Binuclear Organometallic Compounds. Part VII.[1] Trimethylstannyl Complexes of Tantalum(V), Molybdenum(IV), and Tungsten(IV)

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The amine elimination reaction has been examined using some di- or tri-hydrido-transition metal complexes and Me_3SnNMe_2. This has afforded the new hydrido-trimethylstannyl complexes $(cp)_2Ta(H)_2SnMe_3$, $(cp)_2Mo(H)$-$SnMe_3$, and $(cp)_2W(H)SnMe_3$ ($cp = \pi$-C_5H_5). Halogen complexes $(cp)_2M(X)SnMe_3$ (M = Mo or W; X = Cl, Br, or I) were obtained from the hydrido-precursors and suitable organic halides. Some aspects of the chemistry of $(cp)_2M(X')SnMe_3$ (M = Mo or W; X' = H or Cl) have been studied; the new complexes $(cp)_2W(H)Cl$ and $(cp)_2M(SnMe_3)[-C(CO_2Me)=CHCO_2Me]$ have been obtained.

FORMATION of compounds having metal–metal bonds by elimination of a neutral species from suitable precursors, typically an alkali-metal halide, is widely applicable.[2] In Part I,[3] we described such a procedure, which was the amine elimination reaction [equation (1) where

$$Me_3M^1\text{–}NMe_2 + LM^2H \longrightarrow HNMe_2 + Me_3M^1\text{–}M^2L \quad (1)$$

$$Me_3M^1\text{–}NMe_2 + (cp)_2M^2H_{n+1} \longrightarrow (cp)_2M^2(H)_nM^1Me_3 + HNMe_2 \quad (2)$$

M^1 = Si, Ge, or Sn; M^2 = Cr, Mo, W, or Pt). The work now described is in part an extension of reaction (1) to include basic di- and neutral tri-hydrides of transition metals. Thus, reaction (2) has been realised for M^2 = Mo or W, $n = 1$; M^2 = Ta, $n = 2$; and M^1 = Sn. Reactions (2) all proceeded readily in boiling tetrahydrofuran (THF). Using ^1H n.m.r. spectroscopy to follow the reactions, it was shown that (*a*) for equimolar quantities of the reactants, reaction (2) is quantitative and (*b*) the ease of conversion of the hydrides decreases in the order M^2 = Mo > W > Ta. It was only possible to replace one hydride ligand by a trimethylstannyl group, even under more forcing conditions. This may be due to steric hindrance, but it is more probable that the mono-substitution causes deactivation towards nucleophilic attack. The reactivity of only one hydride ligand of $(cp)_2MH_2$ (M = Mo or W) is not uncommon,[4-6] although reactions involving both hydride ligands are also known.[4,7]

The tantalum product, $(cp)_2Ta(H)_2SnMe_3$, is of some interest as a d^0 high oxidation state (formally +5) complex. In any case, only few Group VA–Group IVB metal–metal bonded species are known and those that have been well substantiated [$Ph_3SnM(CO)_6$, $Ph_3SnM(CO)_5PPh_3$, $Ph_3SnTa(CO)_5P(OPh)_3$, Ph_3SnV-$(CO)_5(n\text{-}C_4H_9)_3P$, and $Ph_3SnM(CO)_4\{(Ph)_2PCH_2\}_2$ (M = V, Nb, or Ta)] [8] are of d^4 M^I type. The possibility of

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[7] (*a*) R. L. Cooper and M. L. H. Green, *J. Chem. Soc.* (*A*), 1967, 1155; (*b*) M. L. H. Green and P. J. Knowles, *J. Chem. Soc.* (*A*), 1971, 1508.

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metal–metal π-bonding does not arise for the Ta (d^0) complex, but may be involved in the Mo and W (d^2) compounds. Recent structural work[9] on $(cp)_2Zr(Cl)$-$SiPh_3$,[1] a d^0 Zr^{IV} complex, has revealed the longest known transition metal–silicon bond (Zr–Si, 2·82 Å). The Ta–Sn bond length in $(cp)_2Ta(H)_2SnMe_3$ is therefore also expected to be very long.

Prolonged heating of dimethylaminotrimethylsilane [reaction (2), M^1 = Si] with the di- or tri-hydrides in boiling THF failed to cause a reaction and in each case starting materials were recovered in high yield. With respect to equation (1), reactivity falls in the series Sn > Ge > Si;[3] the Sn/Si difference is attributed in part to the M^1–N thermochemical bond energies [79·1 (Si)[10] and 41·0 (Sn)[11] kcal mol^{-1}], and also to the differences in nucleophilicities (basicities: SnN > SiN).[11]

The new compounds $(cp)_2M^2(H)_nSnMe_3$ contain M–H bonds as potential reactive centres. A study of the chemistry of the complexes $(cp)_2M^2(H)SnMe_3$ (M^2 = Mo or W), was therefore undertaken, with five possibilities in mind: (*a*) replacement of the trimethylstannyl ligand, (*b*) replacement of the hydride ligand, (*c*) a combination of (*a*) and (*b*), (*d*) insertion into the metal–hydrogen bond, and (*e*) reductive elimination of Me_3SnX (X = halide or hydrogen). Only (*a*)—(*d*) have been realised.

It seems that $(cp)_2W(H)SnMe_3$ is unable to exhibit basic properties towards hydrogen halides without W–Sn scission. Thus, hydrogen chloride gas immediately produced a grey precipitate of $(cp)_2W(H)_3Cl$ which with further gas was converted into the blue-black insoluble $(cp)_2WCl_2$. The formation of $(cp)_2W(H)_3Cl$ is well known for $(cp)_2WH_2$ with hydrogen chloride.[12] Thus, the reaction sequence is likely to be that described by equation (3), and [3(a)] was confirmed by using a 1 : 1 stoicheiometric ratio of reagents. The halogeno-complexes $(cp)_2M^2(X)SnMe_3$ (M^2 = Mo or W; X = Cl, Br, or I), were synthesised from the hydride (X = H), but a careful selection of halogenating agents was necessary. [The dihydrides $(cp)_2M^2H_2$ form the dichlorides $(cp)_2M^2Cl_2$, by heating under reflux in chloroform.[7a]] Addition of carbon tetrachloride to $(cp)_2M^2(H)SnMe_3$ produced rapid formation of the insoluble dichloride $(cp)_2M^2Cl_2$; however, using a 1 : 1 stoicheiometric ratio, with THF as solvent, afforded the deep-red $(cp)_2M^2(Cl)$-$SnMe_3$ in high yield (M^2 = Mo, 84%; M^2 = W, 92%). Other chlorides ($PhCH_2Cl$ or $CH_2{:}CHCH_2Cl$) also furnished $(cp)_2W(Cl)SnMe_3$, but in lower yield (40% and 10%, respectively). A 1 : 1 stoicheiometric interaction of carbon tetrabromide and $(cp)_2W(H)SnMe_3$ yielded the insoluble $(cp)_2WBr_2$. However, stirring $(cp)_2M^2(H)$-$SnMe_3$ with benzyl bromide at room temperature produced (M^2 = Mo, 80%; M^2 = W, 72%) the red-brown $(cp)_2M^2(Br)SnMe_3$. The iodo-homologues were prepared in reasonable yield (50%) by stirring allyl or benzyl iodide and $(cp)_2M^2(H)SnMe_3$ at room temperature, or in low yield (M^2 = W, 10%) using methyl iodide. From n.m.r. studies of the three benzyl halide reactions, it was found that the ease of formation of the halide $(cp)_2W(X)SnMe_3$ decreases in the order I > Br > Cl. In every case, use of a large excess of halogenating agent gave the dihalide $(cp)_2M^2X_2$. An attempt to prepare the fluoro-complex $(cp)_2W(F)SnMe_3$, by fluorination of $(cp)_2W(Cl)SnMe_3$ with silver tetrafluoroborate, led to complete decomposition, with identification only of chlorotrimethylstannane. The successful use of silver tetrafluoroborate to fluorinate transition metal Group IVB chlorides, however, has been reported.[13]

$$\begin{tikzcd}
\mathrm{(cp)_2W(H)SnMe_3 + HCl} \arrow[r, "(a)"] & \mathrm{(cp)_2WH_2 + ClSnMe_3} \arrow[d, "\mathrm{HCl}", "(b)"'] & \\
 & \mathrm{(cp)_2W(H)_3Cl} \arrow[r, "\mathrm{HCl}", "(c)"'] & \mathrm{(cp)_2WCl_2}
\end{tikzcd} \qquad (3)$$

Insertion into the metal–hydrogen M^2–H bond, has only been achieved with the substituted acetylene, dimethyl acetylenedicarboxylate. The reactions proceed smoothly either at room temperature (M^2 = Mo) or under reflux (M^2 = W, 65°). It was anticipated that more forcing conditions would be required than for the monoinsertion into the dihydride $(cp)_2M^2H_2$ (M^2 = Mo, 0°; M^2 = W, 25°).[4] Some difficulty was experienced in removing diethyl ether from the orange crystals of the tungsten complex; however, upon heating the crystals to 140° *in vacuo*, ether of crystallisation was lost and red $(cp)_2W(SnMe_3)[-C(CO_2Me)=CHCO_2Me]$ was obtained. Several attempts have been made to insert tin(II) halides into $(cp)_2M^2(X)SnMe_3$, but no pure complexes were isolated; the reactions appear to yield three or four products (M^2 = Mo, X = Cl), or two major products (M^2 = W, X = Cl) one of which seems to be $(cp)_2W$-$(SnCl_3)SnMe_3$. Tin(II) halides are known to undergo monoinsertion into $(cp)_2M^2X_2$ (M^2 = Mo, W; X = Cl, Br, or I).[6]

The stoicheiometric reaction of ethereal hydrogen chloride solution with $(cp)_2W(Cl)SnMe_3$ affords red crystalline $(cp)_2W(H)Cl$. Any excess of hydrogen chloride rapidly forms the dichloride $(cp)_2WCl_2$. This is similar to the reaction of $(cp)_2W(H)Ph$ with dry hydrogen chloride; at first a red solution is formed [presumably $(cp)_2W(H)Cl$], then $(cp)_2WCl_2$, a colourless gas and benzene.[7b] Although reductive elimination of Me_3SnX from $(cp)_2M^2(X)SnMe_3$ has not been realised so far, it has been observed that pyrolysis (200°) of benzene solutions of $(cp)_2M^2(X)SnMe_3$ (M^2 = W, X = Br; or M^2 = Mo, X = Cl, Br, or I) affords an hydrido-metal complex, but not the expected product $(cp)_2M^2(H)Ph$.

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[13] T. J. Marks and A. M. Seyam, *J. Organometallic Chem.*, 1971, **31**, C62.

The reaction is complicated and no pure products have yet been identified.

Some physical properties of the new compounds, together with their hydride precursors[12] are in the Table. The molybdenum and tungsten complexes, $(cp)_2M^2(H)SnMe_3$, possess stability in air similar to that of their dihydride precursors. Thus, the tungsten compound is less sensitive than its molybdenum analogue, although it decomposes after several minutes' atmospheric exposure. The dihydridotantalum derivative, however, appears to be considerably less air-sensitive and more thermally robust than its trihydride precursor in that it melts without decomposition and can be safely manipulated in air. The halogeno-complexes $(cp)_2M^2(X)SnMe_3$ (M^2 = W) possess similar air stability to the parent hydride (X = H). However, the molybdenum complexes show much greater air sensitivity than their hydride precursor, the pure crystals decomposing instantly in air. Halogeno-complexes (M^2 = Mo or W) possess lower thermal stability, decomposing on melting [except $(cp)_2W(Cl)SnMe_3$], and solubility in organic solvents, than their hydride precursors; the solubility decreasing in the order I > Br > Cl. Replacement of the trimethylstannyl ligand by hydrogen in the chloro-complex $(cp)_2W(Cl)SnMe_3$, decreases air and thermal stability to a comparable level to that of $(cp)_2Mo(Cl)SnMe_3$. However, the solubility in organic solvents increases. Insertion of dimethyl acetylenedicarboxylate into the M^2–H bond of $[(cp)_2M^2(H)SnMe_3]$, thus removing the reactive metal–hydrogen bond, considerably increases both thermal and air stability.

Physical data

Compound	Colour	M.p.[a]	¹H N.m.r.[b] cp[c]	Me	H[c]	I.r. M–H stretch (cm⁻¹) (CS_2 solution)
$(cp)_2MoH_2$ [d]	Yellow	183—185 [d]	5·63 (t, 0·5)		18·83	1823
$(cp)_2Mo(H)SnMe_3$	Bright yellow	100—102	5·88 (d, 0·5)	9·65 [e]	18·78	1802
$(cp)_2WH_2$ [d]	Yellow	193—195 [f]	5·77 (t, 0·75)		22·30 [g] (0·75)	1892
$(cp)_2W(H)SnMe_3$	Bright yellow	102—104	5·98 (d, 0·6)	9·73 [h]	22·37 [g] (0·6)	1880
$(cp)_2TaH_3$ [d]	White	187—189d [d]	5·20		11·63 (t, 9·3) 13·02 (d, 9·2)	1735 [i]
$(cp)_2Ta(H)_2SnMe_3$	White	154—156	5·53 (t, 0·45)	9·50 [j]	14·63	1750
$(cp)_2W(Cl)SnMe_3$	Deep red	181—183	5·70	9·50 [k]		(274) [l]
$(cp)_2W(Br)SnMe_3$	Red-brown	170—172d	5·71	9·51 [m]		
$(cp)_2W(I)SnMe_3$	Violet-black	174—177d	5·71	9·43 [n]		
$(cp)_2Mo(Cl)SnMe_3$	Deep red	159—162d	5·63	9·50 [o]		(272) [p]
$(cp)_2Mo(Br)SnMe_3$	Red-brown	157—158d	5·64	9·48 [q]		
$(cp)_2Mo(I)SnMe_3$	Green-black	164—167d	5·63	9·41 [r]		
$(cp)_2W(H)Cl$	Red	192—194d	5·48		21·45	(273)
$(cp)_2Mo(H)[-C(CO_2Me)=CHCO_2Me]$ [s]	Dark red	103—105	(5·32)	(6·46, 6·51) (OMe)	(3·83) (C–H) (20·4)	1845 (1717, 1692) (C=O) (1568) (C=C)
$(cp)_2Mo(SnMe_3)[-C(CO_2Me)=CHCO_2Me]$	Orange-red	153—154	5·63 (5·44)	6·18, 6·52 (OMe); 9·53 [t] (6·41, 6·53) (OMe); (9·77)	3·13 (CH) (4·07 (CH)	(1701, 1675) (C=O) [i] (1540) (C=C)
$(cp)_2W(H)[-C(CO_2Me)=CHCO_2Me]$ [s]	Dark red	103—105	(5·40)	(6·50, 6·60) (OMe)	(4·00) (CH) (23·0)	1890 (1695, 1665) (C=O) (1555) (C=C)
$(cp)_2W(SnMe_3)[-C(CO_2Me)=CHCO_2Me]$	Red	157—160	5·73 (5·49)	6·20, 6·57 (OMe); 9·56 [u] (6·39, 6·54) (OMe); (9·77)	3·10 (CH) (4·01) (CH)	(1700, 1680) (C=O) [i] (1540) (C=C)

[a] In °C, d = decomposition. [b] τ values obtained in C_6H_6 solutions. τ values obtained in CS_2 solutions given in parentheses. [c] Multiplicity (d = doublet, t = triplet) and splitting (Hz) given in parentheses. [d] Ref. 12. [e] $J(^{119}SnC^1H_3)$, 37·0 Hz. [f] Ref. 22, m.p. 163—165° in ref. 12 is incorrect. [g] 7 of 11 peaks observed. [h] $J(^{119}SnC^1H_3)$, 36·2 Hz. [i] Nujol mull. [j] $J(^{119}SnC^1H_3)$, 35·7 Hz. [k] $J(^{119}SnC^1H_3)$ 38·7 Hz. [l] Nujol mull: W–Cl stretch, *cf.* 283 and 266 cm⁻¹ for $(cp)_2WCl_2$ (ref. 7*a*). [m] $J(^{119}SnC^1H_3)$, 39·4 Hz. [n] $J(^{119}SnC^1H_3)$, 39·1 Hz. [o] $J(^{119}SnC^1H_3)$, 41·5 Hz. [p] Nujol mull: Mo–Cl stretch, *cf.* 293 and 262 cm⁻¹ for $(cp)_2MoCl_2$ (ref. 7*a*). [q] $J(^{119}SnC^1H_3)$, 42·3 Hz. [r] $J(^{119}SnC^1H_3)$, 42·2 Hz. [s] Ref. 4. [t] $J(^{119}SnC^1H_3)$, 39·5 Hz. [u] $J(^{119}SnC^1H_3]$, 38·5 Hz

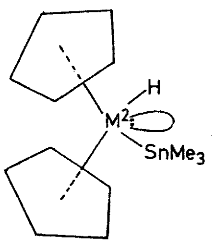
I.r. spectra of the new hydrido-compounds are very similar and show, like their di- or tri-hydride precursors, only a single, strong but broad absorption, due to the metal–hydrogen stretching mode(s). The halides have similar spectra; the values for $\nu(M^2{-}Cl)$ fall between those observed for $(cp)_2M^2Cl_2$.[7a] The complexes $(cp)_2M^2(Y)[-C(CO_2Me)=CHCO_2Me]$ ($Y = SnMe_3$) have similar i.r. spectra to those of the hydrido-analogues (Y = H).[4] Thus, there are two strong absorptions due to ν(C=O) and one strong band assigned to ν(C=C).

X-Ray structural work on $(cp)_2MoH_2$ has shown[14] that the cyclopentadienyl rings are bent, unlike in metallocenes. Furthermore, molecular orbital calculations of such a ring tilt system have shown that there are three hybridised orbitals which are non-bonding towards the rings and which lie in the *xy* plane away from the rings. Two of the orbitals, $spd_{x^2-y^2}$ and d_{z^2} hybrids, are equivalent; the third orbital is an *sp*

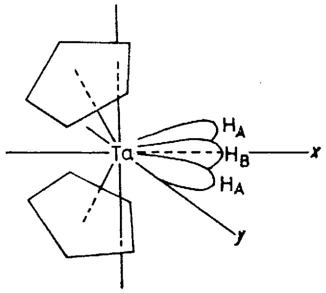
[14] M. Gerloch and R. Mason, *J. Chem. Soc.*, 1965, 296.

hybrid. In the case of $(cp)_2M^2H_2$ (M^2 = Mo or W), n.m.r.[11] and X-ray [14] studies show that the two hydrogens occupy equivalent orbitals, the third orbital being occupied by the lone pair of electrons. Two possible positions for the lone pair orbital have been proposed: one along the x axis (between the hydride ligands) by Balhausen,[15] the other, by Alcock,[16] as being behind the hydride ligands along the y axis. Structural studies [17] on $(cp)_2MX'X''$ (M = Ti or V, X′ = SPh = X″;[17a] M = Zr, X′ = F or I = X″;[17b] M = Mo, X′ = $SnBr_3$, X″ = Br;[17c] M = Zr, Nb, or Mo, X′ = Cl = X″;[17d] M = Re, X′ = Br = X″ [17d]) strongly support the Alcock model; however, the basic properties of the dihydrides $(cp)_2M^2H_2$ (M^2 = Mo or W) and the structure of the trihydrides $(cp)_2M^2H_3$ (M^2 = Nb or Ta) support the Balhausen model. A recent communication [18] has proposed a bonding scheme which incorporates features of both these models. The n.m.r. values (Table) are consistent with the molecular orbital models proposed, in that the dihydrides, $(cp)_2M^2H_2$, show a single high-field hydride resonance which hardly changes position upon mono-substitution by a trimethylstannyl ligand (I). The π-cyclopentadienyl resonance, however, is shifted noticeably to higher field and its splitting (by the hydride ligands) is reduced from a triplet to a doublet. For $(cp)_2TaH_3$, the non-equivalence of orbitals is demonstrated by the A_2B spectrum of the hydride resonances. Mono-substitution provides only a singlet hydride resonance, suggesting substitution of the unique hydrogen (II), the resonance due to the A_2 hydrogen atoms changing from a doublet to a singlet and moving to higher field. The π-cyclopentadienyl resonance (which could not be resolved for the trihydride) appears, as expected, as a triplet. For the hydridochloro-complex $(cp)_2W(H)Cl$, the electronegative chloride ligand causes both the π-cyclopentadienyl and hydride protons to absorb at lower field. Similarly, in the halides $(cp)_2M^2(X)SnMe_3$, both the π-cyclopentadienyl and trimethylstannyl resonances are to lower field than in the corresponding hydride precursors. The complexes $(cp)_2M^2(SnMe_3)[-C(CO_2Me)=CHCO_2Me]$ show the expected spectra with two distinct methoxy-proton resonances, and similar chemical shifts for cp and $SnMe_3$ protons as in $(cp)_2M^2(X)SnMe_3$. Since the i.r. and n.m.r. spectra so clearly resemble the hydrido-σ-alkenyl complexes,[4] the same geometry (*cis*) is assigned to the new trimethylstannyl-σ-alkenyl complexes. Furthermore, such a geometry is clearly sterically favoured. An interesting feature of the trimethylstannyl-σ-alkenyl complexes is that although the methyl coupling constants $J(^{119}SnC^1H_3)$ are similar to those of other trimethylstannyl complexes (Table), the cyclopentadienyl coupling constants $J(^{119}SnC_5{}^1H_5)$ are readily observable (*ca.* 6 Hz), whereas for the halides $(cp)_2M^2(X)SnMe_3$ they are much smaller (*ca.* 2 Hz) and for the parent hydrides (X = H), hardly perceptible. The coupling constants $J(^{119}SnC^1H_3)$ for the new compounds are in the range 35—42 Hz, and are considerably lower than for $cp(OC)_3M\text{-}SnMe_3$ (M = Cr, Mo, or W) (48—49 Hz) [3] or for alkylstannanes which generally fall in the range 50—100 Hz.[19] Such a decrease in the magnitude of the coupling constants implies [19b] a decrease in the s-electron character in the Sn–Me bonds compared with that in the π-cyclopentadienyltricarbonyl analogues.

The marked decrease in m.p. when one of the hydride ligands in the dihydrides (M^2 = Mo or W) is replaced by a trimethylstannyl group is probably due to a substantial loss of symmetry (I). In the case of the trihydride it seems that it is the unique hydride ligand which is substituted (II); the loss of symmetry and decrease in m.p. are therefore less marked.



(I)



(II)

EXPERIMENTAL

General Procedures.—All manipulations were carried out under pure nitrogen or argon, using freshly distilled, dry, degassed solvents. Optimisation of reaction conditions was achieved by exploratory experiments using n.m.r.

^1H N.m.r. spectra were recorded on Varian Associates HA100 or T60 spectrometers. Mass spectra were obtained on an A.E.I. MS 9 instrument by direct insertion of a probe into the electron beam. I.r. spectra were taken with a Perkin-Elmer 457 grating spectrophotometer, either as solutions in KBr cells, or as Nujol mulls between caesium iodide plates. Molecular weights refer to parent ions in mass spectra (based on ^{96}Mo, ^{184}W, and ^{120}Sn), and calculated values refer to molecular weights based on chemical atomic weights.

All the complexes were unstable in solution. Purification involved low pressure sublimation (although for the halides this was a slow process) or recrystallisation.

Dimethylaminotrimethylstannane,[20] dimethylaminotrimethylsilane,[21] dihydridobis(π-cyclopentadienyl)-molybdenum(IV), -tungsten(IV), and trihydridobis(π-cyclopentadienyl)tantalum(V) [12] were prepared by standard methods.

Hydridobis(π-cyclopentadienyl)trimethylstannylmolybdenum(IV).—Dimethylaminotrimethylstannane (0·25 ml, 1·47 mmol) was added to a yellow solution of dihydridobis-

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[16] N. W. Alcock, *J. Chem. Soc. (A)*, 1967, 2001.

[17] L. H. Dahl, 4th Internat. Conf. Organometallic Chem., Bristol 1969; M. A. Bush and G. A. Sim, *J. Chem. Soc. (A)*, 1971, 2225; T. S. Cameron and C. K. Prout, *J.C.S. Dalton*, 1972, 1447; T. S. Cameron, B. Denton, C. K. Prout, and G. V. Rees, unpublished work.

[18] J. C. Green, M. L. H. Green, and C. K. Prout, *J.C.S. Chem. Comm.*, 1972, 421.

[19] (*a*) J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 326; (*b*) N. Flitcroft and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1963, **85**, 1377.

[20] K. Jones and M. F. Lappert, *J. Chem. Soc.*, 1965, 1944.

[21] O. Mjörne, *Svensk Kem. Tidskr.*, 1950, **62**, 120.

(π-cyclopentadienyl)molybdenum(IV) (0·335 g, 1·47 mmol) in THF (10 ml), and the mixture was heated under reflux (2 h, 65°). Gas evolution ceased after *ca.* ¾ h. Removal of volatile materials (20°, 10^{-2} mmHg) left an orange-yellow residue. Sublimation (90°, 10^{-3} mmHg during 8 h) afforded the bright-yellow *hydrido-complex* (0·47 g, 81%), m.p. 100—102° (Found: C, 40·3; H, 5·3%; *M*, 392. $C_{13}H_{20}MoSn$ requires C, 39·9; H, 5·2%; *M*, 390·95).

Hydridobis(π-cyclopentadienyl)trimethylstannyltungsten-(IV).—Similarly, dihydridobis(π-cyclopentadienyl)tungsten-(IV) (1·913 g, 6·05 mmol) in THF (20 ml) and heating under reflux (5 h, 65°) yielded the bright-yellow *hydrido-complex* (2·80 g, 97%), m.p. 102—104° (Found: C, 33·1; H, 4·4%; *M*, 478. $C_{13}H_{20}SnW$ requires C, 32·6; H, 4·2%; *M*, 478·86).

Dihydridobis(π-cyclopentadienyl)trimethylstannyltantalum-(V).—Similarly, trihydridobis(π-cyclopentadienyl)tantalum-(V) (0·119 g, 0·38 mmol) in THF (3 ml) and heating under reflux (6 h, 56°) afforded the white dihydrido-complex (0·13 g, 70%), m.p. 154—156° (Found: C, 33·0; H, 4·3%; *M*, 478. $C_{13}H_{21}SnTa$ requires C, 32·7; H, 4·4%; *M*, 476·96).

Lack of Reaction with Excess of the Tin Amide.—Each of the above three products was treated in turn with an excess of dimethylaminotrimethylstannane and the mixture was heated under reflux in THF for 16—20 h. In no case was a reaction observed; the reactants were recovered quantitatively.

Chlorobis(π-cyclopentadienyl)trimethylstannyltungsten(IV).—Dropwise addition of carbon tetrachloride (0·063 ml, 0·64 mmol) in THF (5 ml) to a yellow solution of hydridobis-(π-cyclopentadienyl)trimethylstannyltungsten(IV) (0·308 g, 0·64 mmol) in THF (5 ml), with cooling (0°), rapidly produced a deep-red solution. Removal of volatiles (20°, 10^{-2} mmHg) followed by very slow sublimation (100°, 10^{-3} mmHg during 115 h) of the deep-red residue afforded deep-red crystals of the *chloro-complex* (0·30 g, 92%), m.p. 181—183° (Found: C, 31·0; H, 3·7; Cl, 6·9%; *M*, 514. $C_{13}H_{19}ClSnW$ requires C, 30·4; H, 3·7; Cl, 6·9%; *M*, 513·3).

Bromobis(π-cyclopentadienyl)trimethylstannyltungsten(IV).—Similarly, benzyl bromide (0·14 ml, 1·18 mmol) and hydridobis(π-cyclopentadienyl)trimethylstannyltungsten-(IV) (0·487 g, 1·02 mmol) in THF (5 ml) after 18 h at 20° afforded red-brown crystals of the *bromo-complex* (0·35 g, 72%), m.p. 170—172° (decomp.) (Found: C, 28·0; H, 3·3; Br, 14·7%; *M*, 558. $C_{13}H_{19}BrSnW$ requires C, 28·0; H, 3·4; Br, 14·4%; *M*, 557·9).

Iodobis(π-cyclopentadienyl)trimethylstannyltungsten(IV).—Similarly, allyl iodide (0·087 ml, 0·95 mmol) and hydridobis-(π-cyclopentadienyl)trimethylstannyltungsten(IV) (0·453 g, 0·95 mmol) in THF (10 ml) after 17 h at 20° afforded violet-black crystals of the *iodo-complex* (0·27 g, 50%), m.p. 174—177° (decomp.) (Found: C, 26·1; H, 3·1; I, 23·0%; *M*, 606. $C_{13}H_{19}ISnW$ requires C, 25·8; H, 3·1; I, 21·0%; *M*, 604·8).

Reaction of Hydridobis(π-cyclopentadienyl)trimethylstannyltungsten(IV) *with Excess of Halogenating Agent.*—For each of the foregoing three halogenations, use of excess of halogenating agent (carbon tetrachloride, benzyl bromide, allyl iodide, respectively) resulted in quantitative conversion into dihalogenobis(π-cyclopentadienyl)tungsten(IV) and halogenotrimethylstannane (both with authentic i.r. and n.m.r. spectra).

Chlorobis(π-cyclopentadienyl)trimethylstannylmolybdenum-(IV).—Using the identical procedure as for the tungsten complex, hydridobis(π-cyclopentadienyl)trimethylstannylmolybdenum(IV) (0·680 g, 1·74 mmol) and carbon tetrachloride (0·17 ml, 1·74 mmol) in THF (15 ml) afforded deep-red crystals of the *chloro-complex* (0·63 g, 84%), m.p. 159—162° (decomp.) (Found: C, 36·9; H, 4·6; Cl, 8·6%; *M*, 425. $C_{13}H_{19}ClSnMo$ requires: C, 36·7; H, 4·5; Cl, 8·3%; *M*, 425·4).

Bromobis(π-cyclopentadienyl)trimethylstannylmolybdenum-(IV).—Similarly, hydridobis(π-cyclopentadienyl)trimethylstannylmolybdenum(IV) (0·30 g, 0·77 mmol) and benzyl bromide (0·10 ml, 0·84 mmol) in THF (5 ml) afforded red-brown crystals of the *bromo-complex* (0·29 g, 80%), m.p. 157—158° (decomp.) (Found: C, 33·2; H, 4·2; Br, 17·3%; *M*, 471. $C_{13}H_{19}BrSnMo$ requires C, 33·2; H, 4·1; Br, 17·0%; *M*, 469·9).

Iodobis(π-cyclopentadienyl)trimethylstannylmolybdenum-(IV).—Similarly, hydridobis(π-cyclopentadienyl)trimethylstannylmolybdenum(IV) (0·43 g, 1·1 mmol) and allyl iodide (0·10 ml, 1·1 mmol) in THF (10 ml) afforded green-black crystals of the *iodo-complex* (0·29 g, 51%), m.p. 164—167° (decomp.) (Found: C, 30·2; H, 3·8; I, 25·0; *M*, 517. $C_{13}H_{19}ISnMo$ requires C, 30·2; H, 3·7; I, 24·6%; *M*, 516·9).

Unsuccessful Synthesis of Fluorobis(π-cyclopentadienyl)-trimethylstannyltungsten(IV).—Silver tetrafluoroborate (0·085 g, 0·43 mmol) in THF (10 ml) was added dropwise, with stirring, to a deep red THF (5 ml) solution of chlorobis(π-pentadienyl)trimethylstannyltungsten(IV) (0·22 g, 0·43 mmol). Rapid decolourisation of the mixture occurred together with formation of a black precipitate and a colourless filtrate, which contained (^{1}H n.m.r.) chlorotrimethylstannane.

Reaction of Hydridobis(π-cyclopentadienyl)trimethylstannyltungsten(IV) *with Hydrogen Chloride.*—Hydrogen chloride gas was passed through a golden yellow THF (5 ml) solution of hydridobis(π-cyclopentadienyl)trimethylstannyltungsten-(IV) (0·355 g, 0·74 mmol). The solution immediately lightened in colour, then a grey precipitate was deposited [isolated and identified (^{1}H n.m.r.) as $(cp)_2W(H)_3Cl$], which progressively darkened to a blue-black solid. Filtration followed by drying (20°, 10^{-3} mmHg) isolated the blue-black dichlorobis(π-cyclopentadienyl)tungsten(IV) (0·169 g, 0·44 mmol, 59%) (Found: C, 31·0; H, 2·9; Cl, 17·6%. Calc. for $C_{10}H_{10}Cl_2W$: C, 31·2; H, 2·6; Cl, 18·4%) (authentic i.r. spectrum).

The bright yellow solution of hydridobis(π-cyclopentadienyl)trimethylstannyltungsten(IV) (0·35 g, 0·73 mmol) in THF (5 ml) rapidly turned pale yellow upon addition of a solution of hydrogen chloride (0·027 g, 0·73 mmol) in THF (5 ml). Removal of volatiles (20°, 10^{-2} mmHg) and sublimation (60°, 10^{-3} mmHg during 10 h) quantitatively afforded pale yellow, crystalline dihydridobis(π-cyclopentadienyl)tungsten(IV) (authentic ^{1}H n.m.r. spectrum).

Lack of Reaction between Hydridobis(π-cyclopentadienyl)-metal Derivatives and Dimethylaminotrimethylsilane.—The silane (0·25 ml, 1·71 mmol) was added to a yellow solution of the dihydridomolybdenum(IV) complex (0·20 g, 0·88 mmol) in THF (10 ml). The mixture was heated under reflux (65°, 6 h). Removal of volatiles (22°, 10^{-2} mmHg), followed by sublimation (80°, 10^{-3} mmHg during 2 h), gave yellow crystals of unreacted dihydridobis(π-cyclopentadienyl)molybdenum(IV) (0·13 g, 65%), m.p. 181—183° (lit.,[12] m.p. 183—185°) (authentic i.r. and ^{1}H n.m.r. spectra).

Similarly, there was no reaction after 16 h at 65° between

(i) the silane (0·14 ml, 1 mmol) and the dihydridotungsten(IV) complex (0·316 g, 1·0 mmol) in THF (8 ml), or (ii) the silane (0·13 ml, 0·94 mmol) and tantalum trihydride (0·294 g, 0·94 mmol) in THF (5 ml).

Chlorobis(π-cyclopentadienyl)hydridotungsten(IV).— Dropwise addition of an ethereal solution of hydrogen chloride (0·023 g, 0·63 mmol) to a benzene (20 ml) solution of chlorobis(π-cyclopentadienyl)trimethylstannyltungsten(IV) (0·322 g, 0·63 mmol) afforded a deep red solution. Filtration, followed by removal of volatiles (22°, 10^{-2} mmHg), addition of toluene, and cooling (−20°) afforded red crystals of the *complex* (0·15 g, 68%), m.p. 192—194° (decomp.) (Found: C, 34·2; H, 3·3%; *M*, 350. $C_{10}H_{11}ClW$ requires C, 34·3; H, 3·2%; *M*, 350·5).

Trimethylstannylbis(π-cyclopentadienyl)[cis-1,2-*bis(methoxycarbonyl)ethenyl*]*tungsten*(IV).—Dimethyl acetylenedicarboxylate (0·09 ml, 1 mmol) and yellow hydridobis(π-cyclopentadienyl)trimethylstannyltungsten(IV) (0·476 g, 1 mmol) were heated at 65° for 7 h in THF (10 ml). Removal of volatiles (22°, 10^{-2} mmHg), followed by extraction of the red residue with diethyl ether, concentration, and cooling (−20°) afforded orange crystals. Heating *in vacuo* (140°) caused loss of ether and formation of red crystals of the *complex* (0·43 g, 70%), m.p. 157—160° (Found: C, 37·0; H, 4·4%; *M*, 622. $C_{19}H_{26}O_4SnW$ requires C, 36·8; H, 4·2%; *M*, 620·97).

Trimethylstannylbis(π-cyclopentadienyl)]cis-1,2-*bis(methoxycarbonyl)ethenyl*]*molybdenum*(IV).—Dropwise addition of dimethyl acetylenedicarboxylate (0·10 ml, 1·1 mmol) in THF (10 ml) to yellow hydridobis(π-cyclopentadienyl)trimethylstannylmolybdenum(IV) (0·43 g, 1·1 mmol) resulted in rapid formation of a red solution. The mixture was left to stir at room temperature overnight. Removal of volatiles (22°, 10^{-2} mmHg), extraction of red residue with diethyl ether, concentration, and cooling (−20°) afforded orange-red crystals of the *complex* (0·41 g, 70%), m.p. 153—154° (Found: C, 42·6; H, 5·1%; *M*, 533. $C_{19}H_{26}O_4SnMo$ requires C, 42·8; H, 4·9%; *M*, 533·1).

Reaction of Chlorobis(π-cyclopentadienyl)trimethylstannyltungsten(IV) *with Tin*(II) *Chloride*.—Dropwise addition of a solution of the chloride (0·116 g, 0·61 mmol) in THF (5 ml) to a deep-red solution of the tungsten complex (0·313 g, 0·61 mmol) in THF (10 ml) produced a darkening in colour. Heating at reflux temperature for 2 h, followed by removal of volatiles, extraction with toluene, and cooling (−20°) afforded a mauve product. N.m.r. and i.r. spectra indicated a mixture possibly of two complexes. Recrystallisation (CH_2Cl_2–C_6H_{14}) failed to achieve a separation.

Pyrolysis of Halogenobis(π-cyclopentadienyl)trimethylstannylmetal Derivatives in Benzene.—Sealed n.m.r. tubes of solutions of $(cp)_2M^2(X)SnMe_3$ (M^2 = Mo or W; X = Cl, Br, or I) in benzene were heated at 200° for 9—12 h. The resultant solutions indicated (n.m.r.) formation in most cases, of a metal hydride. For M^2 = W, X = Cl, no change occurred, and for M^2 = W, X = I only an alkyltin species was observed in the n.m.r. Removal of volatiles and extraction (CS_2) indicated (n.m.r.) that the hydride was not the expected complex $(cp)_2M^2(H)Ph$.[7b]

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[22] D. F. Shriver, *J. Amer. Chem. Soc.*, 1963, **88**, 301.