Casan-Pastor, C. F. Hammer, and L. C. W. Baker, *J. Am. Chem. Soc.*, 1988, **110**, 7697.

<sup>122</sup> R. Thouvenot, A. Tézé, R. Contant, and G. Hervé, *Inorg. Chem.*, 1988, **27**, 524.

<sup>123</sup> C. M. Tourné and G. F. Tourné, *J. Chem. Soc., Dalton Trans.*, 1988, 2411.

<sup>124</sup> R. A. Wheeler and R. Hoffman, *J. Am. Chem. Soc.*, 1988, **110**, 7315.

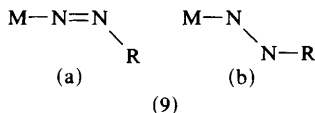
<sup>125</sup> T. Godemeyer, K. Dehnicke, and E. Fluck, *Z. Anorg. Allg. Chem.*, 1988, **565**, 41.

<sup>126</sup> M. A. Bakar, D. L. Hughes, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1988, 2525.

Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; Mn, Tc, Re

acids.<sup>127</sup> A series of compounds have been produced<sup>128</sup> with the formulation  $\text{MoCl}_3(\text{trident})$ , where trident is  $(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{X}$  with  $\text{X} = \text{S}, \text{O}, \text{NH}, \text{NMe}$ , or  $\text{PPh}$ . These were then treated with sodium amalgam under dinitrogen in the presence of a phosphine ligand (L). The products were *trans*- $\text{Mo}(\text{N}_2)_2(\text{trident})\text{L}$ , except for  $\text{X} = \text{PPh}$  where the product was  $\text{Mo}(\text{N}_2)(\text{trident})(\text{L})_2$ .<sup>129</sup> The ability to release ammonia or nitrogen on acid hydrolysis is a marked function of L.

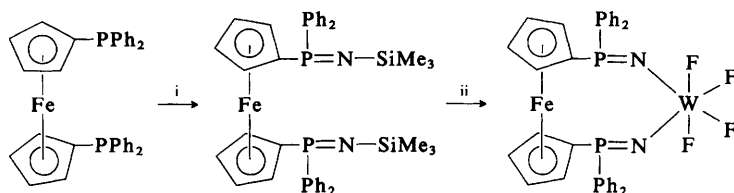
A series of molybdenum, tungsten, and rhenium diazenido complexes make up most of the examples in a paper<sup>130</sup> that correlates the deshielding effect in  $^{15}\text{N}$  n.m.r. with structural points in the ligand. In particular, a distinction is drawn between the two forms of  $\text{M}-\text{NN}-\text{R}$  (9), since the chemical shift from the compound in (9a) is particularly sensitive to the nature of the coordination site. The salt  $(\text{Bu}^n_4\text{N})_3[\text{Mo}(\text{CN})_8]$  has been studied over the range 77–383 K by infrared spectroscopy, measurement of the lattice parameters, and the proton second moment by broad-line n.m.r. Two first-order phase transitions were found.<sup>131</sup> Heating the related salt  $[\text{bipyridylH}]_3[\text{W}(\text{CN})_8]$  followed by extraction with  $\text{PPh}_4\text{Cl}-\text{MeOH}$  gave the complex ion  $[(\text{W}(\text{bipy})(\text{CN})_6)]^{2-}$ , which has intense metal-ligand charge transfer bands.<sup>132</sup>



Addition of  $\text{LiNMe}_2$  to  $\text{Mo}(\text{NMe}_2)_4$  in THF solution, set up the equilibrium shown in Scheme 6. The right-hand species was isolated<sup>133</sup> as a bis-thf solvate and shown to have a near octahedral molybdenum atom,  $(\text{MoN}_6)$ , capped at opposite faces by lithium atoms which, in turn, are made nearly tetrahedral by the thf molecules.



Scheme 6



Reagents: i,  $2\text{Me}_3\text{SiN}_3$ ,  $-\text{N}_2$ ; ii,  $\text{WF}_6$ ,  $-2\text{Me}_3\text{SiF}$

Scheme 7

<sup>127</sup> M. A. Bakar, D. L. Hughes, W. Hussain, G. J. Leigh, C. J. MacDonald, and H. M. Ali, *J. Chem. Soc., Dalton Trans.*, 1988, 2545.

<sup>128</sup> T. A. George and M. A. Jackson, *Inorg. Chem.*, 1988, 27, 924.

<sup>129</sup> T. A. George and R. C. Tisdale, *Inorg. Chem.*, 1988, 27, 2909.

<sup>130</sup> B. L. Haymore, M. Hughes, J. Mason, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1988, 2935.

<sup>131</sup> J. Czerwonka, S. Hodorowicz, A. Kansas, A. Samotus, and S. Sagnowski, *Transition Met. Chem.*, 1988, 13, 190.

<sup>132</sup> J. Szklarzewicz and A. Samotus, *Transition Met. Chem.*, 1988, 13, 69.

<sup>133</sup> M. H. Chisholm, C. E. Hammond, and J. C. Huffman, *Polyhedron*, 1988, 7, 399.

The tungsten product shown in Scheme 7 has been characterized on the strength of n.m.r. spectroscopic evidence.<sup>134</sup> An excess of  $\text{NCl}_3$  reacts with  $\text{W}(\text{CO})_6$  to give  $\text{WCl}_4(\text{NCl})$ , which adds on an acetonitrile to give the distorted octahedral  $\text{WCl}_4(\text{NCl})(\text{NCMe})$ , where the two nitrogens are *trans*.<sup>135</sup> The product of a reaction between  $(\text{NSCl})_3$  and trichloroacetanhydride is  $\text{CCl}_3\text{CO}-\text{NS}_3\text{N}_2$ , which reacts with  $\text{MoCl}_5$  to give a mixture of  $\text{MoCl}_3(\text{N}_3\text{S}_2)$  and  $\text{MoCl}_2(\text{N}_2\text{SCOCCL}_3)$ .<sup>136</sup> Extraction of an acetonitrile solution of  $[\text{MoCl}_3(\text{N}_3\text{S}_2)]_2$  with a mixture of  $\text{NaF}$  and the ether 15-crown-5 gives the ion-pair  $[\text{Na}-15\text{-crown-5}][\text{MoF}_2\text{Cl}_2(\text{N}_3\text{S}_2)]$ .<sup>137</sup> the molybdenum is roughly octahedral, with a planar nitrogen-sulphur ring and the fluorines *trans* to the nitrogens. The sodium is 7-coordinated by the ether O and the fluorine atoms.

A series of papers<sup>138–143</sup> have been published concerning molybdenum with the ligands NO and tris(3,5-dimethylpyrazolyl)borate, ( $\text{L}'$ ). Treatment of the coordinatively unsaturated complex  $\text{Mo}(\text{NO})\text{L}'\text{I}_2$  with saturated cyclic amines such as pyrrolidine or piperidine gave a mixture of a paramagnetic amine complex  $\text{Mo}(\text{NO})\text{L}'(\text{NHC}_n\text{H}_{2n})$  and a diamagnetic amide complex  $\text{Mo}(\text{NO})\text{L}'(\text{NC}_n\text{H}_{2n})$ .<sup>138,139</sup> The amide had  $\text{Mo}-\text{N}$  of 1.937 Å compared to the amine species with  $\text{Mo}-\text{N}$  of 2.241 Å. Alkoxide species  $\text{Mo}(\text{NO})\text{L}'\text{Cl}(\text{OR})$  can be made from  $\text{Mo}(\text{NO})\text{L}'\text{Cl}_2$  by reacting with an alcohol- $\text{NR}_3$  mixture,<sup>140</sup> and the carboxylates  $\text{Mo}(\text{NO})\text{L}'(\text{OR})(\text{OCOR}')$  have also been prepared.<sup>141</sup> A cyclic voltammetric study of mono- and bi-metallic molybdenum and tungsten complexes containing NO and  $\text{L}'$  reveals<sup>142,143</sup> that in the bimetallic species the two metals are strongly, weakly, or negligibly interacting electrochemically, depending on the nature of the link between them. Complexes of the type  $\text{Ml}_2(\text{CO})_3(\text{NCMe})_2$  undergo a series of reactions as shown in Scheme 8.<sup>144–148</sup> Other mixed ligand complexes characterized include  $\text{MoX}_2(\text{CO})_2(\text{bipy})(\text{diphs})$ ,<sup>149</sup> where X is Cl, Br, or I,  $\text{Mo}(\text{NCMe}_3)\text{Cl}_3(\text{PMe}_3)_2$ ,<sup>150</sup>  $\text{Mo}(\text{CO})_2(\text{CNR})_2(\text{PR}'_3)_2$ ,<sup>151</sup> and *fac*- $\text{Mo}(\text{CO})_3(\text{bipy})$ -(tdp),<sup>152</sup> where the ligand (tdp) is as shown in (10) and is coordinated through the trivalent phosphorus. Treatment of compound (11) with  $\text{LiNMe}_2$  results<sup>153</sup> in the

<sup>134</sup> H. W. Roesky, K. Swarat, and F. Edelmann, *Z. Naturforsch., Teil B*, 1988, **43**, 231.

<sup>135</sup> A. Görg, K. Dehnicke, and D. Fenske, *Z. Naturforsch., Teil B*, 1988, **43**, 677.

<sup>136</sup> P. Klinzing, A. El-Kholi, U. Patt-Siebel, U. Müller, and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1988, **562**, 31.

<sup>137</sup> K. Völz, G. Baum, W. Massa, and K. Dehnicke, *Z. Naturforsch., Teil B*, 1988, **43**, 1235.

<sup>138</sup> N. Alobaidi, T. A. Hamor, C. J. Jones, J. A. McCleverty, K. Paxton, A. J. Howes, and M. B. Hursthouse, *Polyhedron*, 1988, **7**, 1931.

<sup>139</sup> N. Alobaidi, C. J. Jones, J. A. McCleverty, A. J. Howes, and M. B. Hursthouse, *Polyhedron*, 1988, **7**, 235.

<sup>140</sup> J. A. McCleverty and A. Włodarczyk, *Polyhedron*, 1988, **7**, 103.

<sup>141</sup> A. Włodarczyk, A. J. Edwards, and J. A. McCleverty, *Polyhedron*, 1988, **7**, 103.

<sup>142</sup> S. M. Charsley, C. J. Jones, J. A. McCleverty, B. D. Neaves, S. J. Reynolds, and G. Denti, *J. Chem. Soc., Dalton Trans.*, 1988, 293.

<sup>143</sup> S. M. Charsley, C. J. Jones, J. A. McCleverty, B. D. Neaves, and S. J. Reynolds, *J. Chem. Soc., Dalton Trans.*, 1988, 301.

<sup>144</sup> P. K. Baker, S. G. Fraser, and M. J. Snowden, *Inorg. Chim. Acta*, 1988, **148**, 247.

<sup>145</sup> P. K. Baker, S. G. Fraser, and T. M. Matthews, *Inorg. Chim. Acta*, 1988, **150**, 217.

<sup>146</sup> P. K. Baker and S. G. Fraser, *Inorg. Chim. Acta*, 1988, **142**, 219.

<sup>147</sup> P. K. Baker and D. Kendrick, *J. Coord. Chem.*, 1988, **17**, 355.

<sup>148</sup> P. K. Baker, S. G. Fraser, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1988, 2729.

<sup>149</sup> F. J. Arnaiz, C. S. Bartolome, G. García, and M. Pérez, *Inorg. Chim. Acta*, 1988, **141**, 57.

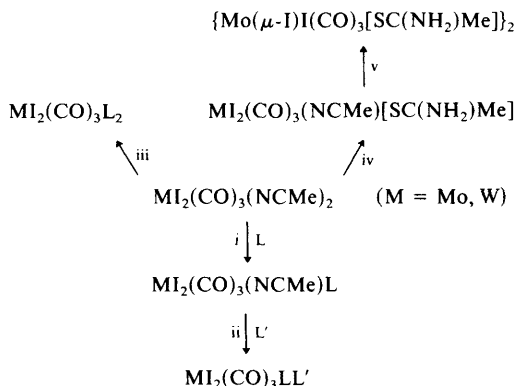
<sup>150</sup> A. J. Nielson, *Polyhedron*, 1988, **7**, 67.

<sup>151</sup> L. D. Detter, K. A. Conner, A. P. Rothwell, and R. A. Walton, *Inorg. Chim. Acta*, 1988, **143**, 109.

<sup>152</sup> J. Granifo, M. E. Vargas, J. Costamagna, and M. A. Francois, *Polyhedron*, 1988, **7**, 489.

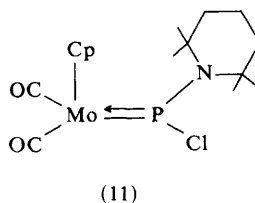
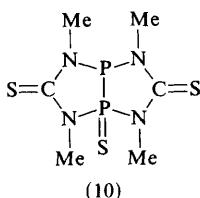
<sup>153</sup> A. H. Cowley, D. M. Giolando, C. M. Nunn, M. Pakulski, D. Westmoreland, and N. C. Norman, *J. Chem. Soc., Dalton Trans.*, 1988, 2127.

Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; Mn, Tc, Re

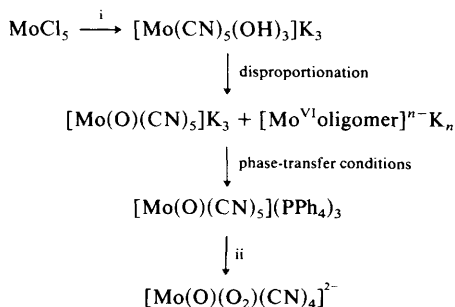


Reagents: i, 1 equiv. of L = PPh<sub>3</sub>, AsPh<sub>3</sub>, SbPh<sub>3</sub>, or BiPh<sub>3</sub>/CH<sub>2</sub>Cl<sub>2</sub>; ii, L' = py or substituted py, or L' = L; iii, 2 equiv. BiPh<sub>3</sub>, SC(NH<sub>2</sub>)Me, or OPHh<sub>3</sub>; iv, 1 equiv. SC(NH<sub>2</sub>)Me. Product isolated for M = W; v, dimerizes for M = Mo

Scheme 8



replacement of the chloro group by NMe<sub>2</sub>. The phosphido ligand functions as a three-electron donor with multiple Mo—P bonding. The molybdenum(IV) cyanide complex formed by disproportionation, as shown in Scheme 9, fails to react with oxygen<sup>154</sup> unless the potassium counterion is the first replaced by PPh<sub>4</sub><sup>+</sup>. Other reports of molybdenum–peroxo species include fluoro<sup>155</sup> and nicotinic acid<sup>156</sup> derivatives.



Reagents: i, KCN/H<sub>2</sub>O; ii, O<sub>2</sub>

Scheme 9

<sup>154</sup> H. Arzoumanian, J.-F. Pétrignani, M. Pierrot, F. Ridouane, and J. Sanchez, *Inorg. Chem.*, 1988, **27**, 3377.

<sup>155</sup> M. C. Chakravorty and D. Bandyopadhyay, *Inorg. Chim. Acta*, 1988, **143**, 247.

<sup>156</sup> C. Djordjevic, B. C. Puryear, N. Vuletic, C. J. Abelt, and S. J. Sheffield, *Inorg. Chem.*, 1988, **27**, 2926.

Two air-stable  $\text{Cr}^{\text{II}}$  complexes  $\text{CrC}_4\text{O}_4 \cdot (\text{H}_2\text{O})_n$ ,  $n = 2$  or  $4$ , with the squarate ion have been characterized.<sup>157</sup> Adduct formation between  $\text{Cr}(\text{acac})_3$  and Freon-113 has been reported.<sup>158</sup>

The alkoxide  $\text{W}(\text{OR})_4$  adopts<sup>159</sup> the rather unusual configuration of a distorted square plane about the tungsten when  $\text{R} = (12)$ . This compound is relatively unreactive, which may be a result of the undoubted steric crowding. The fluoroalkoxide  $[\text{WO}\{(\text{CF}_3)_2\text{C}(\text{O})\text{C}(\text{O})(\text{CF}_3)_2\}_2(\text{thf})]$  has an octahedral structure with the thf *cis* to the oxo group,<sup>160</sup> and with  $\text{W}=\text{O}$  of 1.685 Å,  $\text{W}-\text{OR}$  of 1.951 Å, and  $\text{W}-\text{OR}_2$  of 2.122 Å.

Oxomolybdenum complexes have been characterized with catechol amines<sup>161</sup> and catechols,<sup>162</sup> and with 5'-mononucleotides, where although strong complexes are formed,<sup>163</sup> there is little effect on the average conformation of the nucleotide.

Direct action failed to produce the complex ion  $[\text{WOCl}_4(\text{OPPh}_3)]^-$ , but success was achieved<sup>164</sup> by the partial hydrolysis of  $[\text{WCl}_4(\text{PhC}\equiv\text{CPh})_2]$  in the presence of  $\text{PPh}_3$  with  $\text{CH}_2\text{Cl}_2$  as an oxidizer.

Reaction between  $(\text{Et}_2\text{NH})_2\text{WOS}_3$ ,  $\text{CS}_2$ , and  $\text{O}_2$  gives  $\text{WO}(\text{S}_2)(\text{S}_2\text{CNEt}_2)_2$ , which although there is no apparent change in oxidation state has been shown<sup>165</sup> to proceed by a concealed induced internal electron-transfer *via* both  $\text{W}^{\text{V}}$  and  $\text{W}^{\text{IV}}$  intermediates. A comparative electrochemical study has been made<sup>166</sup> between compounds of the type  $\text{MX}(\text{S}_2)(\text{S}_2\text{CNR}_2)_2$  where  $\text{M} = \text{Mo}$  or  $\text{W}$  and  $\text{X} = \text{O}$  or  $\text{S}$ .

Heating  $\text{WSe}_4^{2-}$  in acetonitrile solution leads to the formation of a number of higher molecular weight ions,<sup>167</sup> which taken with other evidence<sup>168</sup> suggests that  $\text{W}-\text{Se}$  chemistry does not parallel that of  $\text{W}-\text{S}$ , being more complex and having less stable species. The complex salt  $[\text{Mo}(\text{CO})_2(\text{LL})\text{Cl}]_2[\text{Mo}_6\text{O}_{19}]$ , where LL is the chelating ligand  $\text{Ph}_2\text{PCH}_2\text{P}(\text{Se})\text{Ph}_2$ , has the  $\text{Mo}_6\text{O}_{19}^{2-}$  at the centre of symmetry of two seven-coordinate cations each of which is a distorted capped octahedron.<sup>169</sup>

Treatment of  $\text{M}(\text{CO})_6$ , where  $\text{M} = \text{Cr}$  or  $\text{W}$ , with  $\text{K}_2\text{Te}_4$  produces  $[(\text{CO})_4\text{MTe}_4]^{2-}$ , which was shown by single crystal X-ray diffraction analysis<sup>170</sup> to have a five-membered  $\text{CrTe}_4$  envelope-style ring with the chromium at the basal point and near planar tellurium atoms.

Thermal decarbonylation<sup>171</sup> of  $\text{Mo}(\text{CO})_3(\text{thf})_3$  in the presence of iodine leads to a wide range of iodo-complexes (Scheme 10). The complex ions  $[\text{MoBr}_6]^{2+}$  and  $[\text{Mo}_2\text{Br}_{10}]^{2-}$  have been prepared.<sup>172</sup>

<sup>157</sup> K. Michelsen, K. M. Nielsen, and E. Pedersen, *Acta Chem. Scand.*, 1988, **A42**, 724.

<sup>158</sup> L. I. Budarin, N. A. Burlaenko, B. G. Mischanchyk, and L. M. Pogorelaya, *Koord. Khim.*, 1988, **14**, 798.

<sup>159</sup> M. L. Listemann, R. R. Schrock, J. C. Dewan, and R. M. Kolodziej, *Inorg. Chem.*, 1988, **27**, 264.

<sup>160</sup> F. Edelmann, H. Plenio, K. Keller, and H. W. Roesky, *Z. Anorg. Allg. Chem.*, 1988, **565**, 111.

<sup>161</sup> A. M. El-Hendawy, W. P. Griffith, and C. A. Pumphrey, *J. Chem. Soc., Dalton Trans.*, 1988, 1817.

<sup>162</sup> S. F. Gheller, W. E. Newton, L. P. deMajid, J. R. Bradbury, and F. A. Schultz, *Inorg. Chem.*, 1988, **27**, 359.

<sup>163</sup> C. F. G. C. Galdes and M. M. C. A. Castro, *J. Inorg. Biochem.*, 1988, **33**, 47.

<sup>164</sup> M. Kersting, C. Friebe, K. Dehnicke, M. Kreisel, and R. Allmann, *Z. Anorg. Allg. Chem.*, 1988, **563**, 70.

<sup>165</sup> M. A. Ansari, J. Chandrasekaran, and S. Sarkar, *Inorg. Chem.*, 1988, **27**, 763.

<sup>166</sup> A. M. Bond, J. A. Broomhead, and A. F. Hollenkamp, *Inorg. Chem.*, 1988, **27**, 978.

<sup>167</sup> R. W. M. Wardle, S. Bhaduri, C.-N. Chau, and J. A. Ibers, *Inorg. Chem.*, 1988, **27**, 1747.

<sup>168</sup> R. W. M. Wardle, C. H. Mahler, C.-N. Chau, and J. A. Ibers, *Inorg. Chem.*, 1988, **27**, 2790.

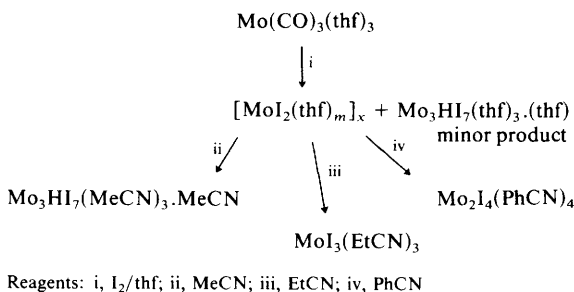
<sup>169</sup> R. Colton, B. F. Hoskins, and P. Panagiotidou, *Aust. J. Chem.*, 1988, **41**, 1295.

<sup>170</sup> W. A. Flomer, S. C. O'Neal, J. W. Kolis, D. Jeter, and A. W. Cordes, *Inorg. Chem.*, 1988, **27**, 969.

<sup>171</sup> F. A. Cotton and R. Poli, *J. Am. Chem. Soc.*, 1988, **110**, 830.

<sup>172</sup> I. Schmidt, U. Patt-Siebel, U. Müller, and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1988, **556**, 57.

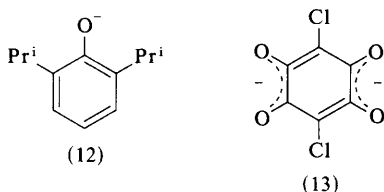
Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; Mn, Tc, Re



Scheme 10

The e.s.r. spectrum of the reaction product of the superoxide ion with [Cr(tpp)Cl], where tpp is tetraphenylporphyrin, shows strong hyperfine interactions between the metal nucleus and the ligand.<sup>173</sup> There is also u.v. spectral evidence to support the probable formation of a Cr<sup>IV</sup>(tpp)/O<sub>2</sub><sup>-</sup> adduct. Molybdenum and tungsten hemoproteins have been used as models for high-valent iron porphyrin centres in myoglobin and horseradish peroxidase.<sup>174</sup> Skilful choice of the Raman resonance excitation profiles allowed the In—M (where M = Mo or W) stretching frequencies (160 and 147 cm<sup>-1</sup>) in (tpp)In—M(CO)<sub>3</sub>Cp to be picked out from the porphyrin bands which dominate the low frequency region of the spectrum.<sup>175</sup> A range of similar species involving thallium porphyrins has also been characterized.<sup>176</sup>

**Cluster Species.**—Reaction of Mo<sub>2</sub>O<sub>7</sub><sup>2-</sup> with tetrachloro-1,2-benzoquinone generates the binuclear complex ion [(MoO<sub>2</sub>Cl<sub>2</sub>)(C<sub>6</sub>O<sub>4</sub>Cl<sub>2</sub>)(MoO<sub>2</sub>Cl<sub>2</sub>)]<sup>2-</sup>,<sup>177</sup> where the central bis-chelating ligand is as shown in (13). Other species of this same broad type



include [(W(CO)<sub>4</sub>(PR<sub>3</sub>)<sub>3</sub>)<sub>2</sub>{CNC<sub>6</sub>H<sub>4</sub>NC}] where infrared and multinuclear n.m.r. spectroscopy suggest strong backbonding,<sup>178</sup> yet the C—N bond length is unchanged between the free ligand and the complex. Photolytic behaviour such as redox processes, bond dissociation, and solvent effects have been followed<sup>179,180</sup> in the series of complexes (OC)<sub>5</sub>M—L—M(CO)<sub>5</sub>, where M is Cr, Mo, or W. The ligands

<sup>173</sup> T. Ozawa and A. Hanaki, *Inorg. Chim. Acta*, 1988, **147**, 103.

<sup>174</sup> Y. Shiro, M. Takeda, and I. Morishima, *J. Am. Chem. Soc.*, 1988, **110**, 4030.

<sup>175</sup> J. Góral, L. M. Proniewicz, K. Nakamoto, Y. Kato, and S. Onaka, *Inorg. Chim. Acta*, 1988, **148**, 169.

<sup>176</sup> R. Guillard, A. Zrineh, M. Ferhat, A. Tabard, Y. Mitaine, C. Swistak, P. Richard, C. Lecomte, and K. M. Kadish, *Inorg. Chem.*, 1988, **27**, 697.

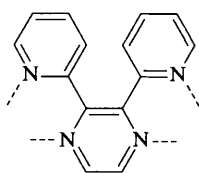
<sup>177</sup> S. N. Shaikh and J. Zubieta, *Inorg. Chim. Acta*, 1986, **146**, 149.

<sup>178</sup> J. S. Rommel, J. B. Weinrach, D. S. Grubisha, and D. W. Bennett, *Inorg. Chem.*, 1988, **27**, 2945.

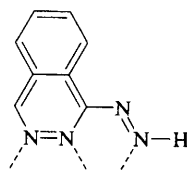
<sup>179</sup> M. M. Zulu and A. J. Lees, *Inorg. Chem.*, 1988, **27**, 1139.

<sup>180</sup> M. M. Zulu and A. J. Lees, *Inorg. Chem.*, 1988, **27**, 3325.

shown in (14) and (15) have been used to link tungsten<sup>181</sup> and molybdenum<sup>182</sup> centres. The Group 6 metals can perform this linking function for other metals and one example involves three chromates linking two iron atoms.<sup>183</sup>



(14)



(15)

Many of the interesting cluster compounds have significance for their relationship to active centres in enzymes and other biologically important entities. Thiomolybdate, for example, is readily absorbed from rat intestine into the organs where it is reversibly bound to proteins.<sup>184</sup> Although it is possible to synthesize pure model compounds,<sup>185,186</sup> there are many problems in the isolation of the naturally occurring materials. Dithionite has frequently been used in the extraction of the Fe—Mo co-factor from *Azotobacter vinelandii*, but a new method<sup>187</sup> of purification has raised questions about both the mechanism of extraction and the properties of the resultant co-factor. Typical studies include redox and e.p.r. measurements<sup>188</sup> on nitrogenases from *A. vinelandii* and *Clostridium pasteurianum*. Contrary to the usual situation the nitrogenase from their hybrid no longer has activity. F.t.-i.r. spectroscopy and normal coordinate analysis were carried out<sup>189</sup> on the linear complex ion  $[\text{Cl}_2\text{Fe}(\text{MoS}_4)\text{FeCl}_2]^{2-}$ . A one-pot synthesis of dimeric  $\text{W}^{\text{V}}$  complexes<sup>190</sup> with the core  $[\text{W}_2\text{XY}(\mu\text{-S})_2]^{2-}$ , where x, y = O or S, and a new entry<sup>191</sup> to the  $[\text{W}_3\text{S}_4]^{4+}$  cluster have been reported. One active area of study is that of the Fe—Mo—S cubane structures. The cage structure  $\text{Fe}_4\text{S}_6(\text{Cp})_4$  remains unperturbed by adduct formation with the fragments  $\text{Mo}(\text{CO})_2$  and  $\text{Mo}(\text{CO})_4$ . The products were studied<sup>192</sup> by various forms of spectroscopy and EXAFS. Cubanes such as  $\text{MoFe}_3\text{S}_4(\text{EtNCS}_2)_5$  can be produced<sup>193</sup> from the linear cluster-type complex ion  $[(\text{FeCl}_2)_2\text{MoCl}_4]$  by reaction with  $\text{Na}(\text{Et}_2\text{NCS}_2)$  in dimethylformamide. Sometimes mixtures of products are achieved.<sup>194</sup>

<sup>181</sup> E. M. Armstrong and P. K. Baker, *Synth. React. Inorg. Met.-Org. Chem.*, 1988, **18**, 1.

<sup>182</sup> S. N. Shaikh and J. Zubietta, *Inorg. Chem.*, 1988, **27**, 1896.

<sup>183</sup> P. Chaudhuri, M. Winter, K. Wieghardt, S. Gehring, W. Haase, B. Nuber, and J. Weiss, *Inorg. Chem.*, 1988, **27**, 1564.

<sup>184</sup> Z. Y. Wang and J. Mason, *J. Inorg. Biochem.*, 1988, **33**, 19.

<sup>185</sup> P. A. Eldredge, R. F. Bryan, E. Sinn, and B. A. Averill, *J. Am. Chem. Soc.*, 1988, **110**, 5573.

<sup>186</sup> A. Müller, A. Hildebrand, M. Penk, H. Bögge, E. Bill, and A. Trautwein, *Inorg. Chim. Acta*, 1988, **148**, 11.

<sup>187</sup> B. Hedman, P. Frank, S. F. Gheller, A. L. Roe, W. E. Newton, and K. O. Hodgson, *J. Am. Chem. Soc.*, 1988, **110**, 3798.

<sup>188</sup> T. V. Morgan, L. E. Mortenson, J. W. McDonald, and G. D. Watt, *J. Inorg. Biochem.*, 1988, **33**, 111.

<sup>189</sup> Z.-Y. Lin, L.-J. He, L.-N. Zhang, and J.-X. Lu, *Acta Chim. Sinica (Engl. Ed.)*, 1988, **1**.

<sup>190</sup> M. A. Ansari, J. Chandrasekaran, and S. Sarkar, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2265.

<sup>191</sup> F. A. Cotton and R. Llusar, *Inorg. Chem.*, 1988, **27**, 1303.

<sup>192</sup> J. Jordanov, H. M. J. Hendriks, N. Dupré, A. Viari, P. Vigny, and G. Diakun, *Inorg. Chem.*, 1988, **27**, 2997.

<sup>193</sup> Q.-T. Liu, L.-R. Huang, Y. Yang, and J.-X. Lu, *Acta Chim. Sinica*, 1988, **46**, 1.

<sup>194</sup> Q.-T. Liu, L.-R. Huang, Y. Yang, and J.-X. Lu, *Acta Chim. Sinica, (Engl. Ed.)*, 1988, 286.

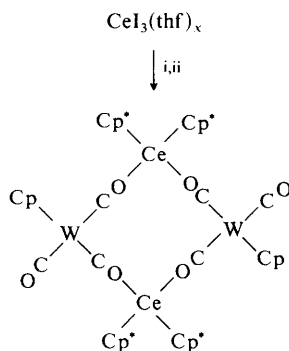


Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; Mn, Tc, Re

A double cubane cluster  $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{SCH}_2\text{CH}_2\text{OH})_9]^{3-}$  forms spontaneously from ferrous ion, tetrathiomolybdate, and 2-mercaptoethanol.<sup>195</sup> It is also possible to use molybdate as the origin of the molybdenum, and thiosulphate as the sulphur source, with both rate and yield being greatly enhanced by the presence of catalytic traces of the enzyme sulphurtransferase rhodanese.

Reaction of  $\text{WF}_6$  with pentafluoroaniline gives<sup>196</sup> a mixture of two imido anions,  $[\text{WF}_5(\text{NC}_6\text{F}_5)]^-$  and the fluoro-bridged species  $[\{(\text{C}_6\text{F}_5\text{N})\text{WF}_4\}_2(\mu\text{-F})]^-$ . One unusual feature is that the dimer exists in two distinct forms, one in which  $\text{W-F-W}$  is  $150.8^\circ$  and the other in which it is  $170.4^\circ$ .

The reaction product shown in Scheme 11 has a 12-membered core that adopts<sup>197</sup> a near-chair configuration, with linear  $\text{W-C-O}$  moieties and with two linear  $\text{Ce-O-C}$  and two at an angle of  $154^\circ$ . The compound was potentially of interest in luminescence studies, but was found to be virtually non-emissive.



Reagents: i,  $\text{Cp}^*\text{K}$ , where  $\text{Cp}^* = \text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ; ii,  $\text{K}[\text{CpW}(\text{CO})_3]$

**Scheme 11**

An interesting example of base-induced intramolecular  $\text{Mo-Mo}$  bond formation has been observed.<sup>198</sup> The hydroxyl bridge in  $[\{\text{LMO}\}_2(\mu\text{-MeCO}_2)_2(\mu\text{-OH})]^{3+}$ , where L is  $N',N'',N'''$ -trimethyl-1,4,7-triazacyclononane, can be deprotonated to form an oxo-bridged complex. In the course of this change, which is reversible, the  $\text{Mo-Mo}$  distance alters from 3.55 Å to 2.885 Å with the formation of a  $\text{Mo-Mo}$  bond.

Treatment of  $\text{WCl}_4$  in 1,2-dimethoxyethane with sodium amalgam followed by three equivalents of  $\text{Li}(\text{NSiMe}_3)_2$  gives<sup>199</sup> small amounts of the quite unprecedented  $\text{C}[\text{W}_2\{\text{N}(\text{SiMe}_3)\text{Si}(\text{Me})_2\text{CH}_2\}_2\{\text{N}(\text{SiMe}_3)\text{SiMe}_2\}_2]_2$ , the skeleton of which is shown in (16).

The chemistry of triply-bonded dimetal species is mostly concerned with amido and alkoxo compounds. The  $\text{W}\equiv\text{W}$  bond in  $\text{W}_2(\text{Me}_2\text{N})$  is cleaved<sup>200</sup> and a  $\text{CS}_2$

<sup>195</sup> R. J. Anglin, F. Bonomi, and D. M. Kurtz, Jr., *Inorg. Chem.*, 1988, **27**, 3434.

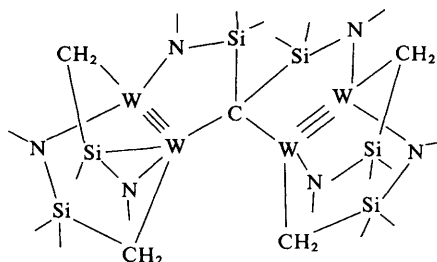
<sup>196</sup> J. Fawcett, G. A. Griffith, R. D. Peacock, and D. R. Russell, *Polyhedron*, 1988, **7**, 2015.

<sup>197</sup> P. N. Hazin, J. C. Huffman, and J. W. Bruno, *J. Chem. Soc., Chem. Commun.*, 1988, 1473.

<sup>198</sup> A. Neves, U. Bossek, K. Wieghardt, B. Nuber, and J. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 685.

<sup>199</sup> D. C. Bradley, H. M. Dawes, M. B. Hursthouse, and H. R. Powell, *Polyhedron*, 1988, **7**, 2049.

<sup>200</sup> M. L. Ziegler, K. Blechschmidt, H. Bock, E. Guggölz, and R. P. Korswagen, *Z. Naturforsch., Teil B*, 1988, **43**, 590.



(16)

group inserted into the W—N bond by reaction either with CS<sub>2</sub> in hexane or Se in CS<sub>2</sub>. On the other hand, addition of NaCp to 1,2-W<sub>2</sub>Cl<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub> in toluene leads<sup>201</sup> to replacement of the chloro groups by Cp, with the molecule taking up the *gauche* conformation.

The reduction of alkynes bonded to M<sub>2</sub>(OR)<sub>6</sub> has been examined.<sup>202</sup> Treatment of hydrocarbon solutions of M<sub>2</sub>(OR)<sub>6</sub> with ligands such as 9,10-phenanthrenequinone or tetrachloro-1,2-benzoquinone, gives rise<sup>203</sup> to M<sub>2</sub>(OR)<sub>m</sub>(LL)<sub>n</sub>, where M is Mo or W and LL is the fully reduced form of the ligand. In favourable cases it was possible to isolate members of a stepwise replacement sequence (*m*, *n*) from (6, 0) through (6, 2), (4, 3), to (2, 4). The replacement is an oxidative addition process with a transformation from (M≡M)<sup>6+</sup> to (M—M)<sup>10+</sup>. U.v. irradiation of a carbon tetrachloride solution of (Ph<sub>4</sub>P)[W<sub>2</sub>Cl<sub>7</sub>(thf)<sub>2</sub>] produces a colour change from green to deep purple and blue crystals of (Ph<sub>4</sub>P)[W<sub>2</sub>Cl<sub>8</sub>(thf)] can<sup>204</sup> be isolated.

The dimolybdenum quadruply bonded complexes Mo<sub>2</sub>X<sub>4</sub>(PMe<sub>3</sub>)<sub>4</sub>, X = NCO or NCS, have been prepared in a 'one-pot' reaction by refluxing Me<sub>3</sub>SiX, phosphine, and Mo<sub>2</sub>(O<sub>2</sub>CMe)<sub>4</sub>.<sup>205</sup> For a series of *ca.* 20 compounds of the type Mo<sub>2</sub>Cl<sub>4</sub>(PR<sub>3</sub>)<sub>4</sub> correlations were achieved<sup>206</sup> between the δ—δ\* transition energy and measures of Π-acidity such as the C—O stretching frequency of the <sup>13</sup>C chemical shift. An attempted correlation with the Mo—Mo bond length was unsuccessful. Some detailed assignments of electronic spectra of similar compounds have been made,<sup>207</sup> and it has also been shown<sup>208</sup> that the Mo—Mo stretching frequency in Mo<sub>2</sub>(O<sub>2</sub>CMe)<sub>4</sub> does not shift on forming Mo<sub>2</sub>(O<sub>2</sub>CCD<sub>3</sub>)<sub>4</sub> although (C—C) and (Mo—O) stretches are sensitive.

Other related papers include<sup>209–211</sup> syntheses of Mo<sub>2</sub>X<sub>2</sub>Y<sub>2</sub>(LL)<sub>1,2</sub>, where X, Y = Cl, Br, or O<sub>2</sub>CMe, and LL is a chelating diphosphine, and oxidative-addition<sup>212</sup> of disulphides and diselenides to M<sub>2</sub>Cl<sub>4</sub>(LL)<sub>2</sub>, where M is Mo or W.

<sup>201</sup> M. H. Chisholm, M. J. Hampden-Smith, J. C. Huffman, J. D. Martin, K. A. Stahl, and K. G. Moodley, *Polyhedron*, 1988, 7, 1991.

<sup>202</sup> M. H. Chisholm, B. K. Conroy, D. L. Clark, and J. C. Huffman, *Polyhedron*, 1988, 7, 903.

<sup>203</sup> T. P. Blatchford, M. H. Chisholm, and J. C. Huffman, *Inorg. Chem.*, 1988, 27, 2059.

<sup>204</sup> D. J. Bergs, M. H. Chisholm, K. Folting, J. C. Huffman, and K. A. Stahl, *Inorg. Chem.*, 1986, 27, 2950.

<sup>205</sup> F. A. Cotton and M. Matusz, *Inorg. Chem.*, 1986, 27, 2127.

<sup>206</sup> F. A. Cotton, L. M. Daniels, G. L. Powell, A. J. Kahaian, T. J. Smith, and E. F. Vogel, *Inorg. Chim. Acta*, 1988, 144, 109.

<sup>207</sup> M. D. Hopkins, V. M. Miskowski, and H. B. Gray, *J. Am. Chem. Soc.*, 1988, 110, 1787.

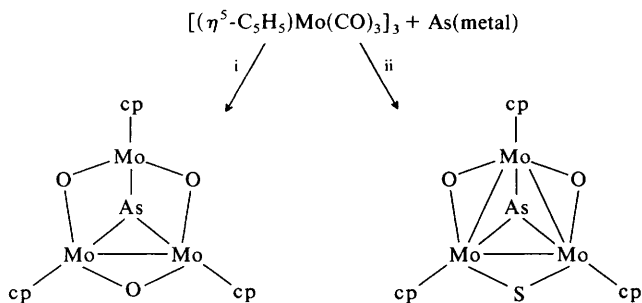
<sup>208</sup> R. J. H. Clark, A. J. Hempleman, and M. Kurmoo, *J. Chem. Soc., Dalton Trans.*, 1988, 973.

<sup>209</sup> M. Bakir and R. A. Walton, *Polyhedron*, 1988, 7, 1279.

<sup>210</sup> M. Bakir, F. A. Cotton, M. M. Cudahy, C. Q. Simpson, T. J. Smith, E. F. Vogel, and R. A. Walton, *Inorg. Chem.*, 1988, 27, 2608.

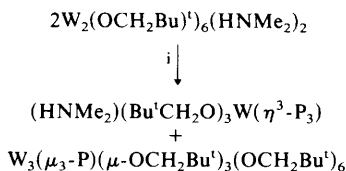
<sup>211</sup> F. A. Cotton and S. Kitagawa, *Polyhedron*, 1988, 7, 1673.

<sup>212</sup> J. A. M. Canich, F. A. Cotton, K. R. Dunbar, and L. R. Falvello, *Inorg. Chem.*, 1988, 27, 804.



Scheme 12

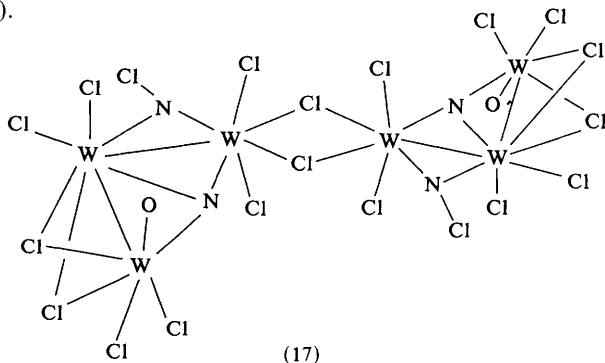
Reaction between  $[\text{CpMo}(\text{CO})_3]_3$  and arsenic produces<sup>213</sup> the products shown in Scheme 12. The structure of the tri-metal complex  $[(\text{MoBr})_3(\mu\text{-Br})_3(\mu\text{-O}_2\text{CMe})_3(\mu_3\text{-O})]$  has been shown<sup>214</sup> to be based around an equilateral metal triangle. The reaction involving phosphorus shown in Scheme 13, produces two products the first of which



Reagent: i,  $\text{P}_4$

Scheme 13

has previously been characterized. The new product<sup>215</sup> is a tri-tungsten complex where each metal has square-based pyramidal coordination with the phosphorus axial to each centre. The treatment of  $\text{WCl}_5$  with  $(\text{Hg}_2\text{N})\text{Br}$  in boiling carbon tetrachloride gives  $\text{W}_2\text{NCl}_7$  which in turn forms<sup>216</sup> several products on addition of a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{PPh}_4\text{Cl}$ . One of these has been characterized as the product shown in (17).



<sup>213</sup> H.-P. Neumann and M. Ziegler, *J. Chem. Soc., Chem. Commun.*, 1988, 498.

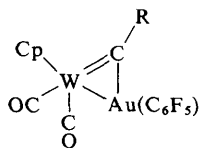
<sup>214</sup> E. L. Akhmedov, A. S. Kotelnikova, T. B. Larina, A. M. Abbasov, M. D. Surazhskaya, and P. A. Kozmin, *Koord. Khim.*, 1988, **14**, 1143.

<sup>215</sup> M. H. Chisholm, K. Folting, and J. W. Pasterczyk, *Inorg. Chem.*, 1988, **27**, 3057.

<sup>216</sup> D. Fenske, Th. Godemeyer, and K. Dehnicke, *Z. Naturforsch., Teil B*, 1988, **43**, 12.

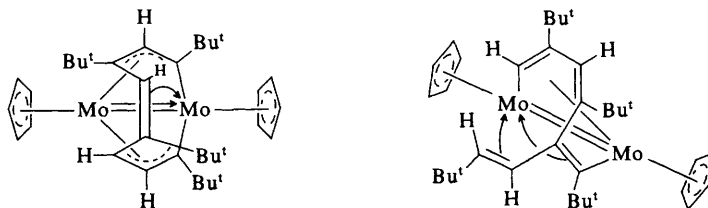
Bonding in tetra-metal clusters has been analysed with the aid of Fenske–Hall calculations.<sup>217</sup> Both capping and edge-bridging ligands can cause charge movement from the metal cluster. The butterfly arrangement is dominated by the influence of capping ligands, and that of the square type by edge-bridging ligands. A butterfly alkoxide complex,  $M_4(OR)_{12}$ , is formed by treating  $M_2(OBu^t)_6$ , where M is Mo or W, with various alcohols. The colour of the solution darkens and it was shown<sup>218</sup> by 2D  $^{13}C-^1H$  n.m.r. spectroscopy that eight different types of alkoxide were present. Other tetra-metal cluster papers include one with halogen ligands,  $Mo_4O_2X_2(OPr^i)_6$ ,<sup>219</sup> and another involving tellurium,  $Mo_4Te_{16}(en)_4$ .<sup>2–220</sup>

The final group of cluster compounds concern those formed with mixed metals, the simplest type of which is (18).<sup>221</sup> In a slightly more complex route, addition of



(18)

$Na[Fe(CO)_2Cp]$  to  $[Mo(NCMe)(Bu^tC_2H)_2Cp]BF_4$  has been shown to give the products indicated in (19).<sup>222</sup>



(19)

The characterization has been reported<sup>223–225</sup> of a wide variety of cage structures produced by the attack of alkynes on  $L_nM-W(\equiv CC_6H_4Me-4)(CO)_4$ , where  $ML_n$  is  $Mo(CO)_3Cp$  or  $Co(CO)_4$ . Comparison has been made<sup>226</sup> of a range of reactions for the series of alkylidyne metal complexes  $Cp(OC)_2M\equiv CR$ , where M is Cr, Mo,

<sup>217</sup> B. E. Bursten, M. H. Chisholm, and D. L. Clark, *Inorg. Chem.*, 1988, **27**, 2084.

<sup>218</sup> M. H. Chisholm, K. Folting, C. E. Hammond, and M. J. Hampden-Smith, *J. Am. Chem. Soc.*, 1988, **110**, 3314.

<sup>219</sup> M. H. Chisholm, D. L. Clark, R. J. Errington, K. Folting, and J. C. Huffman, *Inorg. Chem.*, 1988, **27**, 2071.

<sup>220</sup> B. W. Eichhorn, R. C. Haushalter, F. A. Cotton, and B. Wilson, *Inorg. Chem.*, 1988, **27**, 4084.

<sup>221</sup> G. A. Carriedo, V. Riera, G. Sanchez, and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1988, 1957.

<sup>222</sup> M. Green, N. K. Jetha, R. J. Mercer, N. C. Norman, and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1988, 1843.

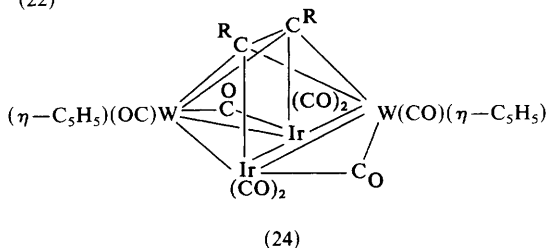
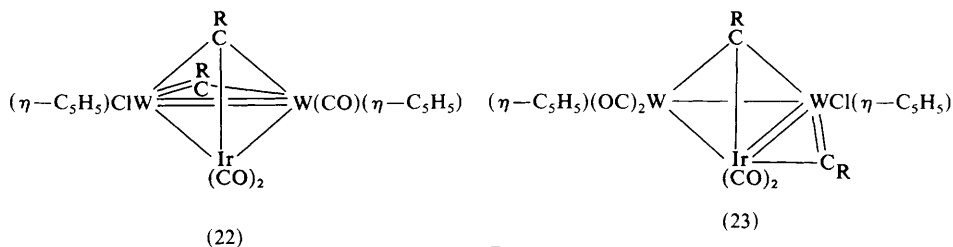
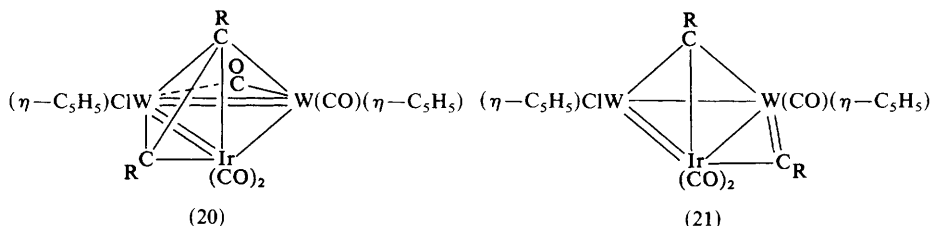
<sup>223</sup> E. Delgado, M. E. Garcia, J. C. Jeffrey, P. Sherwood, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 207.

<sup>224</sup> I. J. Hart, J. C. Jeffrey, M. J. Grosse-Ophoff, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 1867.

<sup>225</sup> I. J. Hart and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 1899.

<sup>226</sup> S. J. Dossett, A. F. Hill, J. C. Jeffrey, F. Marken, P. Sherwood, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 2453.

or W, and R is aryl. The interaction of  $[W(\equiv CC_6H_4Me-4)(CO)_2Cp]$  and  $[IrCl(CO)-(\eta\text{-cyclooctene})]$  forms the five products (20)–(24). These were separated<sup>227</sup> by column chromatography. The construction and characterization of ruthenium clusters with both molybdenum<sup>228</sup> and tungsten<sup>229</sup> has been investigated.



An octanuclear cluster has been produced<sup>230</sup> from  $Pd_4(CO)_4(OAc)_4$  and  $Na[CpMo(CO)_3]$ . The metals in  $Na_2[Pd_4\{CpMo(CO)_3\}_4] \cdot 2(thf)$  are in one plane where the palladium atoms form a square with a molybdenum atom making an isosceles triangle at each edge. The  $[CpMo(CO)_3]^-$  moiety is thus acting as a strong acceptor bridging group.

**Organometallics.**—Prolonged exposure to u.v./visible irradiation of  $Cr(CO)_6$  in an  $O_2$ -doped argon lattice at 12 K results in the formation<sup>231</sup> of  $CrO_2$ . Isotopic-substitution infrared experiments suggest that the  $O-Cr-O$  angle is about  $117^\circ$ .

<sup>227</sup> J. C. Jeffrey, M. A. Ruiz, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 1131.

<sup>228</sup> R. D. Adams, J. E. Babin, and M. Tasi, *Inorg. Chem.*, 1988, **27**, 2618.

<sup>229</sup> F. G. A. Stone and M. L. Williams, *J. Chem. Soc., Dalton Trans.*, 1988, 2467.

<sup>230</sup> T. A. Stomnova, I. N. Busygina, S. B. Katser, A. S. Antsyshkina, M. A. Porai-Koshits, and I. I. Moiseev, *J. Chem. Soc., Dalton Trans.*, 1988, 114.

<sup>231</sup> M. J. Almond and M. Hahne, *J. Chem. Soc., Dalton Trans.*, 1988, 2255.

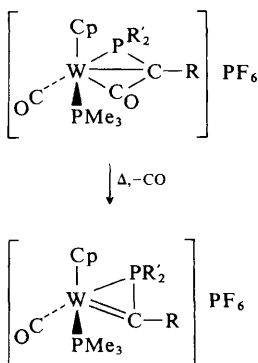
Time-resolved photoacoustic calorimetry has been used<sup>232</sup> to assess the magnitude of the enthalpy changes involved in the replacement of a carbonyl in  $\text{Cr}(\text{CO})_6$  to give  $\text{Cr}(\text{CO})_5\text{L}$ . The photochemical oxidation of  $\text{W}(\text{CO})_6$  in carbon tetrachloride to give species such as  $[\text{W}(\text{CO})_4\text{Cl}_2]_2$  has been applied<sup>233</sup> to the synthesis of  $\text{WCl}_2(\text{CO})_3(\text{PPh}_3)_2$ .

Estimates of the enthalpy changes in the  $\text{Mo}-\text{X}$  bond of  $\text{X}-\text{Mo}(\text{CO})_3\text{Cp}$  have been made<sup>234</sup> for a wide range of entities.

Chemical shifts derived from multinuclear n.m.r. spectroscopic measurements have been used<sup>235</sup> to assess donor strength in complexes of the type  $\text{W}(\text{CO})_{6-n}(\text{CNR})_n$ , and in these species the aliphatic isocyanides were found to be better donors than aromatic isocyanites.

Treatment of  $\text{M}(\text{NBU}^1)_2(\text{OSiR}_3)_2$  with the appropriate Grignard reagent gave<sup>236</sup> the monomeric distorted tetrahedral compound  $\text{M}(\text{NBU}^1)_2(\text{C}_6\text{H}_2\text{Me}_3-2,4,6)_2$ , where M is Cr or Mo.

A phosphinocarbene is produced<sup>237</sup> by mild thermolysis of the cationic tungsta-phospha-bicyclobutanone shown in Scheme 14. Other molybdenum-carbene complexes have also been studied.<sup>238,239</sup>



Scheme 14

A review<sup>240</sup> of arene displacement reactions in  $(\eta^6\text{-arene})\text{Cr}^0$  charts an increasingly complex field that includes the possibility of  $\text{Cr}=\text{Cr}$  intermediates. The synthesis of a variety of perfluorotungstenocenes has been reported.<sup>241</sup> Structural assignments were based on extensive use of n.m.r. spectroscopy.

<sup>232</sup> G. K. Yang, V. Vaida, and K. S. Peters, *Polyhedron*, 1988, 7, 1619.

<sup>233</sup> T. Szymánska-Buzar, *Inorg. Chim. Acta*, 1988, 145, 231.

<sup>234</sup> S. P. Nolan, R. L. de la Vega, S. L. Mukerjee, A. A. Gonzalez, K. Zhang, and C. D. Hoff, *Polyhedron*, 1988, 7, 1491.

<sup>235</sup> M. P. Guy, J. L. Coffey, J. S. Rommel, and D. W. Bennett, *Inorg. Chem.*, 1988, 27, 2942.

<sup>236</sup> A. C. Sullivan, G. Wilkinson, M. Motevalli, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1988, 53.

<sup>237</sup> F. R. Kreissl and M. Wolgruber, *Z. Naturforsch., Teil B*, 1988, 43, 1307.

<sup>238</sup> N. A. Bailey, D. A. Dunn, C. N. Foxcroft, G. R. Harrison, M. J. Winter, and S. Woodward, *J. Chem. Soc., Dalton Trans.*, 1988, 1449.

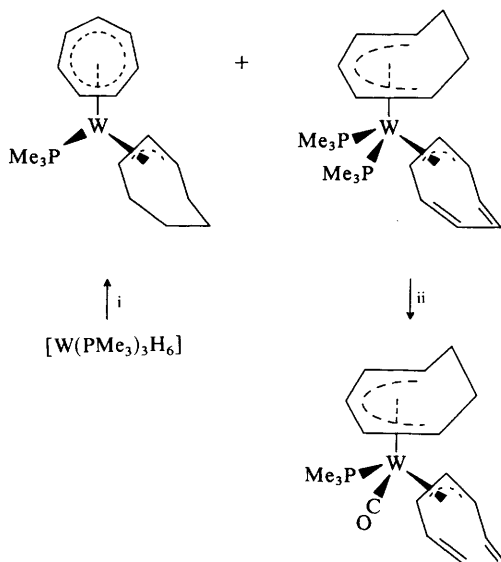
<sup>239</sup> J. G. Yin, J.-B. Chen, W.-H. Xu, and C.-S. Nie, *Acta Chim. Sinica*, 1988, 46, 1020.

<sup>240</sup> I. S. Butler and H. L. Uhm, *Comments Inorg. Chem.*, 1988, 7, 1.

<sup>241</sup> G. Parkin and J. Bercaw, *Polyhedron*, 1988, 7, 2053.

Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; Mn, Tc, Re

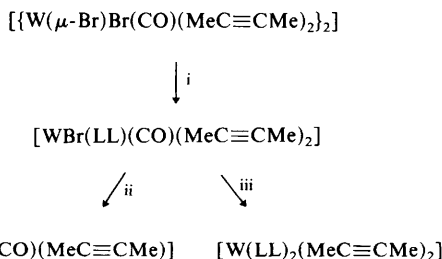
Cycloheptatriene gives two products in reaction<sup>242</sup> with  $W(PMe_3)_6$ , one of which reacts with carbon monoxide (Scheme 15). The synthesis and dynamic properties



Reagents: i, Cycloheptatriene in light petroleum (b.p. 100–120 °C) at 80 °C for 9 d; ii, carbon monoxide (202 650 Pa) in light petroleum (b.p. 40–60 °C) at 50 °C for 4 d

**Scheme 15**

of a range of chelate compounds formed from tungsten but-2-yne complexes (Scheme 16) have been discussed.<sup>243,244</sup> In  $W(acac)_2(CO)(MeC \equiv CMe)$  only the alkyne propeller motion could be observed by n.m.r., but more variety was found in other examples.



Reagents: i,  $LL^- = acac, S_2PMe_2, S_2P(OMe)_2$ ; ii,  $LL^- = acac, S_2P(OMe)_2$ ; iii,  $LL^- = S_2PMe_2$

**Scheme 16**

<sup>242</sup> M. L. H. Green, D. K. Siriwardene, D. O'Hare, and L.-L. Wong, *J. Chem. Soc., Dalton Trans.*, 1988, 2851.

<sup>243</sup> J. L. Davidson and G. Vasapollo, *J. Chem. Soc., Dalton Trans.*, 1988, 2855.

<sup>244</sup> L. Carlton and J. L. Davidson, *J. Chem. Soc., Dalton Trans.*, 1988, 2071.

## 5 Manganese, Technetium, and Rhenium

The Raman spectrum of  $K_3[Mn(CN)_5NO]$  in the excited state shows<sup>245</sup> that the frequency of the C—N stretching vibration decreases by about  $100\text{ cm}^{-1}$  by comparison with the ground state.

Reaction of labelled sodium azide with *mer*- $TcCl_3(Me_2PhP)_3$  produced<sup>246</sup>  $Tc^{15}NCl_2(Me_2PhP)_3$ . The basic configuration of the complex was retained, although the strong *trans* effect of the nitrido ligand is evident in that the Tc—Cl *trans* to the nitrogen is  $2.665\text{ \AA}$  whilst that *trans* to a chlorine is  $2.441\text{ \AA}$ .

A series of manganese complexes  $MnX_2(phos)$ , where X is Cl, Br, or I, and phos is  $P(C_nH_{2n+1})_3$  or  $PPh(C_nH_{2n+1})_2$  with  $n = 12, 14$ , or  $16$ , has been prepared.<sup>247,248</sup> These were found to form highly coloured 1:1 adducts with molecular oxygen in the solid and in toluene or thf solutions. The oxygen binding curves show evidence of cooperativity effects.

<sup>99</sup>Tc n.m.r. chemical shifts have been reported a series of  $Tc^I$  phosphine and phosphite complexes.<sup>249</sup> These were found to correlate well with data from <sup>95</sup>Mo n.m.r. spectral studies of related species, but warnings were given about some recent assignments which may be in error as a result of spectral folding. Other workers have noted<sup>250</sup> that  $Tc^I$  neutral complexes exhibit chemical shifts close to  $-1650\text{ ppm}$  (relative to  $TcO_4^-$ ) but cationic species show a much wider spread of values ranging from *ca.*  $-3500$  for a  $(C_3NP_2)$  donor set, to  $-13\text{ ppm}$  for six phosphorus donor atoms.

Electrochemical measurements have been made<sup>251,252</sup> on some substances *trans*- $M(diphos)_2X_2$  where M is Tc or Re and X is Cl or Br. The value of the redox potential  $M^{III}/M^{II}$  was determined in aqueous solution and in the presence of neutral, anionic, and cationic surfactants. Evidence was obtained for micellar effects dependent upon the lipophilicity of the components of the redox couple.

Various mixed ligand Tc-phosphine complexes have been characterized,<sup>253–255</sup> and there are reports of <sup>31</sup>P n.m.r. measurements of ligand exchange rates of  $TcNX_2(Ph_3Y)_2$  and  $TcNX_3(Me_2PhP)_3$  (X = Cl or Br) and (Y = P or As) with dithiocarbamates.<sup>255</sup>

The reactivity of some rhenium complexes with potentially chelating organohydrazines has been examined.<sup>256</sup> The nature of the alkyl group in  $ReCl_2(PPh_3)_2(NNR)$  was found to be paramount. Thus when R was phthalazine no simple substitution products could be isolated but when  $R = COC_6H_4-p\text{-Cl}$ , donor ligands were able to open up the chelate by displacement of the coordinate carbonyl group. Anthranilic

<sup>245</sup> J.-H. Perng and J. I. Zink, *Inorg. Chem.*, 1988, **27**, 1403.

<sup>246</sup> A. S. Batsanov, Yu. T. Struchkov, B. Lorenz, and B. Olk, *Z. Anorg. Allg. Chem.*, 1988, **564**, 129.

<sup>247</sup> D. S. Barratt, G. A. Gott, and C. A. McAuliffe, *Inorg. Chim. Acta*, 1988, **145**, 289.

<sup>248</sup> D. S. Barratt, G. A. Gott, and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 1988, 2065.

<sup>249</sup> A. Davison, J. K. Kronauge, A. G. Jones, R. M. Pearlstein, and J. R. Thornback, *Inorg. Chem.*, 1988, **27**, 3245.

<sup>250</sup> M. Findeisen, L. Kaden, B. Lorenz, and M. Wahren, *Inorg. Chim. Acta*, 1988, **142**, 3.

<sup>251</sup> J. R. Kirchoff, W. R. Heineman, and E. Deutsch, *Inorg. Chem.*, 1988, **27**, 3608.

<sup>252</sup> K. Libson, M. N. Doyle, R. W. Thomas, T. Nelesnik, M. Woods, J. C. Sullivan, R. C. Elder, and E. Deutsch, *Inorg. Chem.*, 1988, **27**, 3614.

<sup>253</sup> U. Mazzi, F. Refosco, F. Tisato, G. Bandoli, and M. Nicolini, *J. Chem. Soc. Dalton Trans.*, 1988, 847.

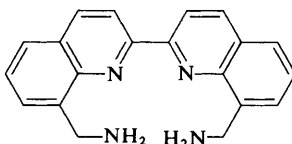
<sup>254</sup> U. Abram, S. Abram, R. Beyer, R. Muenze, L. Kaden, B. Lorenz, and M. Findeisen, *Inorg. Chim. Acta*, 1988, **148**, 141.

<sup>255</sup> U. Abram, B. Lorenz, L. Kaden, and D. Scheller, *Polyhedron*, 1988, **7**, 285.

<sup>256</sup> T. Nicholson and J. Zubietta, *Polyhedron*, 1988, **7**, 171.



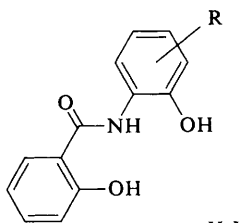
acid reacted<sup>257</sup> in ethanol solution with  $\text{ReOCl}_3(\text{PPh}_3)_2$  to give the rather unusual product with a chelating imido ligand,  $\text{ReCl}(\text{OEt})(\text{PPh}_3)_2(\text{NC}_6\text{H}_4\text{CO}_2)$ . The potentially quadridentate ligand (25) forms  $\text{MnLCl}_2$ , which has been found<sup>258</sup> to be a



(25)

distorted octahedron with  $\text{Cl}-\text{Mn}-\text{Cl}$  of  $175.7^\circ$ . The material  $[\text{Mn}\{15\}\text{aneN}_3\text{Cl}]\text{PF}_6$  contains high spin  $\text{Mn}^{\text{II}}$  and is a 2:1 electrolyte in water but 1:1 in acetonitrile.<sup>259</sup>

Complexes of technetium with heterocyclic amines, e.g.  $\text{TcOCl}_2(\text{py})_2(\text{OR})$ , can be produced<sup>260</sup> either by reacting  $[\text{TcOCl}_4]^-$  with the heterocycle or by reacting  $[\text{TcO}_2(\text{py})_4]^+$  with chloride. A  $\text{Tc}^{\text{V}}$  product is also obtained when the  $\text{Tc}^{\text{VII}}$  complex  $\text{TcO}_3\text{Cl}(\text{LL})$ , where LL is a chelating amine such as bipyridyl or 1,10-phenanthroline, is reacted<sup>261</sup> with an olefin. The olefin is oxidized and a diolate complex can be isolated,  $\text{TcOCl}(\text{OCR}_2\text{CR}_2\text{O})(\text{LL})$ .

 $\text{H}_3\text{L}$ 

(26)  $\text{R} = \text{H}, 5\text{-Me}, 5\text{-Cl}, 5\text{-NO}_2, \text{ or } 4\text{-NO}_2$

The ligand (26) reacts<sup>262</sup> with manganese(II) salts in methanolic potassium hydroxide to give the  $\text{Mn}^{\text{IV}}$  product  $\text{K}_2[\text{MnL}_2]$ , which in the case of the 5-Me ligand can be oxidized by  $\text{Ce}^{\text{IV}}$  to give  $\text{K}[\text{MnL}_2]$ . This was isolated as deep purple crystals. It is stable in the solid, but decomposes in solution, and is a rare example of six coordination in  $\text{Mn}^{\text{V}}$ .

Some complexes of Schiff bases with  $\text{Mn}^{\text{III}}$ <sup>263</sup> and  $\text{Tc}^{\text{V}}$  and  $\text{Re}^{\text{V}}$ <sup>264</sup> have been described.

<sup>257</sup> O. D. Sloan and P. Thornton, *Polyhedron*, 1988, 7, 329.

<sup>258</sup> L.-Y. Chung, E. C. Constable, J. Lewis, P. R. Raithby, and P. T. Kaye, *J. Chem. Soc., Dalton Trans.*, 1988, 2121.

<sup>259</sup> J. E. Newton and S. C. Jackels, *J. Coord. Chem.*, 1988, 19, 265.

<sup>260</sup> R. M. Pearlstein, C. J. L. Lock, R. Faggiani, C. E. Costello, C.-H. Zeng, A. G. Jones, and A. Davison, *Inorg. Chem.*, 1988, 27, 2409.

<sup>261</sup> R. M. Pearlstein and A. Davison, *Polyhedron*, 1988, 7, 1981.

<sup>262</sup> M. Koikawa, H. Okawa, and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1988, 641.

<sup>263</sup> T. Akiu, N. Matsumoto, and H. Okawa, *Bull. Chem. Soc. Jpn.*, 1988, 61, 4155.

<sup>264</sup> F. Refosco, F. Tisato, U. Mazzi, G. Bandoli, and M. Nicolini, *J. Chem. Soc., Dalton Trans.*, 1986, 611.

A complicated range of complexes between the dianion of maltitol and different oxidation states of manganese has been investigated<sup>265</sup> by various potentiometric and spectrophotometric procedures. By vapour pressure and <sup>17</sup>O n.m.r. measurements of acetic acid, exchange between manganese(II) perchlorate and manganese(II) acetate has been followed.<sup>266</sup> The activation volume for the perchlorate was found to be near zero and an interchange mechanism was proposed, whereas for the acetate a positive value was used to support a dissociative interchange mechanism.

Reaction of Mn(hfac)<sub>2</sub> with the stable radical nitronyl nitroxide<sup>267,268</sup> produced 1:1 adducts that proved to be one-dimensional chains. These were found to be ferrimagnetic chains where two different spins are antiferromagnetically coupled.

A series of ten phenolic analogues of amino carboxylic acid ligands has been shown<sup>269</sup> by electrophoretic methods to form complexes with <sup>99m</sup>Tc which may be useful in hepatobiliary scintigraphy.

The extraction by trioctylammonium ion of anionic Tc thiocyanato complexes, following a Sn<sup>II</sup> reduction step of Tc<sup>VII</sup> precursor species, has been found<sup>270</sup> to be sensitive to the concentration of the reducing agent. Both red Tc<sup>IV</sup> or yellow Tc<sup>III</sup> species could be isolated. Technetium tris(acetylacetonate) has been shown<sup>271</sup> to be a near perfect octahedron (O—Tc—O of 90.2°) with Tc—O of 2.025 Å.

Square-pyramidal configurations with basal sulphur donors have been established for the complex ions [TcX(SCOCOS)<sub>2</sub>]<sup>−</sup>, where X is O or N,<sup>272</sup> and for [TcO(SAr)<sub>4</sub>]<sup>−</sup>,<sup>273</sup> where Ar is a bulky aryl group such as 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>. A similar shape was also established<sup>274</sup> for a rare example of an all-sulphur rhenium complex ion [Re(S<sub>4</sub>)<sub>2</sub>S]<sup>−</sup> formed by reaction between Li<sub>2</sub>S<sub>5</sub> and [Re<sub>2</sub>Cl<sub>8</sub>]<sup>2+</sup> in thf.

Electrochemical properties of some mixed ligand thienium complexes involving nitrosyl and chelating ligands such as bipyridyl have been examined.<sup>275</sup>

Treatment of MnX<sub>2</sub>, where X is Br or I, with phosphonium halides gives<sup>276</sup> the complex ion Mn<sub>2</sub>X<sub>6</sub><sup>2+</sup> whose structure is formed from fused tetrahedra. It was also possible to isolate a number of products from thf solutions of MnI<sub>2</sub> and iodine, such as MnI<sub>2</sub>(thf)<sub>3</sub>, [MnI(thf)<sub>5</sub>]I<sub>3</sub>, and [Mn(thf)<sub>6</sub>](I<sub>3</sub>)<sub>2</sub>.<sup>277</sup> A wide range of mixed ligand rhenium species involving NCS and/or SCN with F, Cl, Br, or I have been prepared<sup>278</sup> by oxidative ligand exchange or displacement reactions. Several positional isomers were also separated by ion-exchange chromatography.

Many of the papers dealing with porphyrin ligands are related to molecules of actual, or potential, biological importance. The so-called 'picnic-basket' type of

<sup>265</sup> L. Nagy, T. Gájda, T. Páli, and K. Burger, *Acta Chim. Acad. Sci. Hung.*, 1988, **125**, 403.

<sup>266</sup> M. Ishii, S. Funahashi, and M. Tanaka, *Inorg. Chem.*, 1988, **27**, 3192.

<sup>267</sup> A. Caneschi, D. Gatteschi, P. Rey, and R. Sessoli, *Inorg. Chem.*, 1988, **27**, 1756.

<sup>268</sup> A. Caneschi, D. Gatteschi, J. Laugier, L. Pardi, P. Rey, and C. Zanchini, *Inorg. Chem.*, 1988, **27**, 2027.

<sup>269</sup> J. G. Wilson, *Aust. J. Chem.*, 1988, **41**, 173.

<sup>270</sup> J. G. March and F. Grases, *Can. J. Chem.*, 1988, **66**, 2583.

<sup>271</sup> K. Hashimoto, C. Kabuto, T. Omori, and K. Yoshihara, *Chem. Lett.*, 1988, 1379.

<sup>272</sup> S. F. Colmanet and M. F. McKay, *Inorg. Chim. Acta*, 1988, **147**, 173.

<sup>273</sup> T. A. Hamor, W. Hussain, C. J. Jones, J. A. McCleverty, and A. S. Rothin, *Inorg. Chim. Acta*, 1988, **146**, 181.

<sup>274</sup> F. A. Cotton, P. A. Kibala, and M. Matusz, *Polyhedron*, 1988, **7**, 83.

<sup>275</sup> R. Bhattacharyya, P. S. Roy, and A. K. Dasmahapatra, *J. Chem. Soc., Dalton Trans.*, 1988, 793.

<sup>276</sup> S. Pohl, W. Saak, and P. Stolz, *Z. Naturforsch., Teil B*, 1988, **43**, 171.

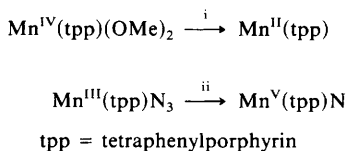
<sup>277</sup> P. Stolz and S. Pohl, *Z. Naturforsch., Teil B*, 1988, **43**, 175.

<sup>278</sup> W. Kelm and W. Preetz, *Z. Anorg. Allg. Chem.*, 1988, **565**, 7.

Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; Mn, Tc, Re

porphyrin have one face sterically shielded and the other face open to influence. Ligand binding studies have been made<sup>279</sup> of Mn<sup>III</sup> examples that show catalytic effects at the open face for olefin epoxidations. Similar cytochrome P-450 model compounds<sup>280</sup> have been shown to control rate, selectivity, and stereoselectivity of reactions by the nature of the axial ligand *trans* to the active site. Other investigations of manganese porphyrins has shown<sup>281</sup> that oxo Mn<sup>IV</sup> complexes can be generated by both chemical and electrochemical oxidation of Mn<sup>III</sup> compounds. These Mn<sup>IV</sup> porphyrins are capable of transferring the oxo group to olefins to make epoxides, and have reactivities quite distinct from their Mn<sup>V</sup>O analogues. In particular, oxygen exchange between the oxo group and water is only slow. The Mn<sup>IV</sup>—O stretching frequency has been located at 754 cm<sup>-1</sup> by the use of resonance Raman spectroscopy.<sup>282</sup>

Pyrolysis experiments<sup>283,284</sup> have been used to generate the porphyrins shown in Scheme 17. The kinetics of the process involved in the transformation of a nitrido to a nitrenoid porphyrin have been followed.<sup>285</sup>



Reagents: i, Δ, 180 °C/10<sup>-4</sup> torr; ii, Δ, 236 °C

Scheme 17

**Cluster Compounds.**—Reaction in toluene between Mn<sub>2</sub>(CO)<sub>10</sub> and Et<sub>3</sub>PTe gives the dimer [(Et<sub>3</sub>P)<sub>2</sub>(CO)<sub>3</sub>MnTe]<sub>2</sub> that has been shown<sup>286</sup> to contain the manganese atoms in a distorted octahedral configuration with *trans*-phosphines, *mer*-carbonyls, and bridged by a ditelluride unit (Mn—Te—Te of 105.5°). Pyrolysis of this product gives MnTe. Treatment of [Mn(CO)<sub>2</sub>Cp\*]<sub>2</sub>(μ-AsCl), where Cp\* represents permethylcyclopentadienyl, with CF<sub>3</sub>SO<sub>3</sub>SiMe<sub>3</sub> gives<sup>287</sup> [{Mn(CO)<sub>2</sub>Cp\*]<sub>2</sub>(μ-As)]CF<sub>3</sub>SO<sub>3</sub> which has been shown to have a near linear Mn—As—Mn bridge (176.3°).

The organization of manganese ions at catalytic sites relevant to photosynthetic processes has been discussed.<sup>288</sup> Spectral evidence seems to favour a cluster with a

<sup>279</sup> J. P. Collman, J. I. Brauman, J. P. Fitzgerald, P. D. Hampton, Y. Naruta, and T. Michida, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 47.

<sup>280</sup> B. Meunier, M.-E. de Carvalho, O. Bartolini, and M. Mometeau, *Inorg. Chem.*, 1988, **27**, 161.

<sup>281</sup> J. T. Groves and M. K. Stern, *J. Am. Chem. Soc.*, 1988, **110**, 8628.

<sup>282</sup> R. S. Czernuszewicz, Y. O. Su, M. K. Stern, K. A. Macor, D. Kim, J. T. Groves, and T. G. Spiro, *J. Am. Chem. Soc.*, 1988, **110**, 4158.

<sup>283</sup> T. Suzuki, T. Imamura, and M. Fujimoto, *Chem. Lett.*, 1988, 257.

<sup>284</sup> Y. Yamamoto, T. Imamura, T. Suzuki, and M. Fujimoto, *Chem. Lett.*, 1988, 261.

<sup>285</sup> L. A. Bottomley and F. L. Neely, *J. Am. Chem. Soc.*, 1988, **110**, 6748.

<sup>286</sup> M. L. Steigerwald and C. E. Rice, *J. Am. Chem. Soc.*, 1988, **110**, 4228.

<sup>287</sup> A. Strube, G. Huttner, and L. Zsolnai, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1529.

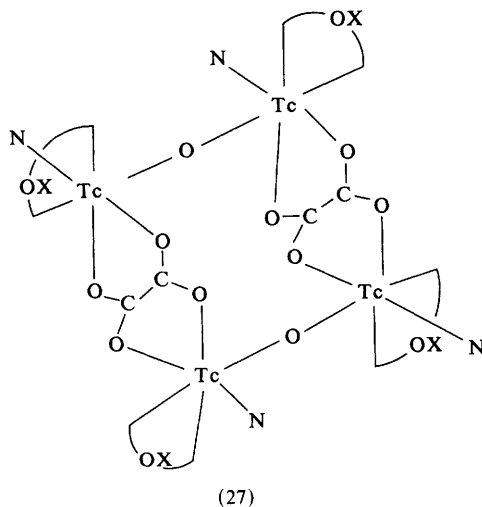
<sup>288</sup> G. C. Dismukes, *Chem. Scr.*, 1988, **28A**, 99.

( $\text{Mn}_4\text{O}_3\text{Cl}$ ) core. Outline structural points about some of the manganese clusters reported<sup>289–294</sup> this year are shown in the Table 1.

**Table 1** Some bridged manganese complexes

Metal atoms	Bridging groups	Ref.
$2\text{Mn}^{\text{III}}$	( $\mu$ -oxo), ( $\mu$ -acetate)	289
$2\text{Mn}^{\text{III}}$	( $\mu$ -oxo), ( $\mu$ -acetate)	290
$\text{Mn}^{\text{III}}, \text{Mn}^{\text{IV}}$	( $\mu$ -oxo)	291
$2\text{Mn}^{\text{IV}}$	( $\mu$ -oxo), ( $\mu$ -acetate)	292
$3\text{Mn}^{\text{III}}$	( $\mu$ -oxo)( $\mu$ -phosphate)	293
$2\text{Mn}^{\text{II}}, 2\text{Mn}^{\text{III}}$	( $\mu$ -oxo)( $\mu$ -carboxylate)	294

Technetium applications are dominated by radiopharmacological uses, such as the reported<sup>295</sup> affinity between the small sulphur-rich proteins, metallothionenes (MT) and  $\text{Tc}^{\text{V}}$ . The MT conjugate with some monoclonal antibodies has been shown to retain the original immunoactivity, and the rapidity of the  $^{99\text{m}}\text{Tc}$  uptake allows labelling to be carried out just prior to use. A tetranuclear technetium cluster,  $[\text{Tc}_4\text{N}_4\text{O}_2(\text{ox})_6]^{4-}$  (27), is formed by reaction of oxalic acid with  $[\text{TcNCl}_4]^-$ , and is notable<sup>296</sup> for the quadridentate bridging oxalates.



<sup>289</sup> Y. Nishida, N. Oshino, and T. Tokii, *Z. Naturforsch., Teil B*, 1988, **43**, 637.

<sup>290</sup> Y. Nishida, *J. Inorg. Biochem.*, 1988, **32**, 277.

<sup>291</sup> K. S. Hagen, W. H. Armstrong, and H. Hope, *Inorg. Chem.*, 1988, **27**, 967.

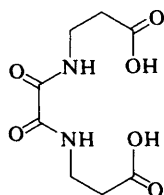
<sup>292</sup> K. Wieghardt, U. Bossek, B. Nuber, J. Weiss, J. Bonvoisin, M. Corbella, S. E. Vitols, and J. J. Girerd, *J. Am. Chem. Soc.*, 1988, **110**, 7398.

<sup>293</sup> K. Wieghardt, U. Bossek, B. Nuber, J. Weiss, S. Gehring, and W. Haase, *J. Chem. Soc., Chem. Commun.*, 1988, 1145.

<sup>294</sup> R. J. Kulawiec, R. H. Crabtree, G. W. Brudvig, and G. K. Schulte, *Inorg. Chem.*, 1988, **27**, 1309.

<sup>295</sup> M. M. Morelock, T. A. Cormier, and G. L. Tolman, *Inorg. Chem.*, 1988, **27**, 3137.

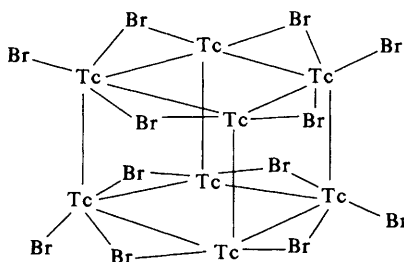
<sup>296</sup> J. Baldas, S. F. Colmanet, and M. F. Mackay, *J. Chem. Soc., Dalton Trans.*, 1988, 1725.



(28)

The ligand ( $H_4L$ ) (28) forms an alternating bimetallic chain compound  $MnCuL(H_2O)_3 \cdot H_2O$  in which the Mn ions have a somewhat distorted octahedral environment whereas the copper ions have a distorted square pyramidal coordination. This product is likely to be the first in a series of species showing interesting and subtly varying magnetic properties.<sup>297</sup>

The rhenium complex  $[ReS_4(CuCl)_3Cl]^{4-}$  adopts<sup>298</sup> a cubane-like cage structure with  $S-Re-S$  of  $110^\circ$  (av.) and heavily distorted tetragonal copper atoms (angles between  $92^\circ$  and  $126^\circ$ ). The structure (29) and properties of a technetium bromide



(29)

cluster  $[Tc_8Br_4(\mu-Br)_8]^+$  have been reported.<sup>299,300</sup> XPS measurements suggest that the metal-metal bonding is much stronger than in many other  $d$ -element clusters.

Structures of some dirhenium compounds  $Re_2Cl_4(Ph_2PCH=CHPh)_2$ <sup>301</sup> and  $[Re_2Cl_4(HCOO)_3]^{-302}$  have been established.

Treatment of  $Re_3(\mu-Cl)_3(CH_2C_6H_4Bu^t-4)_6$  with an excess of  $LiMe$  produces<sup>303</sup>  $Re_3(\mu-Me)_3R_6$  ( $R$  = benzyl group), and mixed chloro/methyl products are obtained by use of a deficiency of the reagent. A central triangular  $Re_3(\mu-X)_3$  unit is common to all these substances.

<sup>297</sup> Y. Pei, O. Kahn, J. Sletten, J.-P. Renard, R. Georges, J.-G. Gianduzzo, J. Curely, and Q. Xu, *Inorg. Chem.*, 1988, **27**, 47.

<sup>298</sup> W. Clegg, C. D. Garner, and C. D. Scattergood, *Acta Cryst.*, 1988, **44C**, 753.

<sup>299</sup> V. I. Spitzin, S. V. Krytchikov, M. S. Grigoriev, and A. F. Kuzina, *Z. Anorg. Allg. Chem.*, 1988, **563**, 136.

<sup>300</sup> S. V. Krytchikov, A. F. Kuzina, and V. I. Spitzin, *Z. Anorg. Allg. Chem.*, 1988, **563**, 153.

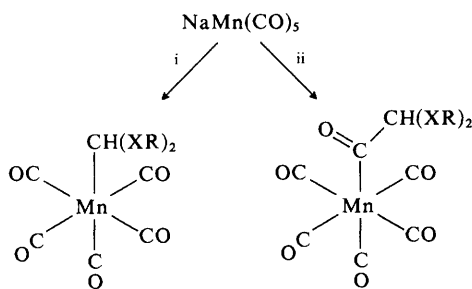
<sup>301</sup> M. Bakir, F. A. Cotton, L. R. Falvello, K. Vidyasagar, and R. A. Walton, *Inorg. Chem.*, 1988, **27**, 2460.

<sup>302</sup> N. S. Osmanov, A. S. Kotelnikova, T. A. Abbasova, B. G. Lebedev, P. A. Kozmin, M. D. Surazhskaya, and T. B. Larina, *Koord. Khim.*, 1988, **14**, 714.

<sup>303</sup> A. C. C. Wong, P. G. Edwards, G. Wilkinson, M. Motevalli, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1988, 219.

Reaction of  $[\text{Re}(\equiv\text{CR})(\text{CO})_2(\text{indenyl})]\text{BF}_4$  with  $[\text{Fe}(\text{CO})_3(\text{NO})]^{2-}$  gives a mixed dimetal complex,<sup>304</sup> but when  $\text{Mo}(\equiv\text{CR})(\text{CO})_2\text{Cp}$  is reacted with  $\text{Re}_2(\mu\text{-H})(\text{CH}=\text{CHBu})(\text{CO})_8$  it gives not a trimetal product but a tetranuclear species<sup>305</sup>  $[\text{Mo}_2\text{Re}_2(\text{CR})_2(\mu\text{-CO})_2(\text{CO})_7\text{Cp}_2]$ .

**Organometallics.**—The gap between organometallic and classical coordination chemistry has been partly bridged in a review of localized and delocalized bonding in polynuclear complexes of the moiety  $\text{Mn}(\text{CO})_2(\text{C}_5\text{R}_5)$ .<sup>306</sup> A general method for the preparation of carbonyl and butenolide products from organomanganese pentacarbonyl complexes has been outlined.<sup>307</sup> Sequential insertion into alkyl- $\text{Mn}(\text{CO})_5$  complexes of carbon monoxide and either alkenes or alkynes at high pressure results in the formation of good yields of acryl-coordinated complexes (manganacycles). Manganese acetal complexes (Scheme 18) have been characterized.<sup>308</sup> The first-order



$\text{RX} = \text{PhO}$  or  $(\text{RX})_2 = 1,2\text{-dioxymethylene}$

Reagents: i,  $(\text{RX})_2\text{CHCl}$ ; ii,  $(\text{RX})_2\text{CHCOCl}$

**Scheme 18**

rate law for ligand substitution by diimine ligands in  $\text{Mn}(\text{CO})_5\text{Br}$  is consistent<sup>309,310</sup> with a limiting dissociative mechanism governed by the rate of loss of a *cis*-CO ligand. In 50% aqueous methanol the dissociation of bromide is also important. The manganese  $\sigma$ -bonded alkyls in Scheme 19 have been characterized<sup>311,312</sup> by crystallographic and e.s.r. procedures. The  $\text{Mn}^{\text{III}}$  species  $[\text{MnOMe}_3]^{2-}$  was isolated as a lithium salt and forms part of a  $\text{Li}-\text{O}$  cluster (12Li and 10 O atoms), with the manganese taking a tetrahedrally-distorted square planar shape. The ions  $[\text{MnMe}_4]^{2-}$  and  $[\text{MnMe}_6]^{2-}$  are tetrahedral and octahedral with  $\text{Mn}-\text{C}$  bond lengths of 2.26 and 2.12 Å respectively.

<sup>304</sup> D. Miguel, U. Steffan, and F. G. A. Stone, *Polyhedron*, 1988, 7, 443.

<sup>305</sup> J. C. Jeffrey, M. J. Parrott, U. Pyell, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 1121.

<sup>306</sup> W. Kaim and R. Goss, *Comments Inorg. Chem.*, 1988, 7, 269.

<sup>307</sup> P. DeShong, D. R. Sidler, P. J. Rybczynski, G. A. Slough, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1988, 110, 2575.

<sup>308</sup> Chr. Löwe, G. Huttner, L. Zsolnai, and H. Berke, *Z. Naturforsch., Teil B*, 1988, 43, 25.

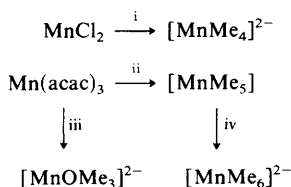
<sup>309</sup> R. bin Ali, J. Burgess, and P. Guardado, *Transition Met. Chem.*, 1988, 13, 126.

<sup>310</sup> G. Schmidt, H. Paulus, R. van Eldick, and H. Elias, *Inorg. Chem.*, 1988, 27, 3211.

<sup>311</sup> R. J. Morris and G. S. Girolami, *Polyhedron*, 1988, 7, 2001.

<sup>312</sup> R. J. Morris and G. S. Girolami, *J. Am. Chem. Soc.*, 1988, 110, 6245.

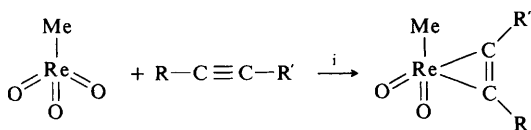
Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; Mn, Tc, Re



Reagents: i, 4LiMe, 2tmed, Et<sub>2</sub>O (tmed = *N,N,N',N'*-tetramethylethylenediamine); ii, 5LiMe, 2tmed; iii, 5LiMe, tmed, Et<sub>2</sub>O; iv, air

Scheme 19

A wide range of products have been identified<sup>313</sup> in the thermolysis at around 200 °C of Re<sub>2</sub>(CO)<sub>10-n</sub>(PPh<sub>3</sub>)<sub>n</sub>, where *n* = 1 or 2. Multinuclear n.m.r. was the main analytical method employed. The use of polymer-bound reagents in reaction with MeRe(O)<sub>3</sub> has been very fruitful (Scheme 20).<sup>314</sup>



R, R' = H, Me, Et, Pr, Bu<sup>t</sup>, C<sub>6</sub>H<sub>5</sub>

Reagent: i, Polymer-bound tri-phenylphosphane

Scheme 20

The eclipsed sandwich compound Re(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub> has been synthesized<sup>315</sup> by a photolytic reaction between rhenium vapour and C<sub>5</sub>Me<sub>5</sub>H. Electronic structures in both solid and solution states were investigated.

<sup>313</sup> H.-J. Haupt, P. Balsaa, and U. Flörke, *Inorg. Chem.*, 198, 27, 280.

<sup>314</sup> J. K. Felixberger, J. G. Kuchler, E. Herdtwerk, R. A. Paciello, and W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1988, 27, 946.

<sup>315</sup> J. A. Bandy, F. G. N. Cloke, G. Cooper, J. P. Day, R. B. Girling, R. G. Graham, J. C. Green, R. Grinter, and R. N. Perutz, *J. Am. Chem. Soc.*, 1988, 110, 5039.