

## 20 Organometallic Chemistry of Monometallic Species

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### 1 Introduction

Important reviews have appeared on monometallic organometallic complexes containing diazo,<sup>1</sup> pyridylphosphine,<sup>2</sup> multidentate isocyanide,<sup>3</sup> and dihydrogen<sup>4</sup> ligands. Reviews on Mo and W 16-electron piano-stool molecules of the type  $[\text{MR}_2(\text{NO})\text{L}]$  (R = alkyl, aryl; L = Cp or Cp\*)<sup>5</sup> and organometallic intermediates<sup>6</sup> also contain material of interest. The use of the *fac*- $\text{Re}^{\text{I}}(\text{CO})_3$  (diimine) chromophore for studying intramolecular electron and energy transfer has been reviewed.<sup>7</sup>

### 2 Ti, Zr, and Hf

The reaction of  $[\text{Ti}(\text{CO})_6]^{2-}$  with  $\text{R}_3\text{SnCl}$  (R = Me, Ph, or Cy) gives the stable anions  $[\text{Ti}(\text{SnR}_3)(\text{CO})_6]^-$ , which are the first examples of this type of titanium carbonyl; the molecular structure of  $[\text{K}(\text{cryptand } 2.2.2)][\text{Ti}(\text{SnCy}_3)(\text{CO})_6]$  has been crystallographically determined.<sup>8</sup> The photopromoted substitution reactions of  $[\text{Ti}(\text{CO})_4(\eta\text{-C}_5\text{R}_5)]^-$  (R = H, Me) with a series of organophosphines afford<sup>9</sup> new zero-valent complexes of the type  $[\text{Ti}(\text{CO})_3(\text{PR}_3)(\eta\text{-C}_5\text{R}_5)]^-$  or  $[\text{Ti}(\text{CO})_2(\text{dmpe})(\eta\text{-C}_5\text{R}_5)]^-$ . The synthesis and molecular structure of the first Group 4 alkyl/alkene hafnium complex,  $[\text{Li}(\text{tmeda})_2][\text{HfEt}_4(\eta^2\text{-C}_2\text{H}_4)]$ , which is an important Ziegler–Natta type intermediate, have been reported.<sup>10</sup> The preparation and X-ray crystal structure of the first stable zirconium alkylidene complex (1), formed *via*  $\alpha$ -hydrogen abstraction, have been described.<sup>11</sup>

The asymmetric epoxidation catalyst (2), which is the first enantiomerically enriched,  $\text{C}_2$  symmetrically bridged  $\text{TiCl}_2$  with homotopic Cp groups, has been synthesized.<sup>12</sup> The unprecedented synthesis of  $\beta$ -substituted zirconacyclobutanes from the thermal rearrangement of diallylpermethylzirconocene and related compounds has

<sup>1</sup> D. Sutton, *Chem. Rev.*, 1993, **93**, 995.

<sup>2</sup> G. R. Newkome, *Chem. Rev.*, 1993, **93**, 2067.

<sup>3</sup> F. E. Hahn, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 650.

<sup>4</sup> D. M. Heinekey and W. J. Oldham, Jr., *Chem. Rev.*, 1993, **93**, 913.

<sup>5</sup> P. Legzdins and J. E. Veltheer, *Acc. Chem. Res.*, 1993, **26**, 41.

<sup>6</sup> R. N. Perutz, *Chem. Soc. Rev.*, 1993, **22**, 361.

<sup>7</sup> K. S. Schanze, D. B. MacQueen, T. A. Perkins, and L. A. Cabana, *Coord. Chem. Rev.*, 1993, **122**, 63.

<sup>8</sup> J. E. Ellis and P. Yuen, *Inorg. Chem.*, 1993, **32**, 4998.

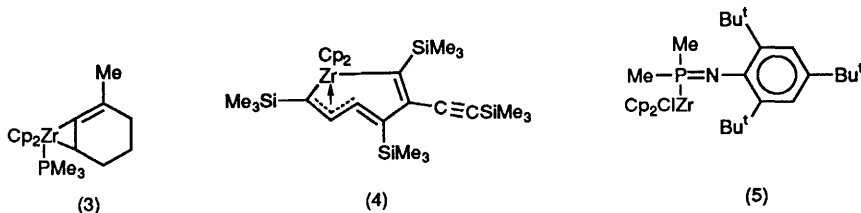
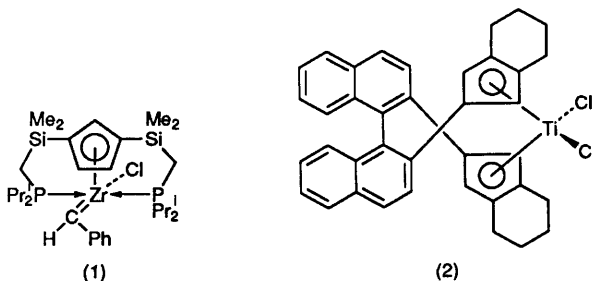
<sup>9</sup> J. E. Ellis, B. K. Stein, and S. R. Frerichs, *J. Am. Chem. Soc.*, 1993, **115**, 4066.

<sup>10</sup> M. D. Spencer, P. M. Morse, S. R. Wilson, and G. S. Girolami, *J. Am. Chem. Soc.*, 1993, **115**, 2057.

<sup>11</sup> M. D. Fryzuk, S. S. H. Mao, M. J. Zaworotko, and L. R. MacGillivray, *J. Am. Chem. Soc.*, 1993, **115**, 5336.

<sup>12</sup> R. L. Halterman and T. M. Ramsey, *Organometallics*, 1993, **12**, 2879.

been described.<sup>13</sup> The unusual  $\eta^3$ -allenyl complex of zirconium(IV), namely  $[\text{ZrMe}\{\eta^3\text{-C(Ph)=C=CH}_2\}\text{Cp}_2]$ , which has been structurally characterized by X-ray crystallography, has been prepared from the reaction of  $[\text{ZrClMeCp}_2]$  with  $\text{PhC}\equiv\text{CCH}_2\text{MgBr}$ .<sup>14</sup> The preparation and molecular structure of (3), which is the first stable allene complex of Zr and the first six-membered-ring-allene-transition-metal complex, have been reported.<sup>15</sup> The seven-membered, cyclic cumulene zirconium complex (4) has been prepared and crystallographically characterized.<sup>16</sup> The preparation and reactivity of (5), the first iminozirconio-phosphorane, a masked iminophosphide, have been described.<sup>17</sup> One or two equivalents of  $\text{Li[PHmes]}$  react with  $[\text{ZrCl}_2(\eta\text{-C}_5\text{Me}_4\text{Et})_2]$  to give the crystallographically characterized complex  $[\text{Zr}\{\text{PmesPmes}\}(\eta\text{-C}_5\text{Me}_4\text{Et})_2]$ ; the molecular structure shows side-on coordination of *trans*-mesP=mes, which is unstable as an uncoordinated ligand.<sup>18</sup> The synthesis and molecular structures of the *ansa*-bridged compounds  $[\text{MClCp}\{\text{Me}_2\text{C}(\eta\text{-C}_5\text{H}_4)_2\}]$  (M = Zr, Hf) have been reported; the hafnium complex is the first tris( $\eta^5$ -cyclopentadienyl) analogue of hafnium.<sup>19</sup> The synthesis and characterization of the novel arene complexes  $[\text{MMe}_2\text{Cp}^*(\eta^6\text{-arene})][\text{BMe}(\text{C}_6\text{F}_5)_3]$  (M = Ti, Zr, Hf; arene =  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_5\text{Me}$ ,  $2,4,6\text{-C}_6\text{H}_3\text{Me}_3$ ,  $\text{C}_6\text{H}_5\text{CH=CH}_2$ ) have been reported.<sup>20</sup> The alkene polymerization catalyst  $[\text{Zr}(\text{CH}_2\text{Ph})_3\{\eta^6\text{-PhCH}_2\}\text{B}(\text{C}_6\text{F}_5)_3]$  reacts with propene initially to give the single-insertion adduct  $[\text{Zr}(\text{CH}_2\text{CHMeCH}_2\text{Ph})(\eta^{\pi}\text{-CH}_2\text{Ph})_2][\text{B}(\text{CH}_2\text{Ph})(\text{C}_6\text{F}_5)_3]$ .<sup>21</sup>



<sup>13</sup> E. B. Tjaden and J. M. Stryker, *J. Am. Chem. Soc.*, 1993, **115**, 2083.

<sup>14</sup> P. W. Blosser, J. C. Gallucci, and A. Wojcicki, *J. Am. Chem. Soc.*, 1993, **115**, 2994.

<sup>15</sup> J. Yin, K. A. Abboud, and W. M. Jones, *J. Am. Chem. Soc.*, 1993, **115**, 3810.

<sup>16</sup> D. P. Hsu, W. M. Davis, and S. L. Buchwald, *J. Am. Chem. Soc.*, 1993, **115**, 10 394.

<sup>17</sup> A. Igau, N. Dufour, A. Mahieu, and J.-P. Majoral, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 95.

<sup>18</sup> S. Kurz and E. Hey-Hawkins, *J. Organomet. Chem.*, 1993, **462**, 203.

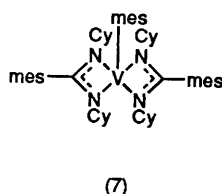
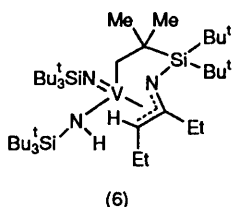
<sup>19</sup> G. M. Diamond, M. L. H. Green, N. A. Popham, and A. N. Chernega, *J. Chem. Soc., Dalton Trans.*, 1993, 2535.

<sup>20</sup> D. J. Gillis, M.-J. Tudoret, and M. C. Baird, *J. Am. Chem. Soc.*, 1993, **115**, 2543.

<sup>21</sup> C. Pellecchia, A. Grassi, and A. Zambelli, *J. Chem. Soc., Chem. Commun.*, 1993, 947.

### 3 V, Nb, and Ta

The preparation and molecular structure of the unusual tetrabromo alkyne complex  $[\text{NEt}_4][\text{NbBr}_4(\text{py})(\eta^2\text{-CF}_3\text{C}\equiv\text{CCF}_3)]$  have been described.<sup>22</sup> Novel [2 + 2] cycloaddition adducts of an imidovanadium complex with ethene and alkynes have been reported; the X-ray crystal structure of (6) reveals this to be the first example of an  $\eta^3$ -azaallyl bonded to a  $d^0$  transition metal.<sup>23</sup> The insertion reactions of carbon monoxide, carbon dioxide, isocyanides, and heterocumulenes into the V–C bond of  $[\text{V}(\text{mes})_3(\text{thf})]$  to give a range of crystallographically characterized complexes, including (7), have been reported.<sup>24</sup> The synthesis, molecular structure, and reactions of the 16-electron complex  $[\text{Ta}(\eta^3\text{-1-phenylallyl})_2\text{Cp}^*]$  have been described; the X-ray structure shows the two allyl groups have supine–supine geometry.<sup>25</sup> The preparation and molecular structures of the unusual tris-selenidotantalum complexes  $[\text{Ta}(\text{Se})_3\text{Li}_3\text{Cl}(\text{thf})_3\text{Cp}^*]$  and  $[\text{Ta}(\text{Se})_3\text{Li}_2(\text{tmeda})_2\text{Cp}^*]$  have been reported.<sup>26</sup>



The complexes  $[\text{NbCl}(\eta^2\text{-C,O-OCRR'})](\eta\text{-C}_5\text{H}_4\text{R})_2]$  ( $\text{R} = \text{H}, \text{SiMe}_3$ ;  $\text{R}' = \text{Me}, \text{Et}, \text{Ph}, \text{etc.}$ ) have been prepared from the electron-rich niobium(III) complexes  $[\text{NbCl}(\eta\text{-C}_5\text{H}_4\text{R})_2]$  and the free ketenes; the molecular structure for  $\text{R} = \text{SiMe}_3$ ,  $\text{R}' = \text{Et}$ ,  $\text{R}'' = \text{Ph}$  shows the *exo-E* geometry in the solid state.<sup>27</sup> The paramagnetic 12-electron complex  $[\text{V}\{\text{CH}(\text{SiMe}_3)_2\}_2\text{Cp}]$  and the 14-electron  $[\text{V}(\text{CH}_2\text{CMe}_2\text{R})_2(\text{PMe}_3)\text{Cp}]$  ( $\text{R} = \text{Me}, \text{Ph}$ ) complexes have been prepared; the complex  $[\text{V}(\text{CH}_2\text{Bu}^t)_2(\text{PMe}_3)\text{Cp}]$  decomposes at ambient temperature in the presence of dmpe to give *via*  $\alpha$ -hydrogen abstraction the first vanadium alkylidene complex,  $[\text{V}(=\text{CHBu}^t)(\text{dmpe})\text{Cp}]$ , which has been crystallographically characterized.<sup>28</sup> Treatment of  $[\text{Nb}(\text{CH}_2\text{SiMe}_3)(\text{CO})\text{Cp}_2]$  with elemental sulfur ( $\text{S}_8$ ) gives the crystallographically characterized complex  $[\text{Nb}(\text{CH}_2\text{SiMe}_3)(\eta^2\text{-COS})\text{Cp}_2]$  by the unprecedented facile addition of sulfur to a metal carbonyl.<sup>29</sup> The reactions of  $[\text{TaH}(=\text{S})(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2]$  with  $\text{HCl}$  and  $\text{PhNCS}$  show an unusually low metal–hydride reactivity; the  $\text{Ta}=\text{S}$  bond undergoes either protonation or [2 + 2] cycloaddition.<sup>30</sup> The

<sup>22</sup> C. Felten, F. Olbrich, and D. Rehder, *Organometallics*, 1993, **12**, 982.

<sup>23</sup> J. de With, A. D. Horton, and A. G. Orpen, *Organometallics*, 1993, **12**, 1493.

<sup>24</sup> M. Vivanco, J. Ruiz, C. Floriani, A. Chiesi-Villa, and C. Rizzoli, *Organometallics*, 1993, **12**, 1794.

<sup>25</sup> K. Mashima, Y. Yamanaka, Y. Gohro, and A. Nakamura, *J. Organomet. Chem.*, 1993, **459**, 131.

<sup>26</sup> K. Tatsumi, H. Kawaguchi, and K. Tani, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 591.

<sup>27</sup> M. C. Fermin, A. S. Hneihen, J. J. Maas, and J. W. Bruno, *Organometallics*, 1993, **12**, 1845.

<sup>28</sup> B. Hessen, J.-K. F. Buijink, A. Meetsma, J. H. Teuben, G. Helgesson, M. Håkansson, S. Jagner, and A. L. Spek, *Organometallics*, 1993, **12**, 2268.

<sup>29</sup> P.-F. Fu, M. A. Khan, and K. M. Nicholas, *Organometallics*, 1993, **12**, 3790.

<sup>30</sup> H. Brunner, M. M. Kubicki, J.-C. Leblanc, C. Moise, F. Volpato, and J. Wachter, *J. Chem. Soc., Chem. Commun.*, 1993, 851.

preparation, molecular structure, and fluxional properties of  $[\text{Nb}(\text{NBu}')(\eta^1\text{-C}_5\text{H}_5)\text{Cp}_2]$  have been reported.<sup>31</sup> The metal-vapour synthesis and crystallographic characterization of the first  $\eta^6$ -pyrazine sandwich complex,  $[\text{V}(\eta^6\text{-Me}_4\text{-pyrazine})_2]$ , have been described.<sup>32</sup>

#### 4 Cr, Mo, and W

The complex  $[\text{Cr}(\text{CO})_5(\eta^2\text{-C}_2\text{H}_4)]$  has been prepared for the first time by UV photolysis of  $[\text{Cr}(\text{CO})_6]$  in supercritical ethene at room temperature.<sup>33</sup> The preparation and molecular structure of  $[\text{PPN}][\text{W}(\eta^1\text{-HCO}_3)(\text{CO})_5]$ , which is an organometallic analogue of carbonic anhydrase, have been described.<sup>34</sup> The neutron structure and also the inelastic neutron scattering of  $[\text{Mo}(\text{CO})(\text{H}_2)\{(\text{C}_6\text{D}_5)_2\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{D}_5)_2\}_2] \cdot 4.5\text{C}_6\text{D}_6$  have been reported; this complex has an extremely low barrier to hydrogen rotation.<sup>35</sup> The preparation, X-ray crystal structure, and reactivity of  $[\text{NEt}_4][\text{W}(\text{CO})_5(\text{PPh}_2\text{CS}_2)]$ , which has unprecedented phosphorus coordination of the diphenyl(dithioformato)phosphine ligand, have been described.<sup>36</sup> Reaction of  $[\text{W}(=\text{NNMe}_2)(\text{CO})_5]$  with *dppm* affords the crystallographically characterized metallocyclic phosphinimine  $[\text{W}(\text{CO})_4\{\text{PPh}_2(\text{CH}_2)\text{PPh}_2\text{N}(\text{NMe}_2\text{-N},\text{P})\}]$ , surprisingly *via* the nucleophilic attack of phosphine at  $\text{N}_\alpha$  of the hydrazido ligand.<sup>37</sup> Isotopic labelling studies show that *trans*, *trans*- $[\text{W}(\text{CO})_2(\text{NH}=\text{NH})(\text{PR}_3)_2(\text{NO})][\text{SO}_3\text{CF}_3]$  ( $\text{R} = \text{Ph}, \text{Cy}$ ) are the first examples in which diazene coordinates as a monodentate ligand to a transition-metal centre.<sup>38</sup>

The synthesis and Diels–Alder and Michael-addition reactions of the first parent alkynyl Fischer carbene complexes of the type  $[\text{M}\{\text{C}(\text{NMe}_2)(\text{C}\equiv\text{CH})\}(\text{CO})_5]$  ( $\text{M} = \text{Cr}, \text{W}$ ) have been reported.<sup>39</sup> The preparation and molecular structure of *trans*- $[\text{W}(\equiv\text{CH})(\text{Bu}^n)(\text{dmpe})_2]$ , which has an unusual  $\text{W}\equiv\text{C}\text{--}\text{H}$  angle of  $162^\circ$  have been described.<sup>40</sup> Reactions of  $[\text{W}\{\text{C}(\text{R})\text{SMe}\}(\text{CO})_2\text{Cp}]^+$  ( $\text{R} = \text{Ph}, p\text{-tol}$ ) with  $\text{X}=\text{C}(\text{NH}_2)_2$  ( $\text{X} = \text{S}, \text{Se}$ ) give the spirocyclic compounds (8) *via* attack at the  $\text{M}=\text{C}_{\text{carbonyl}}$  rather than the  $\text{M}=\text{C}_{\text{carbene}}$  bond.<sup>41</sup> The first stable 2-chromaoxetane complex (9) and its homologues have been prepared from  $\alpha$ -phosphonio(methylidene) complexes of Cr, Mo, and W.<sup>42</sup> The preparation and molecular structure of a new type of tungsten(IV) phenylimido alkylidene complex,  $[\text{W}\{\text{C}=\text{CH}(\text{SiMe}_3)\}(\text{CH}_2\text{SiMe}_3)(=\text{NPh})\{\text{OCPh}_2(2\text{-py})\}]$ , and its triorganotungsten precursor,  $[\text{W}(\text{CH}_2\text{SiMe}_3)_3(=\text{NPh})\{\text{OCPh}_2(2\text{-py})\}]$ , have been reported.<sup>43</sup> The synthesis, X-ray crystal struc-

<sup>31</sup> M. L. H. Green, D. M. Michaelidou, P. Mountford, A. G. Suárez, and L.-L. Wong, *J. Chem. Soc., Dalton Trans.*, 1993, 1593.

<sup>32</sup> W. D. McGhee, A. Sella, D. O'Hare, F. G. N. Cloke, C. Mehnert, and M. L. H. Green, *J. Organomet. Chem.*, 1993, **459**, 125.

<sup>33</sup> J. A. Banister, S. M. Howdle, and M. Poliakoff, *J. Chem. Soc., Chem. Commun.*, 1993, 1814.

<sup>34</sup> D. J. Darensbourg, M. L. M. Jones, and J. H. Reibenspies, *Inorg. Chem.*, 1993, **32**, 4675.

<sup>35</sup> G. J. Kubas, C. J. Burns, J. Eckert, S. W. Johnson, A. C. Larson, P. J. Vergamini, C. J. Unkefer, G. R. K. Khalsa, S. A. Jackson, and O. Eisenstein, *J. Am. Chem. Soc.*, 1993, **115**, 569.

<sup>36</sup> K.-H. Yih, Y.-C. Lin, M.-C. Cheng, and Y. Wang, *J. Chem. Soc., Chem. Commun.*, 1993, 1380.

<sup>37</sup> B. A. Arndtsen, H. F. Sleiman, L. McElwee-White, and A. L. Rheingold, *Organometallics*, 1993, **12**, 2440.

<sup>38</sup> M. R. Smith, III, T.-Y. Cheng, and G. L. Hillhouse, *J. Am. Chem. Soc.*, 1993, **115**, 8638.

<sup>39</sup> A. Rahm, W. D. Wulff, and A. L. Rheingold, *Organometallics*, 1993, **12**, 597.

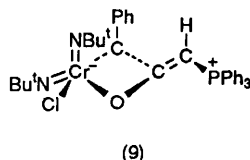
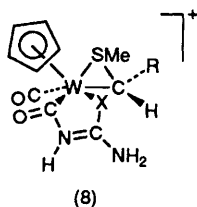
<sup>40</sup> J. Manna, S. J. Geib, and M. D. Hopkins, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 858.

<sup>41</sup> F. R. Kreissl, W. Schütt, J. Ostermeier, and E. Herdtweck, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1152.

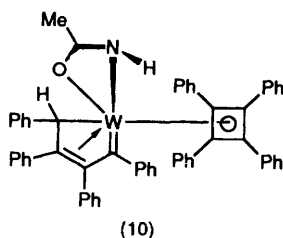
<sup>42</sup> J. Sundermeyer, K. Weber, and H. Pritzkow, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 731.

<sup>43</sup> P. A. van der Schaaf, R. A. T. M. Abbenhuis, D. M. Grove, W. J. J. Smeets, A. L. Spek, and G. van Koten, *J. Chem. Soc., Chem. Commun.*, 1993, 504.

ture, and reactivity of the  $d^2$  pseudo-metallocene complex  $[\text{Mo}(\text{N}-2,6\text{-Pr}_2\text{C}_6\text{H}_3)_2(\text{PMe}_3)_2]$  have been described.<sup>44</sup> Treatment of  $[\text{W}(\text{Te})_2(\text{PMe}_3)_2(\eta^2\text{-OCHR})]$  ( $\text{R} = \text{H}, \text{Ph}$ ) with  $\text{Bu}^+\text{NC}$  yields the structurally characterized  $\eta^2$ -ditellurido complex  $[\text{W}(\text{CNBu}^+)_4(\text{PMe}_3)(\eta^2\text{-Te}_2)]$  via the unprecedented coupling of the *cis*-tellurido ligands.<sup>45</sup>



Reaction of *trans*- $[\text{M}(\equiv\text{CNHMe})(\text{CNMe})(\text{dppe})_2][\text{BF}_4]$  ( $\text{M} = \text{Mo}, \text{W}$ ) with  $[\text{Et}_2\text{OH}][\text{BF}_4]$  affords the bis(amino)alkyne complexes *trans*- $[\text{MF}(\text{dppe})_2(\eta^2\text{-MeHNC}\equiv\text{CNHMe})][\text{BF}_4]$ , which for  $\text{M} = \text{Mo}$  has been structurally characterized; these complexes, previously formulated as *trans*- $[\text{M}(\text{CNHMe})_2(\text{dppe})_2][\text{BF}_4]_2$ , were actually the first examples illustrating the now well-established reductive coupling of isocyanide ligands.<sup>46</sup> The preparation and reactions with neutral donor ligands of the unusual alkyne complexes  $[\text{MoCl}(\text{GeCl}_3)(\text{CO})(\text{NCMe})(\text{PPh}_3)(\eta^2\text{-RC}\equiv\text{CR})]$  ( $\text{R} = \text{Me}, \text{Ph}$ ), which contain six different monodentate ligands, have been described.<sup>47</sup> Treatment of *fac*- $[\text{W}(\text{CO})_3(\text{NCMe})_3]$  or  $[\text{W}(\text{CO})(\eta^2\text{-PhC}\equiv\text{CPh})_3]$  with an excess of  $\text{PhC}\equiv\text{CPh}$  gives the crystallographically characterized complex  $[\text{W}(\text{CO})(\eta^2\text{-PhC}\equiv\text{CPh})\{\eta^5\text{-C}_3\text{Ph}_3(\text{C}_5\text{Ph}_5)\}]$ , which contains a novel cyclopentadienylvinylcarbene moiety, formed from the coupling of four alkyne ligands on the tungsten.<sup>48</sup> Hydrolysis of  $[\text{W}(\text{NCMe})(\eta^2\text{-PhC}\equiv\text{CPh})_2(\eta^4\text{-C}_4\text{Ph}_4)]$  in alkaline solution yields the crystallographically characterized complex (10) via alkyne-alkyne coupling and



hydration of the acetonitrile ligand.<sup>49</sup> The four-electron donor nitrile complexes  $[\text{WCl}(\text{PMe}_3)_2(\text{bipy})(\eta^2\text{-N}\equiv\text{CR})][\text{PF}_6]$  ( $\text{R} = \text{Me}, \text{Bu}^+, \text{Ph}$ ) and  $[\text{WCl}_2(\text{PMe}_3)_3(\eta^2\text{-$

<sup>44</sup> P. W. Dyer, V. C. Gibson, J. A. K. Howard, and C. Wilson, *J. Organomet. Chem.*, 1993, **462**, C15.

<sup>45</sup> D. Rabinovich and G. Parkin, *J. Am. Chem. Soc.*, 1993, **115**, 9822.

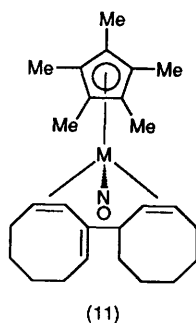
<sup>46</sup> J. J. R. F. da Silva, M. A. Pellinghelli, A. J. L. Pombeiro, R. L. Richards, A. Tiripicchio, and Y. Wang, *J. Organomet. Chem.*, 1993, **454**, C8.

<sup>47</sup> P. K. Baker and D. ap Kendrick, *J. Chem. Soc., Dalton Trans.*, 1993, 1039.

<sup>48</sup> W.-Y. Yeh, S.-M. Peng, and G.-H. Lee, *J. Chem. Soc., Chem. Commun.*, 1993, 1056.

<sup>49</sup> W.-Y. Yeh, S.-M. Peng, and L.-K. Liu, *Inorg. Chem.*, 1993, **32**, 2965.

$\text{N}\equiv\text{CMe}]$ , which has been crystallographically characterized, have been reported.<sup>50</sup> The preparation, molecular structure, and redox properties of the paramagnetic complex  $[\text{Cr}(\text{CO})_3(\eta^5\text{-C}_5\text{Ph}_5)]$  have been described.<sup>51</sup> A detailed study of the synthesis and reactions, including nitrogen–nitrogen bond cleavage, of a series of high oxidation state tungsten hydrazine and hydrazido complexes, such as the crystallographically characterized  $[\text{WMe}_3(\eta^2\text{-MeNNMe})\text{Cp}^*]$ , has been made.<sup>52</sup> Reaction of  $[\text{W}(\text{CH}_2\text{SiMe}_3)_2(\text{NO})\text{Cp}]$  with  $[\text{CPh}_3][\text{PF}_6]$  gives *via* cleavage of the Si–C bond the unsymmetrical dialkyl complex  $[\text{W}(\text{CH}_2\text{SiMe}_3)(\text{CH}_2\text{CPh}_3)(\text{NO})\text{Cp}]$ , which is thermally unstable and in MeCN converts into the metallocyclic complex  $[\text{W}\{\text{CH}_2\text{C}(\text{C}_6\text{H}_4)\text{Ph}_2\}(\text{NCMe})(\text{NO})\text{Cp}]$ ; both of these complexes have been crystallographically characterized.<sup>53</sup> Treatment of  $[\text{M}(\text{CH}_2\text{SiMe}_3)_2(\text{NO})\text{Cp}^*]$  ( $\text{M} = \text{Mo}, \text{W}$ ) with  $\text{H}_2$  in the presence of cycloocta-1,3-diene yields, after the unprecedented coupling of two cycloocta-1,3-dienes in the coordination sphere of the metals, the complexes (11), of which the molybdenum case has been crystallographically characterized.<sup>54</sup>



The preparation and  $^1\text{H}$  NMR spectroscopic characterization of the polyhydride complex  $[\text{MoH}_5(\text{PMe}_3)\text{Cp}^*]$ , which has a pentagonal bipyramidal structure and a long  $T_1$  relaxation time, have been reported.<sup>55</sup> Treatment of  $[\text{MoBr}(\eta^2\text{-MeC}\equiv\text{CR})_2\text{Cp}]$  ( $\text{R} = \text{Me}, \text{Ph}$ ) with  $\text{Li}[\text{N}(\text{SiMe}_3)_2]$  results in dehydrohalogenation and the surprising formation of the three-electron  $\sigma, \eta^2$ -prop-2-ynyl complexes  $[\text{Mo}(\sigma, \eta^2\text{-CH}_2\text{C}_2\text{R})(\eta^2\text{-MeC}\equiv\text{CR})\text{Cp}]$ , which reacts with CO (for  $\text{R} = \text{Me}$ ) to afford the crystallographically characterized  $[\text{Mo}\{\eta^2, \eta^3\text{-}\overline{\text{C}}(\text{Me})\text{C}(\text{O})\text{C}(\text{Me})\text{C}(\text{Me})\text{CH}_2\}(\text{CO})\text{Cp}]$  *via* a novel C–C bond forming reaction.<sup>56</sup> Reaction of  $[\text{MoBr}(\text{CO})(\eta^2\text{-MeC}\equiv\text{CMe})\text{Cp}]$  with isoprene and  $\text{Ag}[\text{BF}_4]$  gives *via* a C–C coupling reaction the crystallographically characterized complex  $[\text{Mo}\{\eta^3, \eta^3\text{CH}(\text{Me})\text{C}(\text{Me})\text{CHCHC}(\text{Me})\text{-}$

<sup>50</sup> J. Barrera, M. Sabat, and W. D. Harman, *Organometallics*, 1993, **12**, 4381.

<sup>51</sup> R. J. Hoobler, M. A. Hutton, M. M. Dillard, M. P. Castellani, A. L. Rheingold, A. L. Rieger, P. H. Rieger, T. C. Richards, and W. E. Geiger, *Organometallics*, 1993, **12**, 116.

<sup>52</sup> R. R. Schrock, T. E. Glassman, M. G. Vale, and M. Kol, *J. Am. Chem. Soc.*, 1993, **115**, 1760.

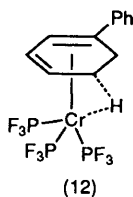
<sup>53</sup> N. Brunet, J. D. Debad, P. Legzdins, J. Trotter, J. E. Veltheer, and V. C. Yee, *Organometallics*, 1993, **12**, 4572.

<sup>54</sup> J. D. Debad, P. Legzdins, M. A. Young, R. J. Batchelor, and F. W. B. Einstein, *J. Am. Chem. Soc.*, 1993, **115**, 2051.

<sup>55</sup> F. Abugideiri, M. A. Kelland, and R. Poli, *Organometallics*, 1993, **12**, 2388.

<sup>56</sup> C. Carfagna, M. Green, M. F. Mahon, S. Rumble, and C. M. Woolhouse, *J. Chem. Soc., Chem. Commun.*, 1993, 879.

$\text{CH}_2\{\text{CO}\}\text{Cp}][\text{BF}_4]$ , which has an unusual  $\eta^3, \eta^3$ -coordinated hexatrienyl ligand.<sup>57</sup> Novel highly stereoselective C–C bond forming reactions initiated by oxoallylmolybdenum complexes have also been described; the molecular structures of  $[\text{Mo}(\text{CO})_2\{\eta^3\text{-CH}_2\text{C}(\text{Ph})=\text{CH}(\text{COPh})\}\text{Cp}]$  and  $[\text{Mo}(\text{CO})_2\{\eta^3\text{-CH}_2\text{C}(\text{Ph})\text{CHC}(\text{Ph})=\text{CH}(\text{COPh})\}\text{Cp}]$  are also discussed in this paper.<sup>58</sup> The first synthesis of sulfinyl-substituted tricarbonyl( $\eta^6$ -arene)chromium(0) complexes, including the crystallographically characterized  $[\text{Cr}(\text{CO})_3\{\eta^6\text{-1-(t-butylsulfinyl)-2-methoxybenzene}\}]$ , has been reported.<sup>59</sup> Sequential nucleophile/proton addition reactions of  $[\text{Cr}(\text{PF}_3)_3(\eta^6\text{-C}_6\text{H}_6)]$  give highly fluxional, agostic cyclohexadiene complexes such as (12), which has been crystallographically characterized.<sup>60</sup>



## 5 Mn, Tc, and Re

Reaction of  $[\text{ReX}(\text{CO})_5]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) with terpy under mild conditions affords the fluxional complexes *fac*- $[\text{ReX}(\text{CO})_3(\eta^2\text{-terpy})]$ , of which the bromine case was crystallographically characterized; under more vigorous conditions ( $\text{X} = \text{Br}$ ) the tridentate complex *cis*- $[\text{ReBr}(\text{CO})_2(\eta^3\text{-terpy})]$  is obtained.<sup>61</sup> The synthesis and molecular structures of the thiocarbonyl complexes  $[\text{Re}(\text{CS})(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNEt}_2)]$  and  $[\text{Re}(\text{CS})(\text{S}_2\text{CNEt}_2)_3]$ , formed from decomposition of the dithiocarbamates during their reaction with  $[\text{ReCl}_3(\text{PMe}_2\text{Ph})_3]$ , have been described.<sup>62</sup> The alkoxide complexes *fac*- $[\text{M}(\text{OR})(\text{CO})_3(\text{L-L})]$  ( $\text{M} = \text{Mn}, \text{Re}$ ;  $\text{R} = \text{Me}, \text{Et}, \text{CH}_2\text{CF}_3$ ;  $\text{L-L} = \text{dppe}, \text{dppp}$ ) react reversibly with  $\text{CO}_2$ , (including that from the atmosphere) to give the carbonato complexes *fac*- $[\text{M}(\text{CO})_3(\text{L-L})\{\text{OC}(\text{O})\text{OR}\}]$ , of which the  $\text{M} = \text{Mn}$ ,  $\text{R} = \text{Me}$ ,  $\text{L-L} = \text{dppe}$  example has been crystallographically characterized.<sup>63</sup> Treatment of *syn*- $[\text{Re}(\equiv\text{CBu}^t)(=\text{CHBu}^t)(\text{OR})_2]$  [ $\text{R} = \text{Bu}^t, \text{CMe}_2(\text{CF}_3)$ ] with ethene yields at low temperatures the trigonal bipyramidal complexes (13) and at higher temperatures the rhenacyclopentene complexes (14) *via* cycloaddition reactions.<sup>64</sup> Reaction of the complexes  $[\text{Re}(\text{O})\text{R}_3(\text{PMe}_3)]$  ( $\text{R} = \text{Me}, \text{CH}_2\text{SiMe}_3$ ) and *cis*- $[\text{Re}(\text{O})\text{Me}_2\text{Cl}(\text{PMe}_2\text{R})_2]$  ( $\text{R} = \text{Me}, \text{Ph}$ ) with ethyne yields  $[\text{Re}(\text{O})\text{R}_3\{\text{CH}=\text{CH}(\text{PMe}_3)\}]$  and  $[\text{Re}(\text{O})\text{Me}_2\{\text{CH}=\text{CH}(\text{PMe}_2\text{R})_2\}]\text{Cl}$ , respectively, as a result of insertion of  $\text{HC}\equiv\text{CH}$  into the  $\text{Re-P}$  bonds;  $[\text{Re}(\text{O})\text{Me}_3(\text{PMe}_3)]$  reacts

<sup>57</sup> C. Carfagna, M. Green, K. R. Nagle, D. J. Williams, and C. M. Woolhouse, *J. Chem. Soc., Dalton Trans.*, 1993, 1761.

<sup>58</sup> J. W. Faller and Y. Ma, *Organometallics*, 1993, 12, 1927.

<sup>59</sup> A. Pérez-Encabo, S. Perrio, A. M. Z. Slawin, S. E. Thomas, A. T. Wierchleyski, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1993, 1059.

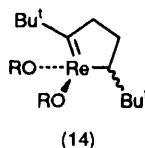
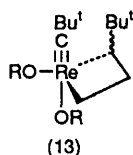
<sup>60</sup> E. P. Kündig, D. Amurrio, G. Bernardinelli, and R. Chowdhury, *Organometallics*, 1993, 12, 4275.

<sup>61</sup> E. W. Abel, V. S. Dimitrov, N. J. Long, K. G. Orrell, A. G. Osborne, H. M. Pain, V. Šik, M. B. Hursthouse, and M. A. Mazid, *J. Chem. Soc., Dalton Trans.*, 1993, 597.

<sup>62</sup> U. Abram and B. Lorenz, *Z. Naturforsch., B Chem. Sci.*, 1993, 48, 771.

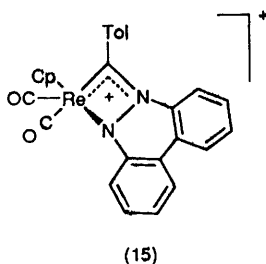
<sup>63</sup> S. K. Mandal, D. M. Ho, and M. Orchin, *Organometallics*, 1993, 12, 1714.

<sup>64</sup> G. A. Vaughan, R. Toreki, R. R. Schrock, and W. M. Davis, *J. Am. Chem. Soc.*, 1993, 115, 2980.



with  $\text{RC}\equiv\text{CR}'$  ( $\text{R} = \text{R}' = \text{Me, Et, Ph}$ ;  $\text{R} = \text{Me, Ph}$ ;  $\text{R}' = \text{H}$ ) to give the alkyne complexes  $[\text{Re}(\text{O})\text{Me}_3(\eta^2\text{-RC}\equiv\text{CR}')]^{65}$

Protonation of the N-pyrrolyl complex  $[\text{Re}(\text{NC}_4\text{H}_4)(\text{PPh}_3)(\text{NO})\text{Cp}]$  with  $\text{HOTf}$  or  $\text{H}[\text{BF}_4]\cdot\text{OEt}_2$  affords the 2H-pyrrole complexes  $[\text{Re}(\text{N}=\text{CHCH}=\text{CHCH}_2)(\text{PPh}_3)(\text{NO})\text{Cp}]\text{X}$ , which rearrange to the carbon-bonded complexes  $[\text{Re}(\text{C}=\text{NHCH}_2\text{CH}=\text{CH})(\text{PPh}_3)(\text{NO})\text{Cp}]\text{X}$ , of which the case for  $\text{X} = \text{OTf}$  has been crystallographically characterized.<sup>66</sup> A series of high oxidation state rhenium complexes that contain ammonia, amido, hydrazine, and hydrazido ligands, derived from  $[\text{ReMe}_3(\text{OTf})\text{Cp}^*]$  and including  $[\text{ReMe}_3(\text{NH}_3)\text{Cp}^*][\text{OTf}]$ , has been reported.<sup>67</sup> The addition and cycloaddition reactions of  $[\text{Re}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2\text{Cp}]$  with propylene sulfide, benzophenone hydrazone, 3,3-dimethyloxetane, 2-methylaziridine, *cis*-azoarenes, epoxides, and benzo[*c*]cinnoline to give a range of novel products, including (15), have been described.<sup>68</sup> The reversible oxidation of norbornene using  $[\text{ReO}_3\text{Cp}^*]$  has been reported.<sup>69</sup> The preparation and X-ray structure of the trimethylsilyl example of  $[\text{Mn}(\text{CO})_3\{\text{exo}-(\text{RCN}_2)-\eta^5\text{-C}_6\text{H}_6\}]$  [ $\text{R} = \text{SiMe}_3$ ,  $(\text{Pr}^i\text{N})_2\text{P}(\text{S})$ ], which are the first examples of a diazo-functionalized ligand on a transition-metal complex, have been described.<sup>70</sup> Treatment of  $[\text{ReH}_7(\text{PPh}_3)_2]$  with indene affords the expected minor product,  $[\text{ReH}_2(\text{PPh}_3)_2(\eta^5\text{-C}_9\text{H}_7)]$ , and the unexpected major product,  $[\text{ReH}_2(\text{PPh}_3)_2(\eta^5\text{-C}_9\text{H}_{11})]$ , in which the Re is  $\eta^5$ -bonded to the six-membered ring.<sup>71</sup> The complexes  $[\text{Mn}(\text{CO})\text{LL}'(\text{endo-}\eta^5\text{-C}_6\text{Me}_n\text{H}_{7-n})]$  ( $n = 0, 3, 6$ ;  $\text{L}, \text{L}' = \text{CO}, \text{PR}_3$ ) transfer hydride to COS and  $\text{CS}_2$  to afford  $\text{HC}(\text{O})\text{S}^-$  and  $\text{HCS}_2^-$ , respectively,<sup>72</sup> and the cationic organometallic complexes  $[\text{Mn}(\text{CO})\text{LL}'(\eta^6\text{-C}_6\text{Me}_n\text{H}_{6-n})]^+$ .



<sup>65</sup> D. M. Hoffman, J. C. Huffman, D. Lappas, and D. A. Wierda, *Organometallics*, 1993, **12**, 4312.

<sup>66</sup> T. J. Johnson, A. M. Arif, and J. A. Gladysz, *Organometallics*, 1993, **12**, 4728.

<sup>67</sup> M. G. Vale and R. R. Schrock, *Organometallics*, 1993, **12**, 1140.

<sup>68</sup> L. A. Mercado, B. M. Handwerker, H. J. MacMillan, G. L. Geoffroy, A. L. Rheingold, and B. E. Owens-Waltermire, *Organometallics*, 1993, **12**, 1559.

<sup>69</sup> K. P. Gable and T. N. Phan, *J. Am. Chem. Soc.*, 1993, **115**, 3036.

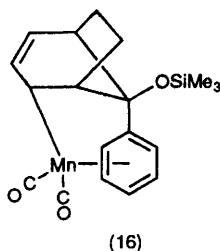
<sup>70</sup> R. Réau, R. W. Reed, F. Dahan, and G. Bertrand, *Organometallics*, 1993, **12**, 1501.

<sup>71</sup> G. P. Rosini and W. D. Jones, *J. Am. Chem. Soc.*, 1993, **115**, 965.

<sup>72</sup> D. B. Snyder, S. J. Schauer, D. P. Eyman, J. L. Moler, and J. J. Weers, *J. Am. Chem. Soc.*, 1993, **115**, 6718.



Reaction of  $[\text{Mn}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]$  with  $\text{PhLi}$  gives the acyl complex  $[\text{Li}(\text{OEt}_2)_2][\text{Mn}(\text{CO})_2\{\text{C}(\text{O})\text{Ph}\}(\eta^5\text{-C}_7\text{H}_9)]$ , which reacts with  $\text{Me}_3\text{SiCl}$  to afford the bicyclo[3.2.1]oct-2-ene complex (16) *via* intramolecular carbene–cycloheptadienyl coupling. Complex (16) reacts with  $\text{PPh}_3$  to yield an unusual complex,  $[\text{Mn}(\text{CO})_2(\text{PPh}_3)\{\eta^3\text{-C}_8\text{H}_9(\text{OSiMe}_3)(\eta^2\text{-Ph})\}]$ , which X-ray crystallography shows has a distorted  $\text{Mn-}\eta^2$ -arene moiety.<sup>73</sup> The metal-vapour synthesis of  $[\text{Mn}(\eta^6\text{-C}_6\text{H}_5\text{Me})_2]\text{I}$ , which is the first structurally characterized bis(arene) $\text{Mn}$  complex, has been described.<sup>74</sup>



## 6 Fe, Ru, and Os

The dehydrohalogenation of  $[\text{RuRCl}(\text{CO})(\text{PMeBu}_2)_2]$  ( $\text{R} = \text{H}$  and  $\text{D}$ ) with  $\text{LiBu}^n$  at low temperature in the presence of  $\text{CH}_2=\text{CHMe}$  affords the rigid complex  $[\text{RuH}(\text{CO})(\text{PMeBu}_2)_2(\eta^3\text{-C}_3\text{H}_5)]$ , which suggests that these are examples of an allylic C–H bond being attacked by a zero-valent ruthenium species.<sup>75</sup> Reaction of  $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$  with  $\text{Sn}(\text{CH}=\text{CH}_2)\text{R}_3$  ( $\text{R} = \text{Me}$ , *p*-tol) yields the coordinatively unsaturated complexes  $[\text{RuCl}(\text{SnR}_3)(\text{CO})(\text{PPh}_3)_2]$  (crystallographically characterized for  $\text{R} = \text{Me}$ ), most likely by insertion of the vinylstannane into the Ru–H bond and a  $\beta$ -stannyl elimination from the resulting  $\beta$ -stannylethyl compound.<sup>76</sup> The 1,3-dipolar cycloaddition reactions of alkynes to  $[\text{Fe}(\text{CO})_2(\text{CNR})(\alpha\text{-diimine})]$ <sup>77</sup> and  $[\text{Fe}(\text{CNR})_3(\alpha\text{-diimine})]$ <sup>78</sup> give a wide range of novel products including (17),<sup>78</sup> of which the  $\text{R} = 2,6\text{-xylyl}$  case was crystallographically characterized. The preparation and molecular structure of the arsaalkyne tetramer  $[\{\text{AsCBu}^1\}_4]$  and its  $\text{Fe}(\text{CO})_4$  derivative (18) have been reported.<sup>79</sup> Treatment of  $[\text{Fe}\{\text{C}(\text{=O})\text{NPr}_2\}\text{CF}_3(\text{CO})_2(\text{PPh}_3)]$  with  $\text{KTp}$  gives the crystallographically characterized ferroxetene complex  $[\text{Fe}\{\text{CF}_2\text{OC}(\text{NPr}_2)\}(\text{CO})\text{Tp}]$ , probably *via* coupling of a difluorocarbene intermediate and the carbamoyl ligand.<sup>80</sup> The preparation, structures, and electron-transfer chemistry of a series of stable iron(I) and iron(II)  $\sigma$ -alkynyl complexes of

<sup>73</sup> C. Wang, J. B. Sheridan, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1993, **115**, 3603.

<sup>74</sup> D. O'Hare, V. Murphy, A. Bland, and P. Scott, *J. Organomet. Chem.*, 1993, **443**, C37.

<sup>75</sup> R. H. Heyn and K. G. Caulton, *J. Am. Chem. Soc.*, 1993, **115**, 3354.

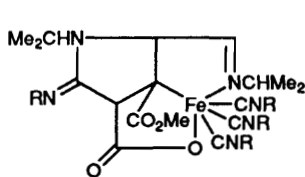
<sup>76</sup> G. R. Clark, K. R. Flower, W. R. Roper, and L. J. Wright, *Organometallics*, 1993, **12**, 259.

<sup>77</sup> P. P. M. de Lange, H.-W. Frühauf, M. J. A. Kraakman, M. van Wijnkoop, M. Kranenburg, A. H. J. P. Groot, K. Vrieze, J. Fraanje, Y. Wang, and M. Numan, *Organometallics*, 1993, **12**, 417.

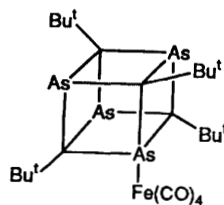
<sup>78</sup> P. P. M. de Lange, M. van Wijnkoop, H.-W. Frühauf, K. Vrieze, and K. Goubitz, *Organometallics*, 1993, **12**, 428.

<sup>79</sup> P. B. Hitchcock, J. A. Johnson, and J. F. Nixon, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 103.

<sup>80</sup> S. Anderson, A. F. Hill, A. M. Z. Slawin, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1993, 266.

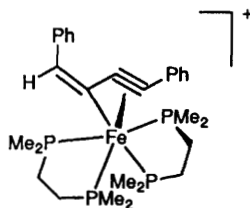


(17)



(18)

the type  $[\text{Fe}(\text{C}\equiv\text{CR})\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]^{n+}$  ( $n = 0, 1$ ;  $\text{R} = \text{Bu}^t, \text{Pr}^n, \text{SiMe}_3, \text{Pe}^n, \text{Ph}$ ) have been described.<sup>81</sup> Treatment of  $[\text{RuH}(\text{dippe})_2][\text{BPh}_4]$  with  $\text{RC}\equiv\text{CH}$  ( $\text{R} = \text{Ph}, \text{CO}_2\text{Me}$ ) affords the dihydrogen complexes  $[\text{Ru}(\text{C}\equiv\text{CR})(\eta^2\text{-H}_2)(\text{dippe})_2][\text{BPh}_4]$ , of which the  $\text{R} = \text{Ph}$  example is the first crystallographically characterized alkynyl-dihydrogen complex.<sup>82</sup> The preparation and reactions of the related complexes  $[\text{OsH}(\text{C}\equiv\text{CR})(\eta^2\text{-H}_2)(\text{CO})(\text{PPr}_3)_2]$  ( $\text{R} = \text{Ph}, \text{SiMe}_3$ ) have been reported.<sup>83</sup> Reactions of  $[\text{FeH}(\eta^2\text{-H}_2)(\text{dmpe})_2][\text{BPh}_4]$  and  $[\text{FeH}(\eta^2\text{-H}_2)(\text{depe})_2][\text{BPh}_4]$  with  $\text{RC}\equiv\text{CH}$  ( $\text{R} = \text{Me}, \text{Pr}^i, \text{Ph}$ ) give a variety of complexes, including (19), which has been crystallographically characterized.<sup>84</sup> The secondary allenylidene complexes *trans*- $[\text{Ru}(\text{C}=\text{C}=\text{CHR})\text{Cl}(\text{dppm})_2][\text{PF}_6]$  ( $\text{R} = \text{Ph}, p\text{-ClC}_6\text{H}_4, \text{trans-CH}=\text{CHPh}$ ) with  $\text{Na}[\text{BH}_4]$  ( $\text{R} = \text{Ph}$ ) and  $\text{Na}[\text{OMe}]$  ( $\text{R} = \text{Ph}, p\text{-ClC}_6\text{H}_4, p\text{-MeOC}_6\text{H}_4$ ) to yield *trans*- $[\text{Ru}(\text{C}\equiv\text{CCH}_2\text{Ph})\text{Cl}(\text{dppm})_2]$  and *trans*- $[\text{Ru}\{\text{C}\equiv\text{CCH}(\text{OMe})\text{R}\}\text{H}(\text{dppm})_2]$ , respectively.<sup>85</sup> The preparation and molecular structures of the related complexes *trans*- $[\text{Ru}(\text{C}=\text{CH}_2)\text{Cl}(\text{dppm})_2][\text{PF}_6]$  and *trans*- $[\text{Ru}(\text{C}\equiv\text{CH})\text{Cl}(\text{dppm})_2]$  have been reported.<sup>86</sup>



(19)

The reaction intermediates  $[\text{Ru}(\text{H}_2\text{O})_5(\eta^2\text{-CH}_2=\text{CH}_2)][p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3]_2$  and  $[\text{Ru}(\text{H}_2\text{O})_4(\eta^2\text{-CH}_2=\text{CH}_2)_2][p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3]_2$  in the aqueous dimerization of ethylene by  $[\text{Ru}(\text{H}_2\text{O})_6][p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3]_2$  have been isolated and characterized in the solid state.<sup>87</sup> The synthesis and X-ray crystal structure of the first stable

<sup>81</sup> C. Bianchini, F. Laschi, D. Masi, F. M. Ottaviani, A. Pastor, M. Peruzzini, P. Zanello, and F. Zanobini, *J. Am. Chem. Soc.*, 1993, **115**, 2723.

<sup>82</sup> M. J. Tenorio, M. C. Puerta, and P. Valerga, *J. Chem. Soc., Chem. Commun.*, 1993, 1750.

<sup>83</sup> J. Espuelas, M. A. Esteruelas, F. J. Lahoz, L. A. Oro, and C. Valero, *Organometallics*, 1993, **12**, 663.

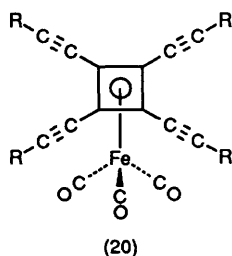
<sup>84</sup> D. L. Hughes, M. J. Jimenez-Tenorio, G. J. Leigh, and A. T. Rowley, *J. Chem. Soc., Dalton Trans.*, 1993, 3151.

<sup>85</sup> N. Pirio, D. Touchard, and P. H. Dixneuf, *J. Organomet. Chem.*, 1993, **462**, C18.

<sup>86</sup> D. Touchard, P. Haquette, N. Pirio, L. Toupet, and P. H. Dixneuf, *Organometallics*, 1993, **12**, 3132.

<sup>87</sup> G. Laurenczy and A. E. Merbach, *J. Chem. Soc., Chem. Commun.*, 1993, 187.

ethene-ethyne transition-metal complex, *trans*-[Os(en)<sub>2</sub>(η<sup>2</sup>-CH<sub>2</sub>=CH<sub>2</sub>)(η<sup>2</sup>-HC≡CH)]Cl<sub>2</sub>·2H<sub>2</sub>O, have been described.<sup>88</sup> The solution structure and reactivity of the catalytically significant η<sup>3</sup>-allyl hydrido complex [FeH(CO)<sub>3</sub>(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)] have been reported.<sup>89</sup> Reaction of H<sub>2</sub>C=C(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> with [MCl<sub>2</sub>(η<sup>6</sup>-arene)]<sub>2</sub> (M = Ru, Os) or [MCl<sub>2</sub>(CO)<sub>3</sub>]<sub>2</sub> (M = Ru, Os) affords the trimethylenemethane complexes [M{η<sup>4</sup>-C(CH<sub>2</sub>)<sub>3</sub>}(η<sup>6</sup>-arene)] and [M(CO)<sub>3</sub>{η<sup>4</sup>-C(CH<sub>2</sub>)<sub>3</sub>}], respectively; the molecular structures of [Ru{η<sup>4</sup>-C(CH<sub>2</sub>)<sub>3</sub>}(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)] and [Ru(CO)<sub>3</sub>{η<sup>4</sup>-C(CH<sub>2</sub>)<sub>3</sub>}] have been crystallographically determined.<sup>90</sup> The preparation and molecular structure (for R = SiMe<sub>3</sub>) of the first complexes with a tetraethynylcyclobutadiene ligand, [Fe(CO)<sub>3</sub>{η<sup>4</sup>-C<sub>4</sub>(C≡CR)<sub>4</sub>}] (R = H, Bu<sup>t</sup>, SiMe<sub>3</sub>, C<sub>8</sub>H<sub>17</sub>) (20), have been described.<sup>91</sup> The electrophilicity scales for organometallic cations such as [Fe(CO)<sub>3</sub>(η<sup>5</sup>-C<sub>6</sub>H<sub>7</sub>)] [BF<sub>4</sub>] and carbenium ions have been integrated following measurements of the rates of the reactions of the former with nucleophiles.<sup>92</sup>



The electron-transfer reactions of a series of alkynyl cyclopentadienyl complexes of the type [Fe(C≡CR)(L-L)(η-C<sub>5</sub>R'<sub>5</sub>)] (R = Bu<sup>t</sup>, CO<sub>2</sub>Me, CO<sub>2</sub>Et, SiMe<sub>3</sub>, Ph, CH<sub>2</sub>OMe; L-L = dpmm; R' = H; or R = Bu<sup>t</sup>, Ph; L-L = dppe; R' = Me) have been reported together with the isolation of the 17-electron iron(III) complexes [Fe(C≡CR)(dppe)Cp\*][PF<sub>6</sub>].<sup>93</sup> Photolysis of several amino-carbene complexes such as [Fe{C(NHCH<sub>2</sub>Ph)Me}(CO)(PPh<sub>3</sub>)Cp] surprisingly gives rise to exclusive loss of PPh<sub>3</sub> rather than CO.<sup>94</sup> The preparation and reactions have been described of the ruthenium-silene complexes [RuH(PR<sub>3</sub>)(η<sup>2</sup>-CH<sub>2</sub>=SiR'<sub>2</sub>)Cp\*] (R = Pr<sup>i</sup>, Cy; R' = Me, Ph), of which the case for R = Pr<sup>i</sup>, R' = Ph has been crystallographically characterized.<sup>95</sup> Intramolecular allylic C-H bond activation occurs when [{RuCl<sub>2</sub>Cp\*}]<sub>2</sub> is reacted with 1,5-Me<sub>2</sub>cod in the presence of AgOTf to give the new bis(allylic) complex (21).<sup>96</sup> A method for preparing the metallophosphorane complex (22), by reacting [Fe(CO)<sub>2</sub>{P(OPh)<sub>3</sub>}Cp][PF<sub>6</sub>] with two equivalents of *o*-HOC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> and one equivalent of BuLi, is unprecedented.<sup>97</sup> Reaction of [Ru(PPh<sub>3</sub>)(η<sup>2</sup>-O<sub>2</sub>CMe)Cp] with

<sup>88</sup> L. Pu, T. Hasegawa, S. Parkin, and H. Taube, *J. Am. Chem. Soc.*, 1993, **115**, 2545.

<sup>89</sup> T. M. Barnhart, J. De Felippis, and R. J. McMahon, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1073.

<sup>90</sup> G. E. Herberich and T. P. Spaniol, *J. Chem. Soc., Dalton Trans.*, 1993, 2471.

<sup>91</sup> U. H. F. Bunz and V. Enkelmann, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1653.

<sup>92</sup> H. Mayr, K.-H. Müller, and D. Rau, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1630.

<sup>93</sup> N. G. Connelly, M. P. Gamasa, J. Gimeno, C. Lapinte, E. Lastra, J. P. Maher, N. Le Narvor, A. L. Rieger, and P. H. Rieger, *J. Chem. Soc., Dalton Trans.*, 1993, 2575.

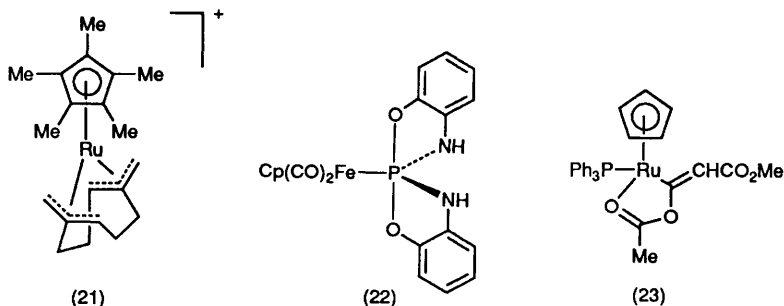
<sup>94</sup> S. G. Davies, M. R. Metzler, K. Yanada, and R. Yanada, *J. Chem. Soc., Chem. Commun.*, 1993, 658.

<sup>95</sup> B. K. Campion, R. H. Heyn, T. D. Tilley, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1993, **115**, 5527.

<sup>96</sup> K. Itoh, K. Masuda, and H. Ikeda, *Organometallics*, 1993, **12**, 2752.

<sup>97</sup> H. Nakazawa, K. Kubo, and K. Miyoshi, *J. Am. Chem. Soc.*, 1993, **115**, 5863.

CO affords  $[\text{Ru}(\text{CO})(\text{PPh}_3)(\eta^1\text{-O}_2\text{CMe})\text{Cp}]$ ; reaction of  $[\text{Ru}(\text{PPh}_3)(\eta^2\text{-O}_2\text{CMe})\text{Cp}]$  with  $\text{HC}\equiv\text{CCO}_2\text{Me}$  gives the unexpected, crystallographically characterized cyclic vinyl ester complex (23) rather than the expected vinylidene complex.<sup>98</sup>



Treatment of  $[\text{RuCp}_2]$  with  $\text{Hg}(\text{OAc})_2$  in  $\text{CH}_2\text{Cl}_2$  under reflux gives  $[\text{Ru}\{\eta^5\text{-C}_5(\text{HgOAc})_s\}_2]$  in high yield; the decahalo complexes  $[\text{Ru}(\eta^5\text{-C}_5\text{X}_5)_2]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) can be prepared by reacting  $[\text{Ru}\{\eta^5\text{-C}_5(\text{HgOAc})_s\}_2]$  with  $\text{CuCl}_2$ ,  $\text{KBr}_3$ , and  $\text{KI}_3$  respectively.<sup>99</sup> The preparation and molecular structure of the stable germanacyclopentadienyl complex  $[\text{RuCp}^*\{\eta^5\text{-C}_5\text{Me}_4\text{GeSi}(\text{SiMe}_3)_3\}]$  have been described.<sup>100</sup> Reaction of  $[\text{Ru}(\eta^6\text{-arene})(\eta^6\text{-C}_{16}\text{H}_{16})][\text{BF}_4]_2$  (arene =  $\text{C}_6\text{H}_6$ , *p*-cymene, 1,2,4,5- $\text{C}_6\text{H}_2\text{Me}_4$ ,  $\text{C}_6\text{HMe}_5$ ,  $\text{C}_6\text{Me}_6$ ) with  $\text{Na}[\text{BH}_4]$  affords the  $\eta^4$ -diene complexes  $[\text{Ru}(\eta^4\text{-diene})(\eta^6\text{-C}_{16}\text{H}_{16})]$  via addition of two hydride nucleophiles to the non-cyclophane ring, which contrasts with previously reported, analogous reactions that gave bis(cyclohexadienyl) type complexes.<sup>101</sup> The derivatized cyclophane complexes  $[\text{RuL}(\text{E-E})(\eta^6\text{-C}_6\text{H}_6)][\text{BF}_4]_2$  ( $\text{L} = \text{NCMe}, \text{NCEt}$ ;  $\text{E-E} = 2,11\text{-dithia}$  or  $2,11\text{-diselena}[3,3]\text{orthocyclophane}$ ) have been synthesized; the bidentate 2,11-diselena derivatives are the first examples of (selenoether)( $\pi$ -benzene) complexes of ruthenium( $\text{II}$ ).<sup>102</sup> Reaction of  $[\text{OsCl}_2(\eta^6\text{-arene})]$  (arene = *p*-cymene,  $\text{C}_6\text{Me}_6$ ) with four equivalents of  $\text{LiNHBu}^t$  yields the imido complexes  $[\text{Os}(\text{NBu}^t)(\eta^6\text{-arene})]$ , of which the case for arene =  $\text{C}_6\text{Me}_6$  has been crystallographically characterized; the cycloaddition reactions of  $[\text{Os}(\text{NBu}^t)(\eta^6\text{-p-cymene})]$  with  $\text{RN}_3$  ( $\text{R} = \text{Bu}^t, \text{CPh}_3, \text{Ph}, \text{SiMe}_3$ ) and  $\text{Bu}^t\text{NCO}$  give the tetraazene complexes (24) (crystallographically characterized for  $\text{R} = \text{Ph}$ ) and the ureylene complex  $[\text{Os}\{(\text{NBu}^t)_2\text{CO}\}(\eta^6\text{-p-cymene})]$ , respectively.<sup>103</sup> The preparation of a series of phosphinoenolato arene complexes,  $[\text{RuCl}\{\eta^2\text{-P,O-OC(R')=C(R'')PPh}_2\}(\eta^6\text{-arene})]$ , and their coupling reactions with  $\text{PhC}\equiv\text{CH}$  to give  $[\text{Ru}\{\eta^3\text{-CH=C(Ph)C(R'')PPh}_2\}(\eta^6\text{-arene})]^+$  have been reported; the latter ( $\text{R}' = \text{Bu}^t$ ,  $\text{R}'' = \text{H}$ , arene = mes) thermally rearranges to a phosphametallo-cyclopropane complex (25), which has been crystallographically characterized.<sup>104</sup> The

<sup>98</sup> T. Daniel, N. Mahr, T. Braun, and H. Werner, *Organometallics*, 1993, **12**, 1475.

<sup>99</sup> C. H. Winter, Y.-H. Han, R. L. Ostrander, and A. L. Rheingold, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1161.

<sup>100</sup> W. P. Freeman, T. D. Tilley, A. L. Rheingold, and R. L. Ostrander, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1744.

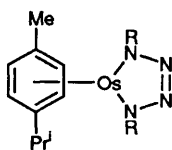
<sup>101</sup> J. W. Steed and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1993, 3187.

<sup>102</sup> L. R. Hanton and T. Kemmitt, *Inorg. Chem.*, 1993, **32**, 3648.

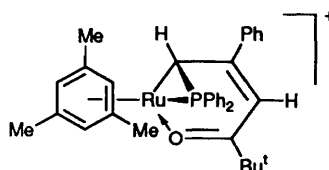
<sup>103</sup> R. I. Michelman, R. G. Bergman, and R. A. Andersen, *Organometallics*, 1993, **12**, 2741.

<sup>104</sup> B. Demerseman, B. Guilbert, C. Renouard, M. Gonzalez, P. H. Dixneuf, D. Masi, and C. Mealli, *Organometallics*, 1993, **12**, 3906.

synthesis and molecular structure of the water-soluble diastereoisomeric Schiff-base complex  $[\text{Ru}(\text{H}_2\text{O})\text{L}^*(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)][\text{ClO}_4]$  [ $\text{HL}^* = (S)\text{-(}\alpha\text{-methylbenzyl)salicylaldimine}$ ] have been described.<sup>105</sup> Several  $\eta^2$ -fullerene ( $\text{C}_{60}$ ) complexes, such as  $[\text{Fe}(\text{CO})_4(\eta^2\text{-C}_{60})]$ , have been reported.<sup>106</sup> Treatment of the 19-electron complex  $[\text{FeCp}(\eta\text{-C}_6\text{Me}_6)]$  with  $\text{C}_{60}$  affords the paramagnetic salts  $[\text{FeCp}(\eta\text{-C}_6\text{Me}_6)][\text{C}_{60}]$ ,  $[\text{FeCp}(\eta\text{-C}_6\text{Me}_6)]_2[\text{C}_{60}]$ , and  $[\text{FeCp}(\eta\text{-C}_6\text{Me}_6)]_3[\text{C}_{60}]$  depending on reaction stoichiometry.<sup>107</sup>



(24)



(25)

## 7 Co, Rh, and Ir

Reaction of  $[\{\text{Ir}(\mu\text{-Cl})(\eta^2\text{-cyclooctene})_2\}_2]$  with  $\text{LiC}_6\text{Cl}_5$  at low temperature gives the unusual homoleptic complex  $\text{Li}_2[\text{Ir}(\text{C}_6\text{Cl}_5)_4]$ , which reacts with CO to yield  $\text{Li}_2[\text{Ir}(\text{C}_6\text{H}_5)_3(\text{CO})]$ ; the molecular structure of  $[\text{PBzPh}_3]_2[\text{Ir}(\text{C}_6\text{Cl}_5)_4]\cdot\text{CH}_2\text{Cl}_2$  shows square planar iridium with the aryl rings all inclined in the same way in a propeller-like manner.<sup>108</sup> The  $\sigma$ -alkynyl complexes  $[\text{NET}_4][\text{RhCl}(\text{C}\equiv\text{CR})(\text{PPr}^i_3)_2]$  ( $\text{R} = \text{CO}_2\text{Et}$ , Ph) have been made by  $\text{SiMe}_3$  abstraction from *trans*- $[\text{RhCl}(\text{RC}\equiv\text{CSiMe}_3)(\text{PPr}^i_3)_2]$  ( $\text{R} = \text{CO}_2\text{Et}$ ) or *trans*- $[\text{RhCl}\{\text{C}=\text{C}(\text{SiMe}_3)\text{R}\}(\text{PPr}^i_3)_2]$  ( $\text{R} = \text{CO}_2\text{Et}$ , Ph); treatment of  $[\text{NET}_4][\text{RhCl}(\text{C}\equiv\text{CR})(\text{PPr}^i_3)_2]$  with MeI surprisingly gives the allene complex *trans*- $[\text{RhCl}(\eta^2\text{-CH}_2=\text{C}=\text{CHCO}_2\text{Et})(\text{PPr}^i_3)_2]$ , which has been crystallographically characterized, or the alkyne complex *trans*- $[\text{RhCl}(\eta^2\text{-MeC}\equiv\text{CPh})(\text{PPr}^i_3)_2]$ .<sup>109</sup> Reaction of  $[\text{Ir}(\text{CO})_3\text{L}_2]^+$  ( $\text{L} = \text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{PET}_3$ ,  $\text{PEt}_2\text{Ph}$ ,  $\text{PETPh}_2$ ) with  $\text{XeF}_2$  yields the fluoroacyl complexes  $[\text{IrF}(\text{COF})(\text{CO})_2\text{L}_2]^+$  via an unusual type of oxidative-addition reaction; treatment of the complex  $[\text{IrF}(\text{COF})(\text{CO})_2(\text{PET}_3)_2]^+$  with  $\text{SiH}_3\text{X}$  ( $\text{X} = \text{CN}$ ,  $\text{NCS}$ , or  $\text{NCO}$ ) affords<sup>110</sup> the novel acyl complexes  $[\text{IrF}(\text{COX})(\text{CO})_2(\text{PET}_3)_2]^+$ . The thermolysis of  $[\text{Ir}(\text{H})_2\text{Et}(\text{triphos})]$  in a range of solvents gives ethane and the intermediate  $[\text{IrH}(\text{triphos})]$ , which inserts into the C–H bonds of either the solvent or 1-alkynes, ethene, etc. generally to give  $\sigma$ -organyl dihydrides,  $[\text{Ir}(\text{H})_2(\sigma\text{-organyl})(\text{triphos})]$  (organyl =  $\text{C}_6\text{H}_5$ ,  $\text{CH}_2\text{CN}$ ,  $\text{C}\equiv\text{CPh}$ ,  $\text{C}\equiv\text{CCO}_2\text{Et}$ ,  $\text{CH}=\text{CH}_2$ ).<sup>111</sup> Treatment of

<sup>105</sup> S. K. Mandal and A. R. Chakravarty, *Inorg. Chem.*, 1993, **32**, 3851.

<sup>106</sup> R. E. Douthwaite, M. L. H. Green, A. H. H. Stephens, and J. F. C. Turner, *J. Chem. Soc., Chem. Commun.*, 1993, 1522.

<sup>107</sup> C. Bossard, S. Rigaut, D. Astruc, M.-H. Delville, G. Félix, A. Février-Bouvier, J. Amiel, S. Flandrois, and P. Delhaès, *J. Chem. Soc., Chem. Commun.*, 1993, 333.

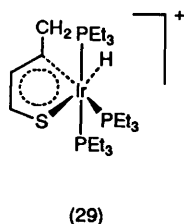
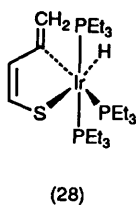
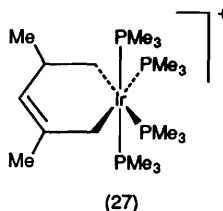
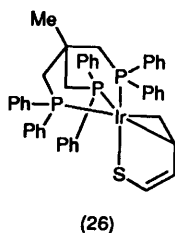
<sup>108</sup> M. P. García, M. V. Jiménez, L. A. Oro, F. J. Lahoz, M. C. Tiripicchio, and A. Tiripicchio, *Organometallics*, 1993, **12**, 4660.

<sup>109</sup> H. Werner, D. Schneider, and M. Schulz, *J. Organomet. Chem.*, 1993, **451**, 175.

<sup>110</sup> E. A. V. Ebsworth, N. Robertson, and L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.*, 1993, 1031.

<sup>111</sup> C. Bianchini, P. Barbaro, A. Meli, M. Peruzzini, A. Vacca, and F. Vizza, *Organometallics*, 1993, **12**, 2505.

$[\text{Ir}(\eta^4\text{-C}_6\text{H}_6)(\text{triphos})][\text{BPh}_4]$  with thiophene affords the iridathiabenzene complex  $[\text{Ir}(\eta^2\text{-C}_4\text{H}_4\text{S})(\text{triphos})][\text{BPh}_4]$ , which can be converted into the butadienethiolate compound (26) *via* the (thiapentadienyl) hydride kinetic intermediate  $[\text{IrH}(\eta^2\text{-C}_4\text{H}_4\text{S})(\text{triphos})]$  after reaction with  $\text{Li}[\text{BHEt}_3]$ .<sup>112</sup> The preparation and spectroscopic characterization of the iridacyclohexene complex (27) and its iridacyclohexadiene analogue have been described.<sup>113</sup> Reaction of the iridathiacycle (28) with strong acids gives (29) *via* protonation at the exocyclic methylene carbon; the *X*-ray crystal structure of the  $[\text{BF}_4]^-$  salt of (29) shows features consistent with aromatic character and is the first example of a metallathiophene.<sup>114</sup> The synthesis of the cationic complexes  $[\text{M}(\eta^4\text{-diene})(\eta^5\text{-L})]^+$  ( $\text{M} = \text{Rh}$ , diene = nbd;  $\text{M} = \text{Ir}$ , diene = cod;  $\text{L} = 2\text{-methylthiophene}$  or  $2,5\text{-dimethylthiophene}$ ) and related complexes has been reported and  $[\text{Rh}(\eta^4\text{-cod})(\eta^5\text{-2,5-dimethylthiophene})][\text{BF}_4]$  has been crystallographically characterized.<sup>115</sup>



The metal-vapour synthesis of the paramagnetic butadiene sandwich complex  $[\text{Co}(\eta^4\text{-C}_4\text{H}_4\text{-1,4-Bu}_2)_2]$  and its reaction with potassium in the presence of 18-crown-6 to give  $[\text{K}(18\text{-crown-6})(\text{thf})_2][\text{Co}(\eta^4\text{-1,4-C}_4\text{H}_4\text{Bu}_2)]$  have been described, the anion of which is the first crystallographically characterized homoleptic butadiene sandwich complex, which is bonded like a genuine diene rather than a metallocyclopentene.<sup>116</sup> Treatment of  $[\{\text{MClL}_2\}_2]$  ( $\text{M} = \text{Rh}$ ,  $\text{L}_2 = \text{cod}$ ,  $\text{L}_2 = (\text{CO})_2$ ;  $\text{M} = \text{Ir}$ ,  $\text{L}_2 = \text{cod}$ ) with  $\text{Li}[\text{CH}\{\text{PPh}_2=\text{N}(\text{p-C}_6\text{H}_4\text{R})_2\}]$  ( $\text{R} = \text{Me}$ ,  $\text{Me}/\text{NO}_2$ ,  $\text{NO}_2$ ) affords the unusual bis(iminophosphoranyl)methanide complexes  $[\text{M}\{\text{CH}(\text{PPh}_2=\text{N}(\text{4-C}_6\text{H}_4\text{R}_2))\}_2\text{L}_2]$  where the ligand is attached as a  $\sigma\text{-N}, \sigma\text{-C}$  chelate; the case when  $\text{M} = \text{Ir}$ ,  $\text{R} = \text{Me}$ ,

<sup>112</sup> C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, P. Frediani, V. Herrera, and R. A. Sanchez-Delgado, *J. Am. Chem. Soc.*, 1993, **115**, 2731.

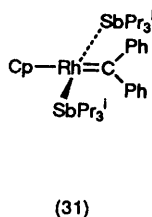
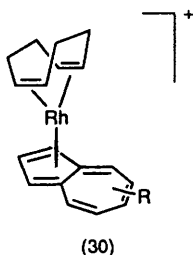
<sup>113</sup> J. R. Bleake, A. M. Rohde, and D. W. Boorsma, *Organometallics*, 1993, **12**, 970.

<sup>114</sup> J. R. Bleake, M. F. Ortwerth, and M. Y. Chiang, *Organometallics*, 1993, **12**, 985.

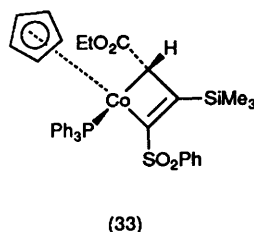
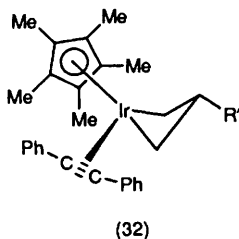
<sup>115</sup> J. R. Polam and L. C. Porter, *Organometallics*, 1993, **12**, 3504.

<sup>116</sup> F. G. N. Cloke, P. B. Hitchcock, and A. McCamley, *J. Chem. Soc., Chem. Commun.*, 1993, 248.

$L_2 = \text{cod}$  has been crystallographically characterized.<sup>117</sup> A series of catalytically active  $\eta^5$ -azulene complexes (30) has been prepared and their fluxionality investigated by  $^1\text{H}$  NMR spectroscopy; the molecular structure when  $R = 1\text{-Me}$ ,  $4\text{-Me}$ , or  $7\text{-Pr}^i$  has been described.<sup>118</sup> The preparation, X-ray crystal structure, and ligand replacement reactions of the first non-heteroatom-stabilized rhodium(I) carbene complex (31) have been reported.<sup>119</sup>



Photolysis of  $[\text{Ir}(\eta^2\text{-C}_3\text{H}_6)(\eta^3\text{-C}_3\text{H}_5)\text{Cp}^*][\text{OTf}]$  gives the inner-sphere triflate complex  $[\text{Ir}(\text{OTf})(\eta^3\text{-C}_3\text{H}_5)\text{Cp}^*]$ , which when reacted with  $\text{RC}\equiv\text{CR}$  ( $R = \text{Me}, \text{Ph}$ ) affords the highly reactive allyl/alkyne complexes  $[\text{Ir}(\eta^2\text{-RC}\equiv\text{CR})(\eta^3\text{-C}_3\text{H}_5)\text{Cp}^*][\text{OTf}]$ , which are inaccessible by conventional routes. The diphenylacetylene complex reacts selectively with nucleophiles to give the metallacyclobutane complexes (32) ( $R' = \text{H}, \text{Me}, \text{CN}$ ) in high yield.<sup>120</sup> Reaction of  $[\text{Co}(\text{PPh}_3)(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSO}_2\text{Ph})\text{Cp}]$  with ethyl diazoacetate gives a mixture of three  $\eta^4$ -diene complexes,  $[\text{Co}\{\eta^4\text{-(}x,y\text{)-CH}(\text{CO}_2\text{Et})=\text{C}(\text{SO}_2\text{Ph})\text{C}(\text{SiMe}_3)=\text{CH}(\text{CO}_2\text{Et})\}\text{Cp}]$  ( $x,y = \text{cis, cis; cis, trans; trans, cis}$ ), and the cobaltacyclobutene complex (33), which



has (*SS*, *RR*) relative stereochemistry.<sup>121</sup> Treatment of the cobaltacyclobutene complex  $[\text{Co}(\text{PPh}_3)\{\text{C}(\text{SO}_2\text{Ph})=\text{C}(\text{SiMe}_3)\text{C}(\text{H})(\text{CO}_2\text{Et})\}\text{Cp}]$  with  $\text{CO}$  at  $75^\circ\text{C}$  yields the  $\eta^4$ -vinylketene complex  $[\text{Co}\{\eta^4\text{-(}E\text{)-C}(\text{CO}_2\text{Et})(\text{H})=\text{C}(\text{SiMe}_3)$

<sup>117</sup> P. Imhoff, R. van Asselt, J. M. Ernsting, K. Vrieze, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, and A. P. M. Kentgens, *Organometallics*, 1993, **12**, 1523.

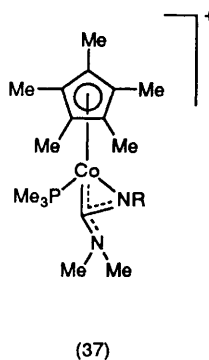
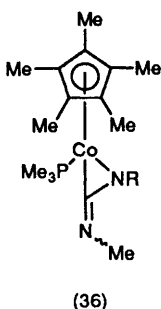
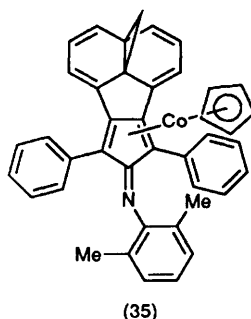
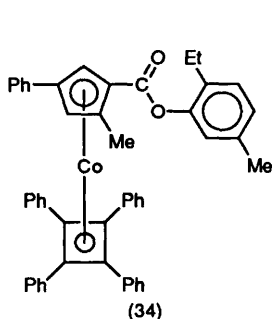
<sup>118</sup> A. J. Rippert, A. Linden, and H.-J. Hansen, *Helv. Chim. Acta*, 1993, **76**, 2876.

<sup>119</sup> P. Schwab, N. Mahr, J. Wolf, and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1480.

<sup>120</sup> K. E. Schwiebert and J. M. Stryker, *Organometallics*, 1993, **12**, 600.

<sup>121</sup> J. M. O'Connor, H.-L. Ji, M. Iranpour, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1993, **115**, 1586.

$C(SO_2Ph)=C=O\}Cp]$ , a small amount of the crystallographically characterized  $\eta^4$ -pyrone complex  $[Co\{\eta^4-C(OEt)=C(SO_2Ph)C(SiMe_3)=C(H)(=O)O\}Cp]$ , and 2-phenylsulfonyl-3-trimethylsilyl-5-ethoxyfuran.<sup>122</sup> A series of diastereoisomerically pure planar-chiral CpCo complexes has been synthesized, such as (34), which has been crystallographically characterized and shows that there are three different chiralities (planar, carbon-centred, helical) in one molecule.<sup>123</sup> Reaction of 2,10-bis(phenylethynyl)-1,6-methano[10]annulene with  $[Co(PPh_3)_2Cp]$  and 2,6-dimethylphenyl isocyanide gives *via* a metallocycle the novel 1,6-methano[10]annulene complex (35), which has a bisnorcaradiene structure.<sup>124</sup> Treatment of  $[Co(CNMe)(PMe_3)Cp^*]$  with Ph or *p*-tolyl azides yields  $\eta^2$ -carbodiimide complexes such as (36), which react with MeI to give the cationic complexes (37), of which the case for R = Ph has been crystallographically characterized thus confirming the bidentate coordination of the amidinyl ligand, in which the positive charge is partially delocalized.<sup>125</sup> Reaction of  $S_c$ - $[CoI_2\{PPh_2NHC^*H(Me)Ph\}Cp]$  with equimolar quantities of dimethyl-, *t*-butyl-, or ethylphosphonite affords the diastereoisomeric *P*-chiral phosphinate Arbuzov products  $(R,S_{Co}; R,S_P; S_c)$ - $[CoI\{PPh_2NHC^*H(Me)Ph\}\{P(O)(OMe)(Bu^t)\}Cp]$  and  $(R,S_{Co}; R,S_P; S_c)$ - $[CoI\{PPh_2NHC^*(Me)Ph\}\{P(O)(OMe)(Et)\}Cp]$ ; the molecular structures of two diastereo-



<sup>122</sup> J. M. O'Connor, H.-L. Ji, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1993, **115**, 9846.

<sup>123</sup> M. Uno, K. Ando, N. Komatsuzaki, T. Tanaka, M. Sawada, and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1993, 1549.

<sup>124</sup> R. Neidlein and U. Kux, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1324.

<sup>125</sup> G. Hörlin, N. Mahr, and H. Werner, *Organometallics*, 1993, **12**, 1775.



isomers of the Bu<sup>t</sup> series and one diastereoisomer of the four isolated for the Et series have been crystallographically characterized.<sup>126</sup>

Several triphosphacyclopentadienyl complexes such as [Rh( $\eta^4$ -diene)( $\eta^5$ -P<sub>2</sub>C<sub>3</sub>Bu<sub>3</sub>)] (diene = cod, hexa-1,5-diene), which has been crystallographically characterized for diene = cod, and the unusual hydride [RhH( $\eta^1$ -P<sub>3</sub>C<sub>2</sub>Bu<sub>2</sub>)(PPh<sub>3</sub>)Cp\*], also crystallographically characterized, have been reported.<sup>127</sup> The preparation and electrochemical properties of the diselenolene complexes [Co{SeC(R<sup>2</sup>)=C(R<sup>3</sup>)Se}( $\eta$ -C<sub>5</sub>R<sub>5</sub>)] [R<sup>1</sup> = H, Me; R<sup>2</sup>-R<sup>3</sup> = (CH<sub>2</sub>)<sub>6</sub>, CH=CH(CH<sub>2</sub>)<sub>4</sub>, CH=CH(CH<sub>2</sub>)<sub>2</sub> CH=CH; R<sup>2</sup> = Ph, R<sup>3</sup> = H; R<sup>2</sup> = R<sup>3</sup> = Ph] have been described.<sup>128</sup> Photolysis of [Rh(PMe<sub>3</sub>)( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)( $\eta$ -C<sub>5</sub>R<sub>5</sub>)] (R = H, Me) with C<sub>6</sub>F<sub>6</sub> gives the unusual complexes [Rh(PMe<sub>3</sub>)( $\eta^2$ -C<sub>6</sub>F<sub>6</sub>)( $\eta$ -C<sub>5</sub>R<sub>5</sub>)]; in the case of R = H the hexafluorobenzene is  $\eta^2$ -coordinated and distorted to generate a planar C<sub>6</sub>F<sub>4</sub> group with the two remaining C-F bonds at 43.8° to this plane. The reactions of [Rh(PMe<sub>3</sub>)( $\eta^2$ -C<sub>6</sub>F<sub>6</sub>)Cp] and related complexes are also discussed.<sup>129</sup> The preparation and temperature-dependent magnetic properties of [Co( $\eta$ -C<sub>6</sub>Me<sub>6</sub>)<sub>2</sub>]X (X = BPh<sub>4</sub>, NbF<sub>6</sub>, PF<sub>6</sub>, SbF<sub>6</sub>) have been reported.<sup>130</sup> Reaction of [RhH(CO)(PPh<sub>3</sub>)<sub>3</sub>] with C<sub>60</sub> gives the crystallographically characterized complex [RhH(CO)(PPh<sub>3</sub>)<sub>2</sub>( $\eta^2$ -C<sub>60</sub>)], in which the hydride remains bonded to Rh and does not transfer to the fullerene.<sup>131</sup>

## 8 Ni, Pd, and Pt

The synthesis of the first palladium(0) complex with secondary phosphines as the only ligands, [Pd(PHBU<sub>2</sub>)<sub>3</sub>], and its oxidative reactions with CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> to give *trans*-[PdCl(CH<sub>2</sub>Cl)(PHBU<sub>2</sub>)<sub>2</sub>] and *trans*-[PdCl(CHCl<sub>2</sub>)(PHBU<sub>2</sub>)<sub>2</sub>] respectively have been described.<sup>132</sup> The synthesis and molecular structure of the platinum(II) hydroxycarbonyl complex [Pt(CO<sub>2</sub>H){C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-2,6}], which has a *trans*-spanning P,C,P-tridentate ligand, have been reported.<sup>133</sup> The mesogenic palladium complexes (38) (*n* = 10, 14) have been synthesized. These have switching times 1000-times faster and transition-temperatures 50 K lower than the first mesogenic palladium complexes and hence it may be possible that these metallomesogens have applications as ferroelectric liquid crystals.<sup>134</sup> Treatment of the metallocyclopentane complex [Ni(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)(bipy)] with N<sub>2</sub>O yields the oxygen-atom transfer product [Ni(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)(bipy)], which has been crystallographically characterized and its reactions investigated.<sup>135</sup> The hydrido-dithiocarbene complex *trans*-[PtH(CSCH<sub>2</sub>CH<sub>2</sub>S)(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] thermally rearranges to the crystallographically characterized complex (39) *via* hydride to carbene migration.<sup>136</sup> Reaction of *trans*-[PtBr{1- $\eta^1$ -cyclohepta-1,3,5-trienyl}(PPh<sub>3</sub>)<sub>2</sub>] with [CPh<sub>3</sub>][BF<sub>4</sub>] affords *trans*-

<sup>126</sup> B. J. Boone, C. R. Jablonski, P. G. Jones, M. J. Newlands, and Y. Yu, *Organometallics*, 1993, **12**, 3042.

<sup>127</sup> P. B. Hitchcock, R. M. Matos, and J. F. Nixon, *J. Organomet. Chem.*, 1993, **462**, 319.

<sup>128</sup> C. P. Morley and R. R. Vaughan, *J. Chem. Soc., Dalton Trans.*, 1993, 703.

<sup>129</sup> S. T. Belt, M. Helliwell, W. D. Jones, M. G. Partridge, and R. N. Perutz, *J. Am. Chem. Soc.*, 1993, **115**, 1429.

<sup>130</sup> D. O'Hare, A. Rai-Chaudhuri, and V. Murphy, *J. Chem. Soc., Dalton Trans.*, 1993, 3071.

<sup>131</sup> A. L. Balch, J. W. Lee, B. C. Noll, and M. M. Olmstead, *Inorg. Chem.*, 1993, **32**, 3577.

<sup>132</sup> P. Leoni, *Organometallics*, 1993, **12**, 2432.

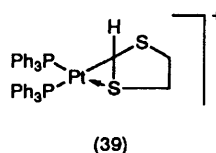
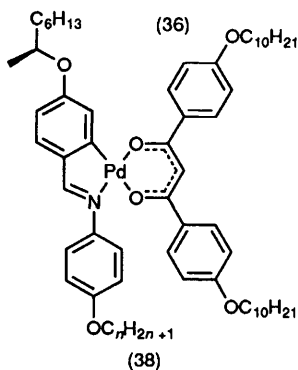
<sup>133</sup> M. A. Bennett, H. Jin, and A. C. Willis, *J. Organomet. Chem.*, 1993, **451**, 249.

<sup>134</sup> M. J. Baena, P. Espinet, M. B. Ros, J. L. Serrano, and A. Ezcurra, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1203.

<sup>135</sup> P. T. Matsunaga, G. L. Hillhouse, and A. L. Rheingold, *J. Am. Chem. Soc.*, 1993, **115**, 2075.

<sup>136</sup> R. A. Michelin, R. Bertani, M. Mozzon, G. Bombieri, F. Benetollo, M. de F. C. Guedes da Silva, and A. J. L. Pombeiro, *Organometallics*, 1993, **12**, 2372.

$[\text{PtBr}(\eta^1\text{-C}_7\text{H}_6)(\text{PPh}_3)_2][\text{BF}_4]$ , in which the  $\text{C}_7\text{H}_6$  exists only in the carbene (tropylium) ion form; the  $\text{Pt}(0)$  complex of  $\text{C}_7\text{H}_6$ ,  $[\text{Pt}(\eta^3\text{-C}_7\text{H}_6)(\text{PPh}_3)_2]$ , prefers the  $\eta^3$ -allene type ground-state structure.<sup>137</sup>



The synthesis, molecular structure, and detailed spectroscopic characterization of  $[\text{Pt}(\text{dmpe})(1,1\text{-dideuterio-2,2-dimethylpent-4-en-1-yl-k}^3\text{C}^{1,4,5})][\text{BF}_4]$  and its 3,3-dideuterio isotopomer have been reported; thermolysis of each of these complexes at  $125^\circ\text{C}$  in several solvents gives a 1 : 1 mixture of these, and the rate of rearrangement is found to be first order.<sup>138</sup> Treatment of *trans*- $[\text{PtX}(\text{SiMe}_3)(\text{PET}_3)_2]$  ( $\text{X} = \text{Br}, \text{I}$ ) with  $\text{RC}\equiv\text{CR}$  ( $\text{R} = \text{Pr}^n, \text{Ph}$ ) yields *trans*-(*E*)- $[\text{PtX}\{\text{SiMe}_3(\text{R})\text{C}\equiv\text{C}(\text{R})\}(\text{PET}_3)_2]$ , which has been crystallographically characterized for  $\text{R} = \text{Ph}$ .<sup>139</sup> *cis*- $[\text{PtX}(\text{Z})(\text{Ph}_2\text{PC}\equiv\text{CPh})_2]$  [ $\text{X} = \text{Z} = \text{Cl}, \text{I}, \text{CF}_3, \text{C}_6\text{F}_5, \text{Me}$ ;  $\text{X}(\text{Z}) = o\text{-C}_6\text{H}_4\text{O}_2, \text{Me}(\text{Cl})$ ] have been crystallographically characterized for  $\text{X} = \text{Z} = \text{Cl}, \text{Me}$  and  $\text{X} = \text{Me}, \text{Z} = \text{Cl}$ ; all of the complexes except for  $\text{X} = \text{Z} = \text{Me}$  thermally rearrange to afford *cis*- $[\text{PtX}(\text{Z})\{o\text{-C}_{16}\text{H}_{10}(\text{PPh}_2)_2\}][\text{BF}_4]$  via intramolecular coupling of the phosphinoalkyne ligands.<sup>140</sup> The preparation, molecular structure, and reactivity towards nucleophiles of the  $\eta^3$ -propargyl/allenyl complex  $[\text{Pt}(\text{PPh}_3)_2(\eta^3\text{-CH}_2\text{C}_2\text{Ph})][\text{O}_3\text{SCF}_3]$  have been reported.<sup>141</sup> Treatment of *trans*- $[\text{PtBr}(\eta^1\text{-CH}=\text{C}=\text{CH}_2)(\text{PPh}_3)_2]$  with  $\text{Ag}[\text{BF}_4]$  gives the  $\eta^3$ -propargyl derivative  $[\text{Pt}(\text{PPh}_3)_2(\eta^3\text{-CH}_2\text{CCH})][\text{BF}_4]$ , the cation of which reacts with  $\text{HOAc}$ ,  $\text{HOME}$ ,  $\text{PhSH}$ ,  $\text{CH}_2(\text{CO}_2\text{Me})_2$ ,  $\text{PhC}\equiv\text{CH}$ , or  $\text{Ph}_2\text{SiH}_2$  to afford  $[\text{Pt}(\text{PPh}_3)_2\{\eta^3\text{-CH}_2\text{C}(\text{Y})\text{CH}_2\}][\text{BF}_4]$  [ $\text{Y} = \text{OAc}, \text{OMe}, \text{SPh}, \text{CH}(\text{CO}_2\text{Me})_2, \text{C}\equiv\text{CPh}, \text{H}$  respectively] thus providing a useful synthetic route to  $\beta$ -substituted  $\pi$ -allyl complexes.<sup>142</sup> The effects of phen-type ligands on the dynamic behaviour of  $\text{Pd}(\eta^3\text{-allyl})$  complexes have been studied using saturation-transfer experiments and measurements of coalescence

<sup>137</sup> Z. Lu, W. M. Jones, and W. R. Winchester, *Organometallics*, 1993, **12**, 1344.

<sup>138</sup> S. P. Ermer, G. E. Struck, S. P. Bitler, R. Richards, R. Bau, and T. C. Flood, *Organometallics*, 1993, **12**, 2634.

<sup>139</sup> H. Yamashita, M. Tanaka, and M. Goto, *Organometallics*, 1993, **12**, 988.

<sup>140</sup> D. K. Johnson, T. Rukachaisirikul, Y. Sun, N. J. Taylor, A. J. Canty, and A. J. Carty, *Inorg. Chem.*, 1993, **32**, 5544.

<sup>141</sup> P. W. Blosser, D. G. Schimpff, J. C. Gallucci, and A. Wojcicki, *Organometallics*, 1993, **12**, 1993.

<sup>142</sup> T.-M. Huang, J.-T. Chen, G.-H. Lee, and Y. Wang, *J. Am. Chem. Soc.*, 1993, **115**, 1170.

temperatures; the X-ray crystal structure of  $[\text{PdCl}(2,9\text{-Me}_2\text{-}1,10\text{-phen})(1,2,3\text{-}\eta^3\text{-CH}_2\text{CHC}(\text{Me})\text{CH}_3)]$  has also been described.<sup>143</sup>

A series of *cis* or *trans* 2- $\sigma$ -butadienyl complexes such as *cis*- $[\text{PtCl}\{\sigma\text{-C}(\text{CH}_2)\text{C}(\text{Et})=\text{CH}_2\}(\text{dppf})]$  reacts with  $\text{TL}[\text{PF}_6]$  to give a range of cationic (1,2,3- $\eta^3$ )-*trans*-butadienyl complexes such as  $[\text{Pt}(\text{PPh}_3)_2\{1,2,3\text{-}\eta^3\text{-trans-CH}_2\text{C}(\text{Et})\text{C}=\text{CH}_2\}][\text{PF}_6]$ , which was characterized by X-ray crystallography.<sup>144</sup> Reaction of  $[\text{NiCp}_2]$  with two equivalents of  $\text{E}(\text{NBu}^t)_2\text{SiMe}_2$  ( $\text{E} = \text{Ge}, \text{Sn}$ ) gives  $[\text{CpNi}\{\text{E}(\text{NBu}^t)_2\text{SiMe}_2\}_2(\mu\text{-Cp})]$  via novel insertions of the carbene homologues into  $\text{Ni-}\eta^5\text{-Cp}$  bonds;<sup>145</sup> the crystallographically characterized sandwich complexes have  $\text{Ge}_2\text{Ni}$  and  $\text{Sn}_2\text{Ni}$  cores. The highly reactive cations of  $[\text{Pt}(\text{solv})_x(\eta\text{-C}_4\text{Me}_4)][\text{O}_3\text{SCF}_3]_2$  react with cyclopentadienes and  $\text{C}_6\text{Me}_6$  to yield the novel sandwich complexes  $[\text{Pt}(\eta\text{-C}_4\text{Me}_4)\text{L}][\text{O}_3\text{SCF}_3]$  ( $\text{L} = \text{Cp}, \text{Cp}', \text{Cp}^*$ ), and  $[\text{Pt}(\eta\text{-C}_4\text{Me}_4)(\eta\text{-C}_6\text{Me}_6)][\text{O}_3\text{SCF}_3]_2$ , which has an average Pt–C distance of 2.138 Å for the  $\text{C}_4\text{Me}_4$  ligand and 2.351 Å for the  $\text{C}_6\text{Me}_6$  ligand suggesting a pronounced structural *trans*-effect.<sup>146</sup> The preparation and molecular structure of the fullerene complex  $[\text{Pd}(\text{PPh}_3)_2(\eta^2\text{-C}_{60})]$  have been described.<sup>147</sup>

<sup>143</sup> S. Hansson, P.-Ola Norrby, M. P. T. Sjögren, B. Åkermark, M. E. Cucciolito, F. Giordano, and A. Vitagliano, *Organometallics*, 1993, **12**, 4940.

<sup>144</sup> S. A. Benyunes, L. Brandt, A. Fries, M. Green, M. F. Mahon, and T. M. T. Papworth, *J. Chem. Soc., Dalton Trans.*, 1993, 3785.

<sup>145</sup> M. Veith and L. Stahl, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 106.

<sup>146</sup> G. E. Herberich, U. Englert, and F. Marken, *J. Chem. Soc., Dalton Trans.*, 1993, 1979.

<sup>147</sup> V. V. Bashilov, P. V. Petrovskii, V. I. Sokolov, S. V. Lindeman, I. A. Guzey, and Y. T. Struchkov, *Organometallics*, 1993, **12**, 991.