

Organogermanium Complexes of Molybdenum and Tungsten

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The complexes $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{M}\cdot\text{GeR}_3$ (M = Mo, W; R = Me, Et, Prⁿ) are stable to water, but are oxidised in air. They are thermally stable to 200° and sublime readily *in vacuo*. Infrared, proton magnetic resonance, and mass spectra are reported. Diethylphosphine displaces one CO group while reaction with Ph₃P gives evidence of an intermediate, $\pi\text{-C}_5\text{H}_5(\text{CO})_3(\text{Ph}_3\text{P})\text{M}\cdot\text{GeR}_3$, which decomposes to $\pi\text{-C}_5\text{H}_5(\text{CO})_2(\text{Ph}_3\text{P})\cdot\text{MGeR}_3$. Reagents which cleave the metal-germanium bond are: HCl, C₂H₄Br₂, EtBr, and I₂. The latter, present in excess, also displaces CO giving $\pi\text{-C}_5\text{H}_5(\text{CO})_2\text{M}\text{I}_3$. Magnesium bromide also cleaves the M-Ge bond forming the transition metal-Grignard reagents which probably involve 3-co-ordinate magnesium, $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{M}\cdot\text{MgBr}(\text{THF})$. Mercuric chloride also cleaves the W-Ge bond giving $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{W}\cdot\text{HgCl}$ which, in preliminary studies, has been further used in the cleavage of other metal-metal bonds.

COMPOUNDS containing bonds between transition metals and metals of the fourth main group have been studied for a number of combinations of metals (*e.g.*, Pt-Si,¹ Pt-Ge,^{2,3} Pd-Ge,⁴ Pt-Sn^{5,6}), and their reactions are often of some interest. This paper is concerned with the formation and reactions of organogermanium complexes of molybdenum and tungsten undertaken to examine the properties of the metal-metal bond. A preliminary

Analyses and some physical properties are shown in the Table. The use of dimethylformamide⁹ which is recommended for the preparation of $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{WNa}$ led to complications in the final stage of the reaction and dibutyl ether was preferred as solvent. All of the complexes (I)–(V) were quite soluble in all common organic solvents (4.5 g. of $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}\cdot\text{GeMe}_3$ dissolved in 5 ml. of tetrahydrofuran at 20°) and were not

MoGe and WGe complexes

Compound	M. p.	Yield ^a (%)	Found		Calc.		$\nu(\text{CO})$ (cm. ⁻¹)	τ^*	
			C	H	C	H		C ₂ H ₅	R
(I) $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}\cdot\text{GeMe}_3$	87–88°	65	36.7	3.7	36.3	3.9	1999, 1929, 1905 ^b	5.42	9.39 ^b
(II) $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}\cdot\text{GeEt}_3$	26.5	45	41.5	4.8	41.5	4.9	1994, 1926, 1907 ^c	5.35	8.82 ^{b,e}
(III) $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}\cdot\text{GePr}^n_3$	< 25	10	Mass spectrometric						
(IV) $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{W}\cdot\text{GeMe}_3$	106–107	50	29.6	3.3	29.3	3.1	2010, 1931, 1908 ^c	4.7	9.37
(V) $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{W}\cdot\text{GeEt}_3$	36	48	34.2	4.2	34.1	4.1	2006, 1923, 1905 ^c	5.37	8.84 ^{b,e}

* Relative to tetramethylsilane.

^a Based on M(CO)₆. ^b Benzene solution. ^c Cyclohexane solution. ^d CCl₄ solution. ^e To centre of complex resonance.

account has been given,⁷ and the two compounds $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}\cdot\text{GePh}_3$ and $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{W}\cdot\text{GePh}_3$ have been described.⁸

Complexes were prepared by the reaction (1).

$$\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MNa} + \text{R}_3\text{GeBr} \longrightarrow \pi\text{-C}_5\text{H}_5(\text{CO})_3\text{M}\cdot\text{GeR}_3 \quad (1)$$
[M = Mo, W. R = Me, Et (and Prⁿ for Mo only)]

¹ F. Glockling and K. A. Hooton, *J. Chem. Soc. (A)*, 1967, 1066.

² R. J. Cross and F. Glockling, *J. Chem. Soc.*, 1965, 5422.

³ F. Glockling and K. A. Hooton, *J. Chem. Soc. (A)*, 1968, 826.

⁴ E. H. Brooks and F. Glockling, *J. Chem. Soc. (A)*, 1966, 1241.

attacked by chloroform or carbon tetrachloride during 1 day. They crystallised readily from cooled pentane or pentane-ether solutions, but this usually led to coloured (yellow, green, or red) products whereas vacuum sublimation gave colourless or buff solids. Their solution infrared spectra in the carbonyl stretching region were as expected for molecules of C_s symmetry having

⁵ R. D. Cramer, R. V. Lindsay, C. T. Prewitt, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1965, **87**, 658.

⁶ M. C. Baird, *J. Inorg. Nuclear Chem.*, 1967, **29**, 367.

⁷ F. Glockling, *Proc. IX Cong. Coord. Chem.*, 1966, 443.

⁸ D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 2222.

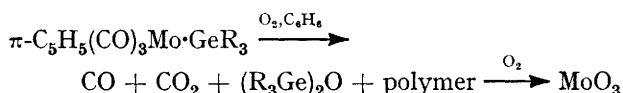
⁹ E. O. Fischer, *Inorg. Synth.*, 1967, **7**, 136.

essentially the same geometry as analogous σ -bonded organic derivatives, $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MR}$.^{10,11}

Proton Magnetic Resonance Spectra.—Both ethyl complexes (II) and (V), at 60 Mc./sec. in benzene solution, showed a complex resonance for the ethyl-group protons. For the tungsten compound (V), the resonance collapsed to virtually a single line although five peaks could just be distinguished with a separation of 1–2 c./sec. The molybdenum complex (II) showed eight lines with a slightly larger separation. In both cases the pattern indicated a ratio of coupling constant to chemical shift for the methyl to methylene protons of about ten. If the straightforward Dailey–Shoolery interpretation of this ratio¹² is taken, the germanium atom has an effective electronegativity close to hydrogen in these complexes. The greater spread of the ethyl resonance in the molybdenum compound suggests that the increase in electronegativity of germanium attached to molybdenum is less than when it is bonded to tungsten.

Chemical reactions on both the Mo–Ge and W–Ge complexes proceeded similarly. In general tungsten compounds were the more stable as with analogous σ -bonded organic derivatives.

Reaction with Oxygen.—Solutions of the three molybdenum complexes were completely oxidised during 18 hr. to give CO, CO₂, (R₃Ge)₂O, and a deep blue, ill-defined molybdenum-containing material which in the early stages of the oxidation retained much carbonyl and hydrocarbon.



The infrared frequencies of the residual carbonyl in this (probably polymeric) material were shifted 20–40 cm.⁻¹ to lower frequency compared with the original material, and the number of carbonyl frequencies increased. In no case was the fate of the cyclopentadienyl group determined. On further contact with oxygen the blue material lost its infrared structure giving one of the blue forms of molybdenum trioxide. During the oxidation the colour of solutions of (I) and (II) changed from pale pink through deep red to yellow-green and were finally deep blue, when they showed a strong Tyndall-cone effect. Mass spectrometry of the partially oxidised blue material gave evidence for the trisgermylmethanol, (R₃Ge)₃COH. Oxygen reacted much more slowly with the crystalline solids (I) and (II) although they rapidly acquired a red-brown surface coating. Some 15% of CO + CO₂ were formed after 3 months at 20°. The methyl complex (I) was explosively oxidised by concentrated nitric acid.

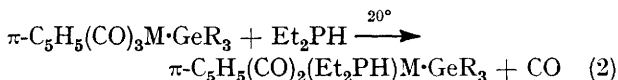
Both tungsten compounds (IV) and (V) were much more stable towards oxygen, especially the methyl complex, which was recovered in 80% yield after remaining in contact with excess of oxygen in benzene

solution for 40 days at 20°. Again the oxidation products isolated were CO, CO₂, (R₃Ge)₂O, and WO₃, but there was no striking colour change. In all oxidation experiments the ratio of CO₂ to CO was about 1 : 3.

Hydrolysis.—All the complexes (I)–(V) were unaffected by air-free water during 2 days at 20°.

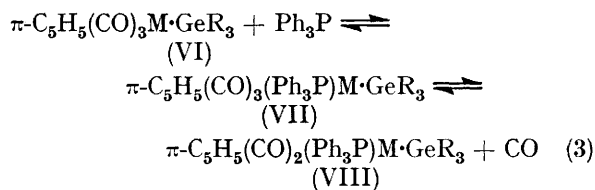
Thermal Decomposition.—Slow thermal decomposition of the molybdenum complex (II) was observed at 150–200° with partial loss of CO and the formation of a small amount of triethylcyclopentadienylgermane. This parallels a rearrangement which is observed under electron impact. Even after 2 days at 200° some 90% of the original complex was present. The tungsten complex (IV) was even more stable and, after 5 days at 190°, 91% of undecomposed complex was recovered together with the red crystalline dimer, $[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{W}]_2$, carbon monoxide, and a green-black material soluble in acetone.

Ligand-exchange Reactions.—For each compound displacement (2) of one carbonyl group occurred quantitatively when dissolved in excess of diethylphosphine.



These mixed carbonyl–diethylphosphine complexes were exceedingly air-sensitive low-melting solids or viscous liquids.

The reaction (3) with triphenylphosphine was more complex, and the evidence described below suggests reversible addition of triphenylphosphine followed by reversible loss of carbon monoxide. In evacuated sealed



tubes the molybdenum complexes and triphenylphosphine, in benzene or cyclohexane, deposited a small proportion of pale brown, flocculent material (VII) after 1–4 hr. at 60°, and roughly the same amount of this material persisted throughout the total period of heating. After 14–20 days at 60–80° the carbon monoxide isolated corresponded to 10–50% reaction based on displacement of 1 CO per mole of complex. Work-up of the mixture gave the orange dicarbonyl–triphenylphosphine complexes (VIII) and in reactions carried out in a stream of nitrogen this substitution product was obtained in high yield after a short period. The dicarbonyl–triphenylphosphine complexes were stable to air during several days. When the tungsten complex $\pi\text{-C}_5\text{H}_5(\text{CO})_2(\text{Ph}_3\text{P})\text{W}\cdot\text{GeMe}_3$ was shaken in an atmosphere of carbon monoxide for 14 days there was infrared and mass spectrometric evidence for the presence of the tricarbonyl complex (IV), and by bubbling CO through a

¹⁰ J. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

¹¹ M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 1963, 273.

¹² B. P. Dailey and J. N. Shoolery, *J. Amer. Chem. Soc.*, 1955, **77**, 3977.

solution of (VIII) ($M = W$, $R = Me$) the tricarbonyl (VI) could be regenerated in >50% yield.

Mass spectrometry of the brown material formed early in the reaction of the molybdenum complexes showed, under low resolution (1:2000), ions due to $\pi-C_5H_5(CO)_3(Ph_3P)Mo \cdot GeEt_3^+$ with a well-defined Mo-Ge isotope pattern.¹³ Infrared examination of this material and crude products from the tungsten reactions showed no evidence for a germyl ketone of the type $M \cdot COGeR_3$ (analogous to σ -organo-derivatives).¹⁴ Moreover the solid (VII) was unaffected by air-free aqueous acetone whereas a germyl ketone would probably have been hydrolysed. Similar intermediates could not be isolated from the action of triphenylphosphine on the tungsten complexes but examination of reaction mixtures and crude products showed three close, but distinct, C-H stretching frequencies attributable to the cyclopentadienyl group, and this prompted an attempt to follow the reaction by changes in the p.m.r. spectrum.

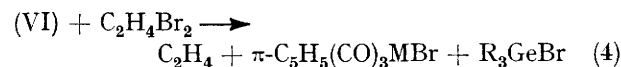
The reaction between $\pi-C_5H_5(CO)_2(Ph_3P)W \cdot GeMe_3$ and CO in deuteriochloroform was carried out in a 1H n.m.r. tube sealed to a bulb containing a ten-fold excess of carbon monoxide at 1 atm. After 1 hr. the singlet resonance due to C_5H_5 protons in the tricarbonyl complex $\pi-C_5H_5(CO)_3W \cdot GeMe_3$ could just be detected. After 10 hr. a second resonance, also a singlet, was detected lying between those due to the C_5H_5 protons in the dicarbonyl-phosphine and tricarbonyl complexes. This new resonance attributed to the complex $\pi-C_5H_5(CO)_3(Ph_3P)W \cdot GeMe_3$, rose to a maximum after 20 hr. and then diminished, whereas the resonance due to the tricarbonyl (IV) grew progressively. After 60 hr. the resonance attributed to the tricarbonyl-triphenylphosphine complex was no longer detectable and at maximum it represented, in terms of peak heights, some 20% of the total C_5H_5 resonance. No other change was detected in the 1H n.m.r. spectrum throughout. The C_5H_5 resonances, relative to tetramethylsilane as internal standard, were $\pi-C_5H_5(CO)_2(Ph_3P)W \cdot GeMe_3$, -302; $\pi-C_5H_5(CO)_3(Ph_3P)W \cdot GeMe_3$, -314; and $\pi-C_5H_5(CO)_3W \cdot GeMe_3$, -323 c./sec., and may perhaps be correlated with deshielding effects due to the increased acceptance of electron density from the metal atom by the entering carbonyl group.

The geometry and bonding in the intermediate (VI) remains uncertain. If the cyclopentadienyl group contributes 6 electrons and the three carbonyl groups remain bonded to the transition metal then a 20-electron complex results in which the transition metal, in oxidation state II, is eight-co-ordinate. On the evidence available the intermediate (VII) could involve a change in the co-ordination of cyclopentadienyl to a π -allyl type of 4-electron ligand in which case an 18-electron complex would result, and the 1H n.m.r. spectrum changes at 35° are not incompatible with this possibility.

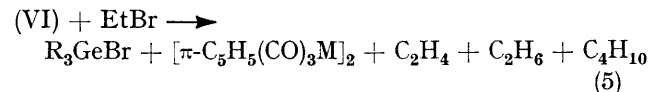
Trimethylphosphine probably reacts in the same way as

triphenylphosphine since after 46 days at 20° it gave carbon monoxide equivalent to 30% of reaction and the complex $\pi-C_5H_5(CO)_2(Me_3P)W \cdot GeMe_3$ was also isolated. Pyridine and the tungsten complex (IV) gave 5% of carbon monoxide after 10 days. The molybdenum complex (II) was only sparingly soluble in di-n-propylamine and less than 1% of CO was formed after 2 months at 20°. In neither of these reactions was a product isolated, but there was mass-spectrometric evidence for the complex $\pi-C_5H_5(CO)_2(C_5H_5N)W \cdot GeMe_3$. The action of the various donor molecules examined in displacing carbon monoxide follows their π -acceptor properties: $Pr^a_2NH < C_5H_5N < Me_3P$, $Ph_3P < Et_2PH$.

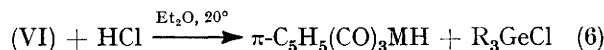
Cleavage of the Metal-Metal Bond.—In contrast to the easy reaction of hydrogen with Pt-Si and Pt-Ge complexes, hydrogenolysis of the Mo-Ge bond in (I) and (II) did not occur even after 5 days at 50°/300 atm. This possibly supports the view that the hydrogenolysis of metal-metal bonds occurs by primary addition of hydrogen to the transition metal, a process which is unlikely in these seven-co-ordinate complexes. Trimethylsilane and phenylacetylene were also unreactive towards the MoGe complexes. With ethylene dibromide an essentially quantitative reaction (4) occurred during 2–4 days at 60°. Ethyl bromide also cleaved the metal-



metal bond (5) in these complexes giving products indicative of radical processes. Reaction (6) with ethereal

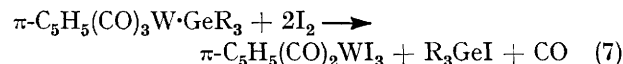


hydrogen chloride gave only two products. The mass



spectrum of the total reaction product showed no ion corresponding to $\pi-C_5H_5(CO)_3MCl$. It is of interest that the molecular ion $\pi-C_5H_5(CO)_3MoH^+$ is of high abundance, in contrast to non-transition metal hydrides, and is some 10 times as abundant as the even-electron ion of highest mass (*i.e.*, $\pi-C_5H_5(CO)_3Mo^+$).

Excess of iodine in benzene solution also cleaved the tungsten-germanium bond with displacement (7) of one carbonyl group giving a tungsten tri-iodide.



Similar molybdenum compounds have been obtained by the action of iodine on the dimer $^{15} [\pi-C_5H_5(CO)_3Mo]_2$.

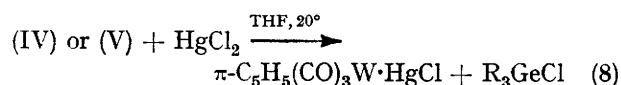
Freshly sublimed mercuric chloride also cleaved the W-Ge bond in (IV) and (V) to give the bright yellow tungsten-mercury chloride complex in an essentially quantitative reaction (8); this complex is air-stable as the

¹³ A. Carrick and F. Glockling, *J. Chem. Soc. (A)*, 1967, 40.

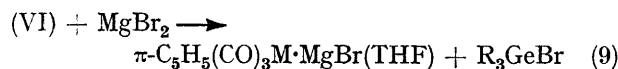
¹⁴ K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, 1967, **6**, 294.

¹⁵ R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc. (A)*, 1966, 1606.

solid at least for several days, but is rather light-sensitive and rapidly decomposes in bright sunlight. A similar

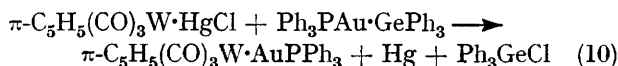


reaction (9) occurred, though somewhat less readily, with anhydrous magnesium bromide in tetrahydrofuran giving the molybdenum- and tungsten-Grignard reagents which have not been previously reported.

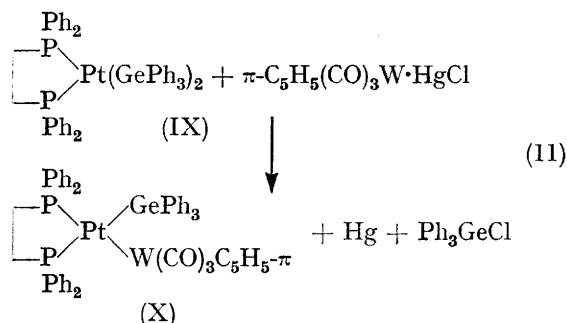


Molecular-weight measurements in freezing benzene indicated that the tungsten compound is monomeric, but the molybdenum compound was too insoluble in benzene for effective measurements. Few examples of 3-co-ordinate magnesium compounds are known¹⁶ and in this case it would probably be sterically difficult to co-ordinate a second tetrahydrofuran molecule. Both the molybdenum and tungsten Grignard reagents were exothermically hydrolysed to the corresponding hydrides, $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MH}$, and an attempt to convert the tungsten Grignard reagent into the σ -phenyl-tungsten complex by reaction with bromobenzene was unsuccessful.

The presence of a potentially reactive -HgCl in the readily handled tungsten-mercury complex prompted us to make a *preliminary* examination of some of its reactions with the aim of forming further metal-metal bonds. Reaction (10) with the gold-germanium complex $\text{Ph}_3\text{PAu}\cdot\text{GePh}_3$ was rapid at room temperature giving mercury and a thin red film of gold on the walls of the reaction vessel. The product, a tungsten-gold complex which formed pale yellow crystals, was isolated in 70% yield.

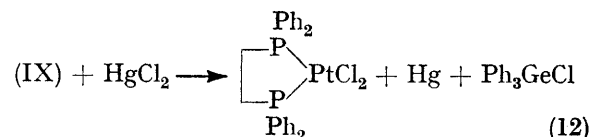


Similarly as an equimolar mixture with a bistrisphenyl-germylplatinum complex (IX) mercury was rapidly precipitated, although the Pt-W complex (X) was isolated with difficulty (reaction 11). Cleavage of Pt-Ge

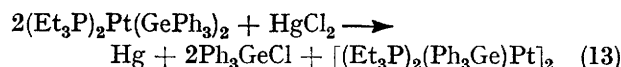


bonds by mercuric chloride was also investigated and is of interest because platinum-Grignard and -lithio-

intermediates have previously been postulated.¹⁷ The chelating phosphine-platinum complex (IX) with 1 mol. of mercuric chloride gave only unchanged material, mercury, and the platinum dihalide complex, possibly because of the low solubility of the starting material (reaction 12). By contrast slow addition of a solution

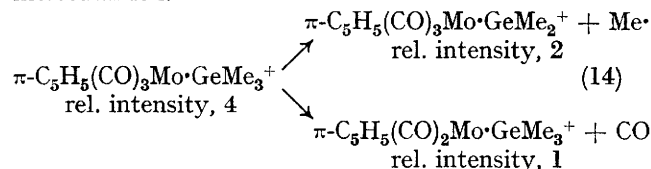


of mercuric chloride to 2 mol. of $(\text{Et}_3\text{P})_2\text{Pt}(\text{GePh}_3)_2$ resulted (13) in an immediate precipitation of mercury with the formation of what is probably a Pt-Pt complex.



Mass Spectra.—Mass and abundance data for Mo-Ge isotope combinations have been given elsewhere;¹³ those for W-Ge and other combinations of polyisotopic elements were obtained in the same way. The mass spectra of the compounds described in this paper are exceedingly complex with many intense (overlapping) metastable peaks and, even under high resolution (1:10,000), only their main features have been elucidated. The compounds (I)–(V) all showed intense molecular ions, most of the ion-current (*ca.* 70–80%) being carried by ions containing the metal-metal bond. This high abundance of molecular ions is in marked contrast to non-transition-metal compounds¹⁸ of the type $\text{R}_3\text{M}\cdot\text{M}'\text{R}'_3$ where the most abundant species are even-electron ions, which implies that it is a bonding electron which is removed by ionisation of the non-transition-metal compounds. In these molybdenum and tungsten complexes it is probably a non-bonding *d*-electron which is removed on ionisation so that structure and stability relationships based on whether the number of electrons is odd or even lose their meaning.

Considerable differences were observed between the methyl complexes (I) and (IV). The Mo complex (I) showed ions corresponding to loss (14) of a methyl radical together with ions due to loss of CO from the molecular ion.



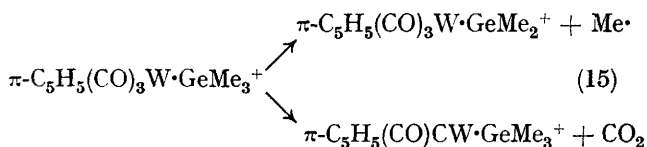
By contrast the molecular ion of the tungsten complex (V) lost $\text{Me}\cdot$ and CO_2 (reaction 15) and unfortunately the region of the metastable peak for CO_2 elimination contained intense metastable peaks due to other transitions. The molybdenum complex also showed ions due to loss of CO_2 , but only after elimination of two methyl groups. Cleavage of the metal-germanium bond must

¹⁶ G. E. Coates and D. Ridley, *J. Chem. Soc. (A)*, 1967, 56.

¹⁷ R. J. Cross and F. Glockling, *J. Organometallic Chem.*, 1965, 3, 253.

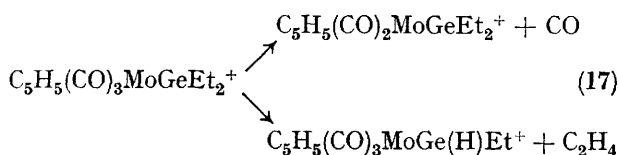
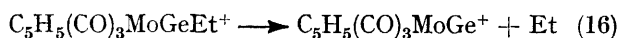
¹⁸ D. B. Chambers and F. Glockling, *J. Chem. Soc. (A)*, 1968, 735.

also occur since the ion Me_3Ge^+ is relatively of high abundance. There was evidence for the ion



$\text{C}_5\text{H}_5\text{M}\cdot\text{GeH}_2^+$ which implies loss of CH_2 or C_2H_4 from the $\text{M}\cdot\text{GeMe}_3$ group, and these elimination reactions have been observed in methylgermanes.¹⁹ Germanium hydride ions were even more abundant in the spectra of (II), (III), and (V) where they are formed by alkene elimination (*e.g.*, $\text{M}\cdot\text{GeEt}^+ \rightarrow \text{M}\cdot\text{GeH}^+ + \text{C}_2\text{H}_4$). The $\text{Mo}\cdot\text{Ge}$ complex (I) showed fragments corresponding to loss of 15, 16, 28, 29, 30, and 44 mass fragments which are probably CH_3 , $(\text{O}\cdot\text{CH}_3)$, $(\text{CO}\cdot\text{C}_2\text{H}_4)$, HCO , H_2CO , and CO_2 respectively. No ion containing only molybdenum or tungsten fragments such as $\text{C}_5\text{H}_5\text{M}^+$ was detected although the spectra were particularly complex in these regions. Fragmentation of the cyclopentadienyl group in $\text{C}_5\text{H}_5\text{MGe}$ gave ions corresponding to loss of H , H_2 , CH , and C_2H_2 . The production of the $\text{C}_5\text{H}_5\text{Ge}^+$ ion in all of the spectra is probably analogous to the ions produced by the transfer of alkyl or aryl groups between metal atoms in compounds of the type $\text{R}_3\text{M}\cdot\text{M}'\text{R}'_3$.¹⁸

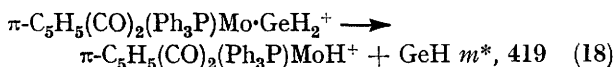
For the ethyl and propyl complexes (II), (III), and (V) the most abundant ion was formed by loss of an R' radical from the molecular ion and, in contrast to the methyl complexes, loss of CO or CO_2 from the molecular ions gave ions of low abundance. The further fragmentation of the ethyl and propyl complexes was extremely complex, producing overlapping patterns owing to loss of CO , HCO , H_2CO , alkyl radical, and alkene with no particularly dominant process (reactions 16, 17).



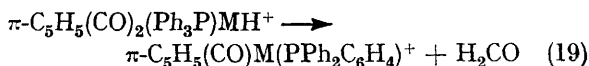
A number of doubly charged ions were visible in the spectra. For the tungsten-methyl compound (IV) these corresponded to all the major $\text{W}\cdot\text{Ge}$ -containing fragments, $\text{C}_5\text{H}_5(\text{CO})_n\text{W}\cdot\text{GeMe}_m$ ($n = 0-3$; $m = 0-2$). The molybdenum analogue (I) showed fewer doubly charged ions and these were in general of lower abundance. One interesting feature is that the abundances of the doubly charged ions increased uniformly from high to low mass whereas those of the singly charged species for the tungsten compound, showed a roughly alternating abundance [*e.g.*, $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{W}\cdot\text{GeMe}_2^+ > \pi\text{-C}_5\text{H}_5(\text{CO})_2\text{W}\cdot\text{GeMe}_2^+$ whereas $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{W}\cdot\text{GeMe}_2^{2+} < \pi\text{-C}_5\text{H}_5(\text{CO})_2\text{W}\cdot\text{GeMe}_2^{2+}$]. In the mass spectrum of the molybdenum-ethyl compound (II) which showed the ions $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoGe}^{2+}$, $\pi\text{-C}_5\text{H}_5(\text{CO})_2\text{MoGe}^{2+}$, $\pi\text{-C}_5\text{H}_5(\text{CO})\text{MoGe}^{2+}$, and $\pi\text{-C}_5\text{H}_5\text{MoGe}^{2+}$ the reverse order

of abundances was observed with $\pi\text{-C}_5\text{H}_5(\text{CO})_2\text{MoGe}^{2+}$ as the most abundant species.

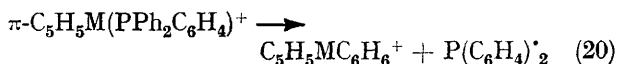
In the dicarbonyl-triphenylphosphine complexes (VIII) the proportion of the ion current carried by ions containing the metal-germanium bond is considerably lower, but the molecular ions were still detected. In contrast to the tricarbonyl compounds (I)–(V) the phosphine complexes showed intense ions containing the transition metal without germanium, and a metastable-supported transition was observed for the elimination (18) of a neutral germanium-containing fragment:



Similar transitions have been observed in organogermanes and result in a characteristic shape of the metastable peak.^{18,19} Elimination (19) of H_2CO was also metastable-supported, and the resultant ion, after loss



of the remaining carbonyl group, eliminated $[\text{P}(\text{C}_6\text{H}_4)_2]$ to give (20) a high-intensity ion $\text{C}_5\text{H}_5\text{MC}_6\text{H}_6^+$ which, if both hydrocarbons are π -bonded to the metal, is a 16-electron ion.



Two doubly charged ions $[\text{C}_5\text{H}_5\text{MP}(\text{C}_6\text{H}_4)_2]^{2+}$ and $[\text{C}_5\text{H}_5\text{MPPh}_3]^{2+}$ were present. In the diethylphosphine complexes $\pi\text{-C}_5\text{H}_5(\text{CO})_2(\text{Et}_2\text{PH})\text{M}\cdot\text{GeR}_3$, fragment ions containing the metal-metal bond were more abundant than in the triphenylphosphine complexes, but the most abundant ion was $\pi\text{-C}_5\text{H}_5(\text{CO})_2(\text{Et}_2\text{PH})\text{M}^+$.

EXPERIMENTAL

π -Cyclopentadienyltrimethylgermyltricarboxylmolybdenum (I).—Freshly cracked cyclopentadiene (4.0 g., 62 mmoles) was added slowly to a stirred suspension of sodium (1.2 g., 48 mmoles) in tetrahydrofuran (THF, 120 ml.) and the pink solution refluxed for 2 hr. Molybdenum hexacarbonyl (12.6 g., 476 mmoles) was added and the mixture refluxed, with stirring, for 15 hr. Vigorous effervescence occurred during the first hour of reflux and the colour of the solution slowly changed to a clear orange. Trimethylbromogermane (9.5 g., 48 mmoles) in THF (50 ml.) was added slowly at room temperature, where upon the solution became yellow with formation of a thick white precipitate. After reflux for 3 hr., the colour changed to orange-red. The solution was filtered (under nitrogen), the THF removed *in vacuo*, replaced by pentane (40 ml.) and the solution again filtered to remove sodium bromide which had been dissolved in the THF. Lustrous plates were deposited from the solution at -10° . The mother-liquors were decanted and the crystals washed with pentane at -78° , and recrystallised to give pale pink crystals of the complex (11.5 g., 65%) (analyses are in the Table). Sublimation at $50-55^\circ/10^{-4}$ mm. gave the complex as virtually colourless plates.

¹⁹ F. Glockling and J. R. C. Light, *J. Chem. Soc. (A)*, 1968, 717.

π -Cyclopentadienyltriethylgermyltricarbornylmolybdenum (II).—This was prepared analogously from sodium cyclopentadienide (74 mmoles), molybdenum hexacarbonyl (16.3 g., 62 mmoles), and triethylbromogermane (15 g., 62 mmoles). It crystallised as pink needles from pentane at -60° (yield, 9.6 g., 46%). Its ultraviolet spectrum in ethanol showed three main bands: λ_{max} 207 m μ , $\log \epsilon$ 3.44; λ_{max} 263 m μ , $\log \epsilon$ 3.00; λ_{max} 320 m μ , $\log \epsilon$ 2.40.

Similarly tri-*n*-propylbromogermane (12 g.) and the sodium salt of *π -cyclopentadienyltricarbonylmolybdenum* (43 mmoles) in THF yielded the brick red complex *cyclopentadienyltri-*n*-propylgermyltricarbornylmolybdenum* (III). Some difficulty was experienced in the isolation of this material because of its great solubility in all common solvents, and it was crystallised from pentane at -78° with considerable loss. Its low m.p. (*ca.* 25°) added to the difficulties and only mass spectrometric and infrared characterisation were obtained.

The tungsten complexes *π -cyclopentadienyltrimethylgermyltricarbornyltungsten* (IV) and the *triethylgermyl analogue* (V) were prepared in a similar way, but in di-*n*-butyl ether as a medium. The sodium 'shot' for the reactions was prepared *in situ* in this solvent and refluxed for 12 hr. to ensure complete reaction with the added cyclopentadiene. White crystals of sodium cyclopentadienide formed on cooling the solution, and after addition of the tungsten carbonyl the mixture was refluxed for 36 hr. before addition of the germanium halide. Addition of 30% (v/v) of THF increased the solubility of the reactants. All the complexes had characteristic, sweetish, nauseating odours.

Reactions of the Complexes.—Oxidation. The molybdenum complex (I) (91 mg., 0.25 mmole) was dissolved in benzene (2.5 ml.) in a 'break-seal' tube, which was then filled with dry oxygen (25 ml.), sealed, and shaken for 20 days. During the first 17 hr. the colour changed as described in the text. Fractional condensation of the volatile products gave CO [9.07 c.c.s at S.T.P. (N-c.c.), identified by its infrared and mass spectrum and estimated by combustion], CO₂ (2.18 N-c.c., infrared, and mass-spectroscopic identification), ratio of complex to CO and CO₂, 1 : 1.61 : 0.57 respectively. Examination of the solvent by vapour-phase chromatography (v.p.c.) confirmed the presence of hexamethyldigermoxane. The crude blue residue showed considerable infrared structure and the mass spectrum of this material showed peaks due to (Me₃Ge)₂O and others ascribable to a compound of the formula (Me₃Ge)₃COH. Mass spectrometry on other blue residues from similar experiments showed peaks which could be ascribed to the latter compound under low resolution, but high-resolution confirmation of this formulation could not be obtained. No significant amount of the blue residue could be Soxhlet-extracted with benzene, and on further exposure to air it lost its infrared bands, other than a broad metal-oxygen vibration centred on 12 μ , and failed to yield any mass spectrum from a direct insertion probe.

The crystalline molybdenum complex (II) sealed in oxygen gave after 3 months at 20° a small amount of CO and CO₂ (<1 N-c.c.) and a brown-black solid [Found: C, 35.4; H, 4.4. C₁₄H₂₀GeMoO₇, *i.e.*, C₅H₅(CO)₃(O₄)MoGeEt₃, requires C, 35.8; H, 4.3%], which showed four vibrations in the carbonyl stretching region (1961, 1946, 1916, 1883 cm.⁻¹ in KBr). This material did not melt below 350° , and was slightly soluble in benzene and methanol to give orange-red solutions which became blue on exposure to air. Starting material was also recovered.

After 40 days in contact with oxygen (410 N-c.c.) a benzene solution of the tungsten complex (IV) (436 mg.) gave CO₂ (6.5 N-c.c.) and CO (27 N-c.c.) and unchanged material. V.p.c. showed the presence of (Me₃Ge)₂O in the solvent.

Pyrolysis. The molybdenum complex (II) (210 mg., 0.51 mmole) was heated in a vacuum for 6 days at 150 – 160° . Carbon monoxide (0.40 N-c.c.), was collected and further heating at 200° for two days produced additional gas (<0.05 N-c.c.). Sublimation of the solid *in vacuo* gave starting material (185 mg., 89%) and a red solid (10 mg.) [Found: C, 40.3; H, 4.2%; M, 615–740 (v.p. osmometer, benzene solution)] part of which slowly sublimed at 60 – $70^\circ/10^{-5}$ mm. to give scarlet crystals. Complex (I) behaved similarly, little decomposition occurring below 200° .

A small quantity of the molybdenum complex (II) was heated to 200° for 15 min. in the hot inlet system of the mass spectrometer and then the volatile products were admitted to the ionisation chamber. C₅H₅GeEt₃ was characterised together with peaks at higher masses ascribable to ion fragments from the unaltered complex.

Heating the tungsten complex (IV) (138 mg.) in a small (6 ml.) break-seal tube for 5 days at 180 – 190° gave CO (0.614 N-c.c.). Sublimation of the residual solid from the tube gave starting material (91%) and a few milligrams of light red crystals identified (by infrared) as [*π -C₅H₅W(CO)₃*]₂. A small amount (*ca.* 1 mg.) of a green-black, involatile, acetone-soluble material remained in the reaction vessel after the sublimation.

Reactions with Diethylphosphine.—The molybdenum complex (II) (17 mg., 0.42 mmole) was sealed with freshly distilled diethylphosphine (3 ml.) in an evacuated break-seal tube. After 28 days at room temperature, the solution yielded carbon monoxide (8.65 N-c.c., 92%). Removal of the excess of phosphine *in vacuo* and crystallisation of the residue from pentane at -20° , gave the pale yellow, highly air-sensitive, low-melting complex *π -cyclopentadienyltriethylgermyldiethylphosphinedicarbonylmolybdenum* [*v*(P–H) 2286, *v*(CO) 1942s, 1910m,sh, 1848s, *v*(CH) of C₅H₅ 3106 cm.⁻¹; M (¹⁷⁰MoGe) 468]. No further characterisation of this material was obtained. (Note: ¹⁷⁰MoGe here and in similar cases means that the sum of the atomic weights is 170 for the most abundant isotope combination.)

A similar reaction between the tungsten complex (IV) (160 mg.) and diethylphosphine (2.5 ml.) gave CO (7.98 N-c.c., 100%) after 14 days at room temperature and *π -cyclopentadienyltrimethylgermyldiethylphosphinedicarbonyltungsten* as a golden yellow air-sensitive liquid [Found: C, 32.6; H, 4.9%; M (²⁵⁶WGe), 512. C₁₅H₂₅GeO₂PW, *i.e.*, C₅H₅(CO)₂(Et₂PH)WGeMe₃ requires C, 32.8; H, 4.9%; M (²⁵⁶WGe), 512], *v*(CO) 1941s, 1861s, *v*(P–H) 2286 cm.⁻¹ (in CCl₄).

Triphenylphosphine Reactions.—(a) *In sealed systems.* The molybdenum complex (I) (325 mg., 0.895 mmole) and triphenylphosphine (620 mg., 2.4 mmoles) were dissolved in benzene (5 ml.) and heated in a break-seal tube for 24 days at 65° . Carbon monoxide (6.53 N-c.c., 32%) was collected and the yellow-brown material (25 mg.) which formed during the first 4 hr. of heating was filtered off from the solution and the infrared spectra of this solid and the solution were rapidly examined in the region 4.5–6.5 μ . Three major bands occurred in this range (1818s, 1894m, 2016m cm.⁻¹ in KBr) none of which could be ascribed to the grouping MoCOGeMe₃. The mass spectrum of the solid showed

under unit resolution rather ill-defined ions corresponding to $C_5H_5(CO)_3(PPh_3)Mo \cdot GeMe_3$. Aqueous acetone had no effect on the infrared spectrum or appearance of the remainder of the benzene solution of the crude product, and gave no additional gas. Replacement of the benzene by methylcyclohexane gave at -40° pale yellow crystals of π -cyclopentadienyltrimethylgermyltriphenylphosphinedicarbonylmolybdenum, m.p. $215-216^\circ$ (sealed tube) [Found: C, 57.2; H, 5.01; P, 5.9. $C_{28}H_{29}GeMoO_2P$, i.e., $\pi-C_5H_5(PPh_3)(CO)_2MoGeMe_3$, requires C, 56.3; H, 4.9; P, 5.1%], $\nu(CO)$ in $CDCl_3$, 1911s, 1894m,sh, 1831 cm^{-1} . The 1H n.m.r. spectrum of this material (50 mg./c.c. in $CDCl_3$) showed resonances corresponding to $\pi-C_5H_5$, τ 5.18, C_6H_5 , τ 2.53, and CH_3 , τ 9.42 in the ratio 5.2 : 15.0 : 9.7.

A tube containing the molybdenum complex (I) (324 mg.) and triphenylphosphine (910 mg.) in benzene (1 ml.) gave, after heating for 24 hr. at 65° , CO (4.7 N-c.c., 24%) and, on immediate removal of benzene and washing of the resultant solid with light petroleum (b.p. $40-60^\circ$), a buff powder, m.p. $100-200^\circ$ (decomp.) (Found: C, 52.3; H, 4.6; P, 5.7%) whose mass spectrum under low source-pressure conditions showed ions ascribable to $C_5H_5(CO)_3(PPh_3)Mo \cdot GeMe_3$. A similar experiment using twice the amount of triphenylphosphine gave 2.44 N-c.c. (12%) of CO after 24 days at room temperature, together with the yellow-brown intermediate (35 mg.). Again the dicarbonyl-phosphine complex was the major product, crystallising from a brown solution in methylcyclohexane.

The molybdenum complex (II) with either an excess or 1:1 molar ratio of triphenylphosphine in methylcyclohexane yielded, after heating at $65-70^\circ$ for 1-7 days, 25-31% of CO and buff crystals of π -cyclopentadienyltrimethylgermyltriphenylphosphinedicarbonylmolybdenum (25%), m.p. $165-170^\circ$ decomp., $\nu(CO)$, 1937s, 1898w, 1858 cm^{-1} [Found: C, 58.3; H, 4.3; P, 6.8%; M ($^{170}MoGe$), 612. $C_{32}H_{35}GeMoO_2$, i.e., $C_5H_5(CO)_2(PPh_3)MoGeEt_3$, requires C, 57.6; H, 5.3; P, 4.6%; M , 612]. The initial light brown precipitate gave a reproducible mass spectrum under low-pressure conditions, showing ions corresponding to $C_5H_5(CO)_3(PPh_3)Mo \cdot GeEt_3$ with the required MoGe isotope pattern, but satisfactory high-resolution mass measurements were not obtained. In all experiments starting materials were recovered.

Similar experiments with the tungsten complex (IV) (1.06 mmoles) and Ph_3P (1.23 mmoles) in methylcyclohexane (5 ml.) gave 22.5% (5.29 N-c.c.) of CO after 30 days at 65° . Normal work-up gave π -cyclopentadienyltrimethylgermyltriphenylphosphinedicarbonyltungsten (243 mg., 34%) [Found: C, 52.8; H, 3.9; P, 6.3%; M (^{256}WGe), 684. $C_{28}H_{29}GeO_2PW$, i.e., $C_5H_5(CO)_2(PPh_3)WGeMe_3$, requires C, 49.1; H, 4.3; P, 4.5%; M , 684]. From a reaction of (IV) with a 3-fold excess of triphenylphosphine at 65° , 17% of CO was isolated. The infrared spectrum of the crude reaction products showed, in addition to three $\nu(CO)$ bands, three $\nu(C-H)$ bands for the C_5H_5 unit at 3135, 3125, 3096 cm^{-1} .

(b) *In an open system.* To the molybdenum complex (II) (3.6 g., 0.086 mole) in pentane (8 ml.) in a double Schlenk tube, was added a benzene solution of triphenylphosphine (2.4 g., 0.092 mole). During the first 15 min. of stirring, a small amount of buff material separated. The brown solution was stirred at room temperature overnight, filtered, and the solvent removed *in vacuo* to give the phosphine-dicarbonyl complex (4 g., 75%) from methylcyclohexane.

Reaction of $\pi-C_5H_5(CO)_2(Ph_3P)W \cdot GeR_3$ with Carbon Mon-

oxide.—(a) *Sealed system.* The complex (48 mg.) in 1:1 benzene-acetone (6 ml.) was sealed in a 120 ml. flask containing CO at 1 atm., and shaken for 14 days at 18° . The infrared spectrum of the recovered material (38 mg. of solid) showed three major carbonyl stretching frequencies, and the mass spectrum of this material showed unequivocally the presence of the tricarbonyl complex ($\pi-C_5H_5(CO)_3WGeMe_3$). Exposure of the crude reaction product (as a semi-solid before crystallisation) gave large Ph_3PO^+ and $Ph_3PO_2^+$ ions in the mass spectrum which were not observed in the spectra of the dicarbonyl-phosphine complexes and these ions are attributed to oxidation of the tricarbonyl-phosphine intermediate.

(b) *Open system.* A slow current of carbon monoxide was passed through a refluxing solution of the dicarbonyl-phosphine complex (33 mg.) in benzene (5 ml.). After 18 hr. the infrared spectrum of the solution showed the three major carbonyl stretching frequencies (2026s, 1929s, 1835s cm^{-1}) of the tricarbonyl compound. The mass spectrum of the solid residue (33 mg.) was determined without further treatment. This showed ions due to $\pi-C_5H_5(CO)_3W \cdot GeMe_3$ (mol. ion intensity 1.2) and $\pi-C_5H_5(CO)_2(PPh_3)W \cdot GeMe_3$ (mol. ion intensity 1.0) but none due to a tricarbonyl-phosphine complex $\pi-C_5H_5(CO)_3(PPh_3)W \cdot GeMe_3$. The infrared spectrum of the solid also corresponded to a mixture of the dicarbonyl-phosphine and tricarbonyl complexes.

Reaction with Trimethylphosphine.—The tungsten complex (IV) (440 mg.), trimethylphosphine (1.2 mmoles), and benzene (5 ml.) were introduced into a break-seal tube. Work-up of the solution after 44 days at 20° yielded CO (6.9 N-c.c., 32%) and from methylcyclohexane yellow crystals of π -cyclopentadienyltrimethylgermyltrimethylphosphinedicarbonyltungsten, m.p. 80° $\nu(CO)$ 1887s, 1799s cm^{-1} [Found: C, 31.5; H, 4.6%; M (^{256}WGe), 588. $C_{13}H_{25}GeO_2PW$, i.e., $C_5H_5(CO)_2(PMe_3)WGeMe_3$ requires C, 31.3; H, 4.6%; M , 588]. The complex smelled strongly of trimethylphosphine.

Cleavage by 1,2-Dibromoethane.—The molybdenum complex (I) (376 mg., 1.03 mmoles) in 1,2-dibromoethane (5.1 g.) gave after heating for 4 days at 75° ethylene (21.7 N-c.c., 94%), Me_3GeBr (by v.p.c.), and lustrous dark red crystals of π -cyclopentadienyltricarbonylmolybdenum bromide (from pentane) [Found: C, 29.5; H, 1.9; Br, 23.8. $C_5H_5BrMoO_3$ requires C, 29.6; H, 1.5; Br, 24.6%].

Cleavage by Ethyl Bromide.—The molybdenum complex (II) (145 mg., 0.349 mmole) and ethyl bromide (5 ml.) gave a red solution after 4 months at room temperature. Fractional condensation of the volatile products gave a mixture of ethylene and ethane (5.1 N-c.c.). V.p.c. of the excess of ethyl bromide showed the presence of triethylbromogermane and butane. The residual red solid was separated by fractional crystallisation from benzene-pentane into starting material and bis-(π -cyclopentadienyltricarbonylmolybdenum) (characterised by infrared spectroscopy).

A similar experiment in which the tungsten complex (IV) (368 mg., 0.819 mmole) and ethyl bromide (5 ml.) were heated for 9 days at 65° gave ethane-ethylene (9.57 N-c.c.), carbon monoxide (1.3 N-c.c.), C_4H_{10} , Me_3GeBr , starting material, and $[\pi-C_5H_5W(CO)_3]_2$ (74 mg.).

Cleavage by Hydrogen Chloride.—The molybdenum complex (I) (332 mg., 0.915 mmole) and dry diethyl ether (5 ml.) saturated with hydrogen chloride were stirred magnetically in a vacuum apparatus at room temperature for four days. The clear solution became orange and deposited

yellow crystals of π -cyclopentadienyltricarbonylmolybdenum hydride [$\nu_{\text{Mo-H}}$ 1786 cm^{-1} (CS_2), M (^{98}Mo), 248]. The mass spectrum of this hydride showed intense molecular ions with a clean Mo isotope pattern and no trace of the halide $\text{C}_5\text{H}_5(\text{CO})_3\text{MoCl}$. V.p.c. examination of the ether showed trimethylchlorogermane and no trace of trimethylgermane.

Dry hydrogen chloride bubbled through a benzene solution of the molybdenum-ethyl complex also yielded the molybdenum hydride and triethylchlorogermane.

Cleavage by Iodine.—The tungsten complex (393 mg., 0.872 mmole), iodine (634 mg., 2.50 mmoles), and benzene (15 ml.) gave after 76 days at room temperature, carbon monoxide (19.3 N.c.c., 99%). The excess of iodine was removed by vacuum sublimation at 45° leaving π -cyclopentadienyldicarbonyltri-iodotungsten (439 mg., 73%), $\nu(\text{CO})$ 2062s, 2020s, 2004s, sh cm^{-1} [Found: C, 12.2; H, 1.2; I, 56.7. $\text{C}_7\text{H}_5\text{O}_2\text{I}_3\text{W}$, i.e., $\text{C}_5\text{H}_5(\text{CO})_2\text{WI}_3$, requires C, C, 12.3; H, 0.7; I, 55.5%]. At a source temperature of 200° it yielded a mass spectrum showing large I_2^+ and $[\text{C}_5\text{H}_5(\text{CO})_2\text{IW}]_2^+$ ions. The presence of Me_3GeI in the benzene solvent was confirmed by mass spectrometry.

Cleavage by Mercuric Chloride.—To the tungsten complex (IV) (487 mg., 1.08 mmoles) in THF (2 ml.) was added freshly sublimed mercuric chloride (296 mg., 1.09 mmole) in THF (3 ml.). After stirring at room temperature overnight solvent was removed giving the bright yellow solid π -cyclopentadienyltricarbonyl tungsten mercury chloride (181 mg., 32%), m.p. 196 – 197° (decomp.) [Found: C, 17.1; H, 1.1. $\text{C}_5\text{H}_5\text{ClHgO}_3\text{W}$, i.e., $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{W}\cdot\text{HgCl}$, requires C, 16.9; H, 0.9%], $\nu(\text{CO})$ 1923, 2015 cm^{-1} in C_6H_6 . The compound crystallised on slow evaporation of a THF solution. It was air-stable during 2–3 days, but darkened rapidly in sunlight (15–30 min.), depositing mercury.

In a similar experiment the tungsten complex (V) (940 mg.) and mercuric chloride (520 mg.) in THF (15 ml.) gave after 2 hours' stirring at room temperature the same tungsten-mercury compound (733 mg., 68%). At a source temperature of 190° , molecular ions of this compound were not visible in its mass spectrum but large Hg^+ and $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{W}^+$ ions were found.

Cleavage by Magnesium Bromide.—Anhydrous magnesium bromide was prepared in one limb of a double Schlenk tube from magnesium turnings (520 mg.) and 1,2-dibromoethane (1.0 g.) in THF (12 ml.). To this filtered solution was added a solution of the tungsten complex (V) (795 mg.) in THF (8 ml.) and the mixture was stirred at room temperature for 4 days. The THF was then removed *in vacuo* and the residual pink solid extracted with benzene to give a red solution. The benzene was removed from this solution and the extraction repeated, giving finally π -cyclopentadienyltricarbonyltungstenmagnesium bromide tetrahydrofuranate (0.4 g.) as a pink solid, $\nu(\text{CO})$ 1916s, 2025s, 2044w cm^{-1} (in C_6H_6) [Found: C, 25.5; H, 2.8%; M , 546. $\text{C}_{13}\text{H}_{13}\text{BrMgO}_4\text{W}$, i.e., $\text{C}_5\text{H}_5(\text{CO})_3\text{WMgBr}(\text{C}_4\text{H}_9\text{O})$, requires C, 28.3; H, 2.6%; M , 509. $\text{C}_5\text{H}_5(\text{CO})_3\text{WMgBr}$ requires C, 22.0; H, 1.1. $\text{C}_5\text{H}_5(\text{CO})_3\text{WMgBr}\cdot 2\text{THF}$ requires C, 33.1; H, 3.6%]. The ^1H n.m.r. spectrum of a saturated solution of the compound in benzene showed the C_5H_5 singlet at τ 5.44, the THF 'triplet' resonance at τ 6.00, and the THF high-field resonance centred on τ 8.58, with relative intensities 15:12:13 respectively.

The corresponding white molybdenum complex, prepared in the same way, was much less soluble in benzene (Found: C, 34.8; H, 4.2; Br, 17.8. $\text{C}_{12}\text{H}_{12}\text{BrMgMoO}_4$ requires

C, 34.2; H, 3.1; Br, 19.0%). Hydrolysis gave the hydride, $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{MoH}$.

Reactions of the Tungsten-Mercury Compound $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{WHgCl}$.—(i) *With triphenylgermyltriphenylphosphinegold.* The gold complex, $\text{Ph}_3\text{PAu}\cdot\text{GePh}_3$ (620 mg.), in 1:1 THF-benzene (6 ml.) was treated with the tungsten-mercury compound (512 mg.) in THF (3 ml.) with immediate blackening of the solution as mercury was deposited. A thin red film of gold formed on the walls of container. The mixture was stirred for 15 min. and filtered to give a yellow solution from which a buff powder, π -cyclopentadienyltricarbonyltungsten-triphenylphosphinegold (442 mg., 68%) was obtained [Found: C, 41.6; H, 3.0; P, 3.5. $\text{C}_{68}\text{H}_{20}\text{AuO}_3\text{PW}$, i.e., $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{W}\cdot\text{AuPPh}_3$ requires C, 39.4; H, 2.5; P, 3.9%].

(ii) *With 1,2-bis(diphenylphosphino)ethanebistriphenylgermylplatinum.* To a suspension of the platinum complex (125 mg.) in THF (15 ml.) was added a THF solution (5 ml.) of the tungsten-mercury compound (653 mg.). Mercury was precipitated and the platinum complex slowly went into solution. The yellow solution was filtered and, on removal of solvent, yielded from pentane 1,2-bis(diphenylphosphino)ethanetriphenylgermyl- π -cyclopentadienyltricarbonyltungstenplatinum (X) (841 mg., 68%) as a light yellow solid, m.p. 200° (decomp) [Found: C, 47.4; H, 3.9; P, 3.7. $\text{C}_{54}\text{H}_{44}\text{O}_3\text{P}_2\text{PtWGe}$, i.e., $(\text{Ph}_2\text{PCH}_2)_2\text{Pt}(\text{GePh}_3)\text{W}(\text{CO})\pi\text{-C}_5\text{H}_5$, requires C, 50.8; H, 3.6; P, 5.0%]. The mass spectrum at a source temperature of 200° showed the ions Ph_3Ge^+ and $\text{C}_5\text{H}_5(\text{CO})_3\text{W}^+$ and ions with a PtWGe isotope pattern up to mass 990. Weak ions in the region of the molecular ions (mass 1230) could be detected but their isotope pattern could not be distinguished. The compound was air-sensitive, darkening after 10 days' exposure. The pentane mother-liquors contained Ph_3GeCl .

Mercuric Chloride and $(\text{Ph}_2\text{PCH}_2)_2\text{Pt}(\text{GePh}_3)_2$.—To a suspension of the platinum complex (651 mg.) in THF (15 ml.) was added a THF solution (1.5 ml.) of freshly sublimed mercuric chloride (147 mg.). Mercury was slowly formed during two days' stirring at room temperature. The solution yielded starting material, and Ph_3GeCl by fractional crystallisation.

Mercuric Chloride and $(\text{Et}_3\text{P})_2\text{Pt}(\text{GePh}_3)_2$.—A THF solution (1 ml.) of mercuric chloride (388 mg.) was added dropwise during 15 min. to a stirred solution of the platinum complex (295 mg.) in THF (5 ml.). Mercury was precipitated during the addition and after 30 min. the dull yellow-brown solution was filtered and concentrated. Slow addition of light petroleum gave a light brown, microcrystalline solid, *di*[triphenylgermylbis(triethylphosphine)-platinum] [Found: C, 50.9; H, 5.8; P, 7.5. $\text{C}_{60}\text{H}_{90}\text{Ge}_2\text{P}_4\text{Pt}_2$, i.e., $[(\text{Et}_3\text{P})_2\text{Pt}\cdot\text{GePh}_3]_2$, requires C, 49.0; H, 6.2; P, 8.4%], m.p. 151 – 152° . The infrared spectrum of this material was closely similar to that of $(\text{Et}_3\text{P})_2\text{Pt}(\text{GePh}_3)_2$, showing only intensity differences in the bands due to GePh_3 . Its mass spectrum at a source temperature of 190° showed a number of differences from the uninuclear platinum complex at high masses and ions with Pt_2Ge_2 isotope patterns were observed at masses from 950 to 1500.

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