Trimethylsilylmethyl and other Alkyls of Chromium, Molybdenum, Ruthenium, and Rhodium from Interaction of Magnesium Dialkyls with Metal–Metal Bonded Binuclear Acetates of Chromium(II), Molybdenum(II), Ruthenium(II, III), and Rhodium(II) †

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The interaction between dialkylmagnesium MgR_2 (R = Me, CH_2SiMe_3, or CH_2CMe_3) and binuclear transition-metal acetates $M_2^{II}(O_2CMe)_4$ (M = Cr, Mo, and Rh) and $Ru_2^{II,III}(O_2CMe)_4Cl$, containing metal–metal bonds in the presence of trimethylphosphine yields either monomeric or dimeric alkyls. In the latter the metal–metal bond is retained as in $Mo_2Me_4(PMe_3)_4$ or $Mo_2(Bu^tCH_2)_2(O_2CMe)_2(PMe_3)_2$. Loss of a hydrogen from a methyl group of CH_2SiMe_3 results in the formation of metallacycles $\overline{M-CH_2SiMe_2-CH_2}$ and $\overline{M{\equiv}M-CH_2-SiMe_2-CH_2}$. The various compounds have been studied by ^1H, ^{13}C and ^{31}P n.m.r. and i.r. spectroscopy and the results of structural determinations by X-ray crystallography are reported.

ALTHOUGH dimolybdenum(II) tetra-acetate, $Mo_2(O_2CMe)_4$, and dichlorodirhenium(III) tetra-acetate, $Re_2Cl_2(O_2CMe)_4$, react with methyl-lithium to give lithium compounds $Li_4[Mo_2Me_8]$ and $Li_2[Re_2Me_8]$ respectively,[1,2] attempts to obtain neutral alkyls from these acetates and from $Rh_2(O_2CMe)_4$ by action of Grignard reagents led to decomposition; with $Mo_2(O_2CMe)_4$, MgMeI gave a red insoluble pyrophoric substance. However, in the presence of trimethylphosphine the binuclear acetates react with magnesium dialkyls,[3] MgR_2 (R = Me, CH_2SiMe_3, and CH_2CMe_3), to give neutral, crystalline alkyl derivatives that may be either monomeric, or dimeric where the metal–metal bond is retained. For the new compounds described here, analytical data are given in Table 1, and spectroscopic data in Tables 2 and 3.

(1) *Chromium Compounds*.—In diethyl ether at 0 °C, tetra-μ-acetato-dichromium(II) reacts with $Mg(CH_2SiMe_3)_2$ in the presence of PMe_3 to give a dark red pyrophoric dimer of stoicheiometry $Cr_2(CH_2SiMe_3)_4(PMe_3)_2$

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† No reprints available.

[1] F. A. Cotton, J. M. Troup, R. T. Webb, D. H. Williamson, and G. Wilkinson, *J. Amer. Chem. Soc.*, 1974, **96**, 3824.

[2] F. A. Cotton, L. D. Gage, K. Mertis, L. W. Shive, and G. Wilkinson, *J. Amer. Chem. Soc.*, 1976, **98**, 6922.

[3] Preliminary note: R. A. Andersen, R. A. Jones, G. Wilkinson, K. M. A. Malik, and M. B. Hursthouse, *J.C.S. Chem. Comm.*, 1977, 283.

TABLE 1

Analytical data for alkyl compounds

	Compound	Colour	M.p. (θ_c/°C)	Found (%) C	Found (%) H	Found (%) P	Found (%) M[a]	Required (%) C	Required (%) H	Required (%) P	Required (%) M
(A)	$\mathrm{Cr_2(CH_2SiMe_3)_4(PMe_3)_2}$	Deep red	80—100 *	43.0	10.2	10.1	560	44.0	9.7	10.3	605
(B)	$\mathrm{Mo_2Me_4(PMe_3)_4}$	Blue	220 *	34.7	8.5	23.6	510	34.6	8.6	22.3	556
(C)	$\mathrm{Mo_2Me_4(PMe_2Ph)_4}$	Blue	130	54.8	7.4	14.1		53.8	7.0	15.4	
(D)	$\mathrm{Mo_2(CH_2SiMe_3)_2(O_2CMe)_2(PMe_3)_2}$	Orange	151—153 *	34.3	7.3	9.8		34.0	7.2	9.8	
(E)	$\mathrm{Mo_2(CH_2SiMe_3)_2\{(CH_2)_2SiMe_2\}(PMe_3)_3}$	Red	143—145	36.3	8.1	14.5	619	37.1	8.7	13.7	680
(F)	$\mathrm{Mo_2(CH_2SiMe_3)_2\{(CH_2)_2SiMe_2\}\{P(OMe)_3\}_3}$	Green	122—124 *	30.9	7.6	11.0	792	30.6	7.2	11.3	824
(G)	$\mathrm{Mo_2(CH_2CMe_3)_2(O_2CMe)_2(PMe_3)_2}$	Red	130—150 *	40.2	7.9	8.8	589	39.8	7.6	10.3	604
(H)	*cis*-$\mathrm{RuMe_2(PMe_3)_4}$	White	200—210 *	38.9	9.6	29.0	427	38.6	9.7	28.5	435
(I)	$\mathrm{Ru\{(CH_2)_2SiMe_2\}(PMe_3)_4}$	Pale yellow	150—151	39.0	9.4	24.9	480	39.1	9.4	25.2	491
(J)	$\mathrm{Ru\{(CH_2)_2CMe_2\}(PMe_3)_4}$	Pale yellow	172—175 *	39.8	9.3	26.9	515	41.7	9.3	27.0	475
(K)	*fac*-$\mathrm{RhMe_3(PMe_3)_3}$	Yellow	106—108	38.1	9.3	23.3	378	38.3	9.6	24.7	376
(L)	$\mathrm{Rh(CH_2SiMe_3)\{(CH_2)_2SiMe_2\}(PMe_3)_3}$	Yellow	100—101 *	40.4	9.7	18.8	535	40.6	9.6	18.5	504

[a] Cryoscopically in benzene.

* Decomposed.

TABLE 2

^{1}H and ^{13}C{^{1}H} nuclear magnetic resonance spectra of alkyl compounds

Compound	δ Values [a]	J/Hz	Assignment	^{13}C{^{1}H} [b]	$J_{C,P}$/Hz
(A)	1.25, s (1)		$\mathrm{P}Me_3$	16.60, s	
	0.58, s (1)		μ-$\mathrm{CH_2Si}Me_3$ [c]	5.25, s	
	0.25, s (1)		$\mathrm{CH_2Si}Me_3$ [c]	6.86, s	
(B)	1.30, m (36)		$\mathrm{P}Me_3$	16.5, t	9.3
	−0.37, t (12)	$^3J_{H,P} = 6$	Me	2.69, t	6.0
(C)	6.45, m (20)		$\mathrm{PMe_2}Ph$		
	0.93, t (24)	$^2J_{H,P} = 6$	$\mathrm{P}Me_2\mathrm{Ph}$		
	−0.80, t (12)	$^3J_{H,P} = 6$	Me		
(D)	2.60, s (3)		$\mathrm{O_2C}Me$	23.36, s	
	1.10, d (9)	$^2J_{H,P} = 6$	$\mathrm{P}Me_3$	12.63, d	20.4
	0.25, s (9)		$\mathrm{CH_2Si}Me_3$	3.99, s	
			$\mathrm{O_2}C\mathrm{Me}$	182.40, s	
	d		$\mathrm{C}H_2\mathrm{SiMe_3}$	9.05, d	29.2
(E)	1.30, m (27)		$\mathrm{P}Me_3$	23.67, d	17.5
				16.84, t	18.2
			$\mathrm{C}H_2\mathrm{SiMe_3}$	43.81, s	
	0.28, s (18)		$\mathrm{CH_2Si}Me_3$	3.46, s	
			$(CH_2)_2\mathrm{SiMe_2}$	73.62, s	
	0.84, s (8) [e]		$\mathrm{(CH_2)_2Si}Me_2$	8.93, s	
(F)	3.60, d	$J_{H,P} = 9$	$\mathrm{P(O}Me\mathrm{)_3}$	52.22, d	12.7
	3.46, t (27)	$J_{H,P} = 9$		14.98, m	
			$CH_2\mathrm{SiMe_3}$	73.19, s	
	0.25, s (24)		$\mathrm{CH_2Si}Me_3$	3.63, s	
			$(CH_2)_2\mathrm{SiMe_2}$	79.87, s	
	0.89, s (8) [e]		$\mathrm{(CH_2)_2Si}Me_2$	8.35, s	
(G)	2.81, s (6)		$\mathrm{O_2C}Me$	−1.92, s	
	1.24, d (36)	$^2J_{H,P} = 6$	$\mathrm{PMe_3}$	−15.72, d	18.0
	1.21, s (18)		$\mathrm{CH_2C}Me_3$	13.86, s	
			$\mathrm{O_2}C\mathrm{Me}$	193.91, s	
	1.96, s (4)		$C\mathrm{H_2CMe_3}$	21.75, dd	30.0, 5.0
			$\mathrm{CH_2}C\mathrm{Me_3}$	11:97, s	
(H)	1.20, d (18)	$^2J_{H,P} = 4.8$	*cis*-$\mathrm{P}Me_3$ [c]	25.39, t	17.3
	1.21, t (18)	$^2J_{H,P} = 4.8$	*trans*-$\mathrm{P}Me_3$	19.76, tt	23.7, 2.4
	−0.26, td (6)	$^3J_{H,P} = 4$	$Me\mathrm{Ru}$ [e]	−3.38, dq	63.8, 12.6
(I)	1.13, d (18)	$^2J_{H,P} = 6$	*cis*-$\mathrm{P}Me_3$ [c]	25.54, t	19.4
	1.43, t (18)	$^2J_{H,P} = 5$	*trans*-$\mathrm{P}Me_3$	22.10, tt	22.6, 3.6
	0.56, s (6)		$\mathrm{(CH_2)_2Si}Me_2$	10.36, t	2.7
	−1.36, t (4)	$^3J_{H,P} = 11$	$(\mathrm{C}H_2)_2\mathrm{SiMe_2}$	−28.98, dq	46.0, 7.7
(J)	1.3, m [e]				
(K)	1.10, d (27)	$^2J_{H,P} = 5$	$\mathrm{P}Me_3$	18.71, td	20.2, 1.9
	0.40, br d (9) [f]	$J_{H,P} = 12$	$Me\mathrm{Rh}$	7.64, br d [g]	100.0
(L)	1.13, t (27)	$J_{H,P} = 12$	$\mathrm{P}Me_3$	20.12, m	
	0.60, s (3)		$\mathrm{(CH_2)_2Si}Me_2$	10.78, s	
	0.42, s (3)			8.41, s	
	0.50, s (2)		$(\mathrm{C}H_2)_2\mathrm{SiMe_2}$		
	0.13, s (2)			−16.12, br d	72.7
	−0.80, br d (2) [h]	$J_{H,P} = 8$	$C\mathrm{H_2SiMe_3}$		
	0.54, s (9)		$\mathrm{CH_2Si}Me_3$	6.9, s	

[a] Measured in benzene as solvent and internal reference (δ 7.27) and referenced to $\mathrm{SiMe_4}$ (δ 0.0) at 60 MHz and 35 °C. Relative intensity in parentheses. [b] Measured in [^{2}H$_6$]benzene as solvent and internal reference (δ 128.7) and referenced to $\mathrm{SiMe_4}$ (δ 0.0) at 25.2 MHz. Peaks to high frequency (low field) of $\mathrm{SiMe_4}$ are taken as positive. [c] These assignments may be reversed. [d] Not observed. Resonances due to $C\mathrm{H_2SiMe_3}$ are probably masked by other peaks. [e] See text. [f] Broad doublet possibly due to splitting by phosphorus nuclei *trans* to Me. Further splitting by Rh and *cis* P atoms not resolved. [g] As for (H). Broad doublet from *trans* P coupling (J = 100 Hz). Further splitting by Rh and *cis* P atoms not resolved. [h] At 0 °C a doublet of doublets is obtained ($J_{H,Rh}$ = 9 Hz and $J_{H,P}$ = 6 Hz).

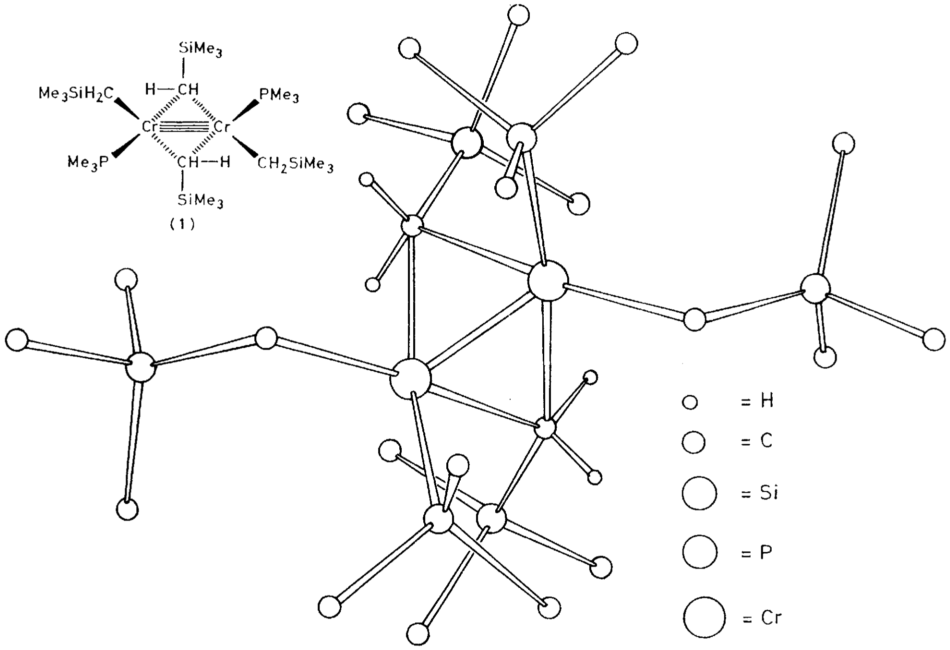
TABLE 3

$^{31}P\{^1H\}$ N.m.r. spectra of alkyl compounds

Compound	$^{31}P\{H\}$ [a]	$J_{P,P}$/Hz	$J_{P,Rh}$/Hz
(A)	−17.35 [b]		
(B)	−1.88, s		
(C)			
(D)	−11.51, s		
(E)	−0.83, d	10.2	
	−4.24, t	21.2	
(F)	−17.4, d	35.1	
	−35.2, t	34.0	
(G)	−16.38, s		
(H)	−1.08, t	25.5	
	−11.64, t	26.0	
(I)	−6.21, t	29.4	
	−17.2, t	29.6	
(J)	−5.50, t [c]	27.9	
	−20.67, t	27.8	
(K)	−17.9, d		82.8
(L)	−17.8, dt	18.9	91.1
	−22.7, dd	18.9	86.3

[a] Measured in [$^2H_6$]benzene (10%)-benzene and referenced to external 85% H_3PO_4 (δ 0.0) at 40.5 MHz. Peaks to high frequency (low field) of reference are taken as positive. [b] [$^2H_6$]benzene (10%)-toluene at −80 °C. [c] [$^2H_6$]Benzene (10%)-tetrahydrofuran.

(A). The compound has feeble paramagnetism, like other metal–metal bonded chromium(II) species ($\mu_{eff.}$ *ca.* 0.9 B.M. per Cr atom in solution), but no e.s.r. spectrum was observed in frozen benzene at −180 °C. The ^1H n.m.r. spectrum showed three rather broad bands of equal area at 35 °C, which sharpen somewhat at −10 °C and broaden further on cooling. The $^{13}C\{^1H\}$ spectrum also has three approximately equal peaks but the $^{31}P\{^1H\}$ spectrum had only a single broad peak (δ −17.35) at −80 °C. The spectra were inadequate to allow structural characterisation but are consistent with structure (1) and Figure 1, determined by *X*-ray diffraction.[3,4]



(1)

FIGURE 1

The molecule has a short Cr–Cr bond (2.10 Å) corresponding to a quadruple metal–metal bond and two bridging trimethylsilylmethyl groups similar to those found in $[Mn(CH_2SiMe_3)_2]_n$,[5] arranged in a *cis*-configuration with a dihedral angle between the two Cr–C–Cr planes of 101°. There is a slight asymmetry of the Cr–C bridge bonds and also one of the hydrogen atoms from each bridging CH_2 group shows a close approach (*ca.* 2.3 Å) to one of the chromium atoms. These features probably result from the packing requirements of the bulky ligands in the crystal.

Similar reactions using other phosphines led to decomposition but by using PMe_3 with $MgMe_2$ and $Mg(CH_2Bu^t)_2$ at 0 °C, small yields of extremely pyrophoric petroleum-soluble compounds were formed.

(2) *Molybdenum Compounds*.—(a) *Methyl*. Tetra-μ-acetato-dimolybdenum(II), $Mo_2(O_2CMe)_4$, reacts with $MgMe_2$ in ether containing PMe_3 within 2—3 h at 25 °C and from the blue solutions can be isolated the blue, air-stable and volatile molybdenum(II) methyl, $Mo_2Me_4(PMe_3)_4$ (B); structure (2) for it is readily deduced from n.m.r. data. There are mutually *trans* P and C atoms bound to each metal and the structure is similar to the blue chloro-complexes[6] $Mo_2Cl_4(PR_3)_4$. Thus the Mo–CH_3, ^1H n.m.r. resonance is a triplet (δ − 0.37, $^3J_{H,P}$ = 6 Hz) due to coupling to two equivalent phosphorus atoms; the PMe_3 region is quite complex. The $^{31}P\{^1H\}$

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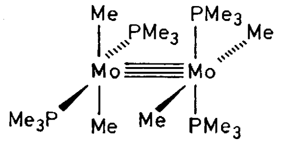
[4] K. M. A. Malik and M. B. Hursthouse, to be published.

[5] R. A. Andersen, E. Carmona-Guzman, J. F. Gibson, and G. Wilkinson, *J.C.S. Dalton*, 1976, 2204.

[6] J. San Filippo, *Inorg. Chem.*, 1972, **11**, 3140; H. D. Glicksman, A. D. Hamer, T. J. Smith, and R. A. Walton, *ibid.*, 1976, **15**, 2205; J. San Filippo and H. J. Swiadoch, *ibid.*, p. 2209; E. Caroma-Guzman and G. Wilkinson, *J.C.S. Dalton*, 1977, 1716.

spectrum is a singlet from −80 to +35 °C indicating only one type of P atom. The $^{13}C\{^1H\}$ spectrum is absolutely diagnostic consisting of a triplet (δ 16.5, $^1J = 9.3$ Hz) due to P–CH_3 groups and a triplet (δ 2.69, $J = 6.0$ Hz) due to Mo–CH_3; the former indicates *trans* PMe_3 groups on each molybdenum since only thus can the value of $J_{C,P}$ be sufficiently large to give a virtually coupled triplet. Although the relative orientations cannot be deduced, an eclipsed geometry for (2) is favoured on steric grounds as in $Mo_2Cl_4(PR_3)_4$, so that each formally Mo^{II}, d^4, ion gives a quadruple bond $\sigma^2\pi^4\delta^2$ and the population of the δ orbital corresponds with the eclipsed form.

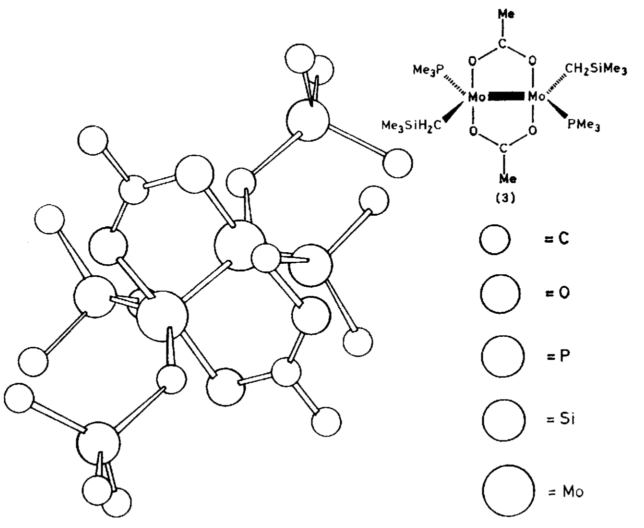


(2)

The compound does not react with H_2, CO, or alkenes at 1 atm and 25 °C but with methanolic HCl it forms $Mo_2Cl_4(PMe_3)_4$.

No complexes could be obtained using $PMePh_2$, PPh_3, or $P(OMe)_3$ but with the less bulky PMe_2Ph a similar blue compound $Mo_2Me_4(PMe_2Ph)_4$ (C) was obtained.

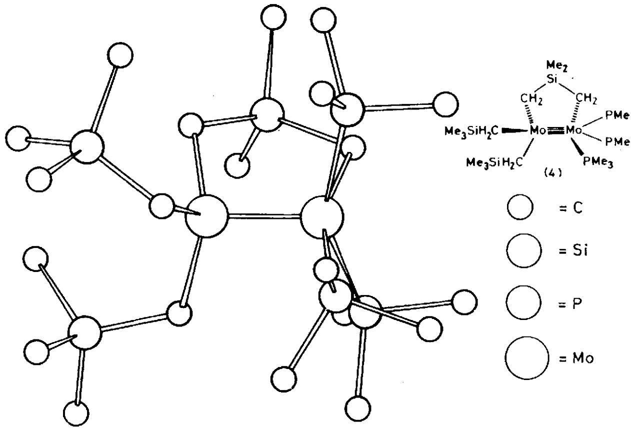
(b) *Trimethylsilylmethyl.* The interaction of $Mo_2(O_2CMe)_4$ with $Mg(CH_2SiMe_3)_2$ and PMe_3 gives a compound (D) that still retains acetate and has formula $Mo_2(O_2CMe)_2(CH_2SiMe_3)_2(PMe_3)_2$ when the reaction stoicheiometry $MgR_2 : Mo_2(O_2CMe)_4 = 2 : 1$ was used. The i.r. and n.m.r. data are consistent with structure (3) and Figure 2, determined by an *X*-ray diffraction study.[4] The acetates are bridging and the phosphine groups are *trans* to each other with respect to the Mo–Mo quadruple bond.



(3)

FIGURE 2

Using an excess of $Mg(CH_2SiMe_3)_2$ leads to a very air-sensitive, red crystalline compound of stoicheiometry $Mo_2(CH_2SiMe_3)_2\{(CH_2)_2SiMe_2\}(PMe_3)_3$ (E). This compound is also obtained when (D) is treated with an excess of $Mg(CH_2SiMe_3)_2$ and PMe_3. While much information can be obtained from n.m.r. data, the assignments (Tables 2 and 3) have been made on the basis of structure (4) and Figure 3, as determined by *X*-ray diffraction.[4] A similar complex of trimethyl phosphite, $Mo_2(CH_2SiMe_3)_2\{(CH_2)_2SiMe_2\}\{P(OMe)_3\}_3$ (F) has also been isolated. Structure (4) has two molybdenum atoms linked by a strong metal–metal bond (2.16 Å), bridged by one $(CH_2)_2SiMe_2$ group forming a novel five-membered heterocycle. Three PMe_3 groups are bonded to one molybdenum atom while two normal CH_2SiMe_3 groups are attached to the other.



(4)

FIGURE 3

The ^1H n.m.r. spectrum is deceptively simple consisting of a multiplet (area 27) due to the PMe_3 groups and two singlets (δ 0.84 and 0.28) (areas *ca.* 8 : 18). Peaks due to the various methylene protons are not observed although integration of the spectrum indicates that they are probably masked by either of the two SiMe resonances.

The AX_2 triplet–doublet pattern of the $^{31}P\{^1H\}$ n.m.r. confirms the presence of three phosphine groups attached to one molybdenum atom in solution as in the crystalline state. Two are *trans* and equivalent while the third is *cis* to both of them.

The methylene carbon atoms of the bridging $(CH_2)_2SiMe_2$ unit should give two separate peaks in the $^{13}C\{^1H\}$ n.m.r. spectrum. However only one slightly broadened peak (δ 73.62) which can be assigned to these atoms is observed.

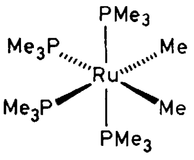
The bridging $(CH_2)_2SiMe_2$ group is no doubt formed by the elimination of a γ-hydrogen from a $MoCH_2SiMe_3$ group. A similar process probably occurs in the formation of the four-membered heterocycles (I) and (L) obtained from $Ru_2(O_2CMe)_4Cl$ and $Rh_2(O_2CMe)_4$ respectively (see later). However the methylene unit which is generated in this case becomes attached to the other molybdenum atom. There is no obvious explanation for the unsymmetrical structure of this alkyl which formally has Mo^I and Mo^{III} atoms.

(c) *Neopentyl.* The neopentyl analogue of (D), namely $Mo_2(CH_2CMe_3)_2(O_2CMe)_2(PMe_3)_2$ (G) is readily obtained and spectroscopic data for the red air-sensitive compound indicate that it has a structure similar to (3) with acetato-bridges.

When a large excess of alkylating agent was used a deep-green, air-sensitive and petroleum-soluble substance was obtained. However we have been unable to obtain pure samples of this oily material. There is no acetate present according to n.m.r. spectral results.

(3) *Ruthenium Compounds.*—(a) *Methyl.* Although $Ru_2^{II,III}Cl(O_2CMe)_4$ does not react with $MgMe_2$ and PMe_3 in diethyl ether over 5 days at ambient temperature, the reaction in tetrahydrofuran is complete within a few hours. From the reaction mixture the pale yellow, volatile and only moderately air-sensitive complex *cis*-$RuMe_2(PMe_3)_4$ (H) can be isolated.

The structure of *cis*-$RuMe_2(PMe_3)_4$ (5) is readily deduced from the n.m.r. data. Thus in the ^1H spectra, the two $P(CH_3)_3$ resonances appear as a pseudotriplet (δ 1.21, $J = 4.8$ Hz) and a doublet (δ 1.20, $J_{H,P} = 4.8$ Hz) which requires two *trans* and two *cis* P atoms.*



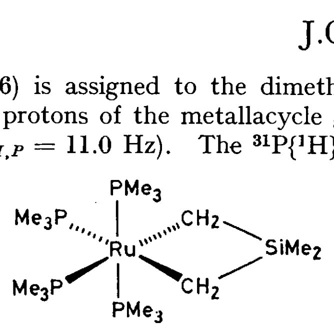
(5)

The CH_3–Ru protons give a complex symmetrical second-order pattern which can be roughly described as a doublet of triplets, each line of the multiplet being separated by *ca.* 4 Hz. We have not attempted a detailed analysis.

The $^{31}P\{^1H\}$ A_2X_2 type spectrum confirms the phosphine group stereochemistry. The $^{13}C\{^1H\}$ spectrum consists of a triplet and a triplet of triplets assigned to the two different types of phosphines. The Ru–CH_3 carbons give a doublet of quartets. The spectrum is, doubtless, second order (although it appears to approximate to a first-order situation) and we have not attempted to analyse it in detail.

(b) *Trimethylsilylmethyl.* Reaction of $Ru_2(O_2CMe)_4Cl$ with $(Me_3SiCH_2)_2Mg$ and PMe_3 in tetrahydrofuran yields a yellow diamagnetic, mononuclear complex $Ru\{(CH_2)_2SiMe_2\}(PMe_3)_4$ (I). N.m.r. data indicate that structure (6) contains a metallacycle similar to the phosphorometallacycles $M{-}CH_2{-}PMe_2{-}CH_2$ [7] and metallacyclobutanes in $(\pi\text{-}C_5H_5)_2W{-}CH_2{-}CHR{-}CH_2$ [8] and $(py)_2Cl_2Pt{-}CH_2{-}CH_2{-}CHPh$.[9]

The ^1H n.m.r. spectrum is similar to that of the methyl analogue; in addition to the phosphine resonances, a singlet (δ 0.56) is assigned to the dimethylsilyl group and the CH_2 protons of the metallacycle give a triplet (δ −1.36, $^3J_{H,P} = 11.0$ Hz). The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ n.m.r. spectra are very similar to those of the methyl compound. The $^{13}C\{^1H\}$ n.m.r. contains a triplet (δ 10.36, $^4J_{C,P} = 2.7$ Hz) and a doublet of quartets in addition to the resonances due to the phosphine groups. The triplet is assigned to the carbon atoms of the $Me_2Si(CH_2)_2$ group possibly coupling with the two mutually *cis* phosphorus atoms and the doublet of quartets to the methylene carbons of the metallacycle (as in the methyl analogue).



(6)

In contrast to that of *cis*-$RuMe_2(PMe_3)_4$, the ^1H n.m.r. spectrum of the metallacycle is temperature dependent. The triplets due to the *trans*-PMe_3 groups and the methylene protons both begin to broaden at +60 °C, while the doublet due to the *cis*-PMe_3 groups remains sharp and can be observed up to +70 °C. At 85 °C the doublet is lost although two distinct phosphine environments are observed. These finally coalesce to a single, broad resonance at 90 °C becoming sharp at 110 °C. The Me_2Si signal remains sharp throughout the temperature range. On cooling to +35 °C the original spectrum is observed indicating that irreversible decomposition is not responsible for the spectral changes. One explanation for these observations is that a rapid intermolecular exchange of PMe_3 groups occurs at elevated temperatures, the rate being faster for the mutually *trans* phosphines rather than those *trans* to CH_2. No new peaks are observed which indicates that any other species involved in the process is not present in significant concentrations.

(c) *Neopentyl.* In tetrahydrofuran, $Ru_2(O_2CMe)_4Cl$ reacts readily within 30 min with $Mg(CH_2Bu^t)_2$ and PMe_3 to give a pale yellow clear solution from which needles of $Ru\{(CH_2)_2CMe_2\}(PMe_3)_4$ (J) can be obtained in high yield. The ^1H n.m.r. spectrum of this air-sensitive, diamagnetic compound is uninterpretable as all the peaks occur over a narrow range. However the $^{31}P\{^1H\}$ n.m.r. is virtually identical with that of the methyl and trimethylsilyl compounds indicating two *cis* and two *trans* phosphines. Unfortunately the compound decomposes in CD_2Cl_2 and $CDCl_3$ and was not sufficiently soluble in other common deuterated solvents (C_6D_6, C_7D_8) for a reliable $^{13}C\{^1H\}$ n.m.r. spectrum to be obtained.

The data available are consistent with a metallacyclobutane structure (7) as found with the trimethylsilyl-

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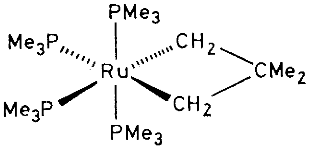
* *Note added in proof.* The iron analogue is now known (H. H. Karsch, *Chem. Ber.*, 1977, **110**, 2699).

[7] H. H. Karsch and H. Schmidtbauer, *Chem. Ber.*, 1974, **107**, 3684.

[8] M. Ephritikhine, M. L. H. Green, and R. E. Mackenzie, *J.C.S. Chem. Comm.*, 1976, 619.

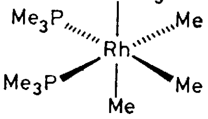
[9] R. J. Puddephat, M. A. Quyser, and C. F. Tipper, *J.C.S. Chem. Comm.*, 1976, 626.

methyl compound. An *X*-ray crystallographic study is in progress.[4]



(7)

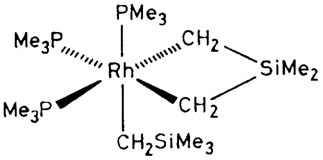
(4) *Rhodium Compounds.*—(a) *Methyl.* Rhodium(II) acetate, $Rh_2(O_2CMe)_4$, reacts with $MgMe_2$ in the presence of PMe_3 at 0 °C to give yellow needles of *fac*-$RhMe_3(PMe_3)_3$ (K). The structure of this non-volatile, diamagnetic alkyl can be easily deduced from n.m.r. data. The $^{31}P\{^1H\}$ n.m.r. spectrum consists of a doublet (δ −17.9, $^1J_{P,Rh} = 82.8$ Hz) indicating that all the PMe_3 groups are chemically equivalent, while the ^1H and $^{13}C\{^1H\}$ n.m.r. spectra are consistent with structure (8).



(8)

Surprisingly rhodium(III) alkyls could not be prepared[10] from $RhCl_3(PR_3)_3$ although the PMe_3 complex was not used. However the iridium analogues are well known for PEt_3 and PEt_2Ph,[11] and $CoMe_3(PMe_3)_3$ is also known.[12]

(b) *Trimethylsilylmethyl.* Pale-yellow crystals of $Rh(CH_2SiMe_3)\{(CH_2)_2SiMe_2\}(PMe_3)_3$ (L) may be obtained from the reaction of $Rh_2(O_2CMe)_4$ with PMe_3 and $Mg(CH_2SiMe_3)_2$. Structure (9) has a metallacycle similar to that in the ruthenium compound. A well resolved ^1H n.m.r. spectrum is obtained at 0 °C in which singlets (δ 0.6 and 0.42, area 3) are assigned to the two chemically non-equivalent SiMe groups of the metallacycle. Similarly, two singlets (δ 0.50 and 0.13, area 2) are obtained for the methylene protons of the $\overline{Rh-CH_2-SiMe_2-CH_2}$ unit. None of these resonances appears to be coupled to rhodium or phosphorus.



(9)

The $^{31}P\{^1H\}$ n.m.r. is a triplet–doublet pattern indicating two like and one unlike phosphine environments. The $^{13}C\{^1H\}$ n.m.r. spectrum is similar to that of the ruthenium metallacycle; the methylene carbon atoms of the metallacycle and possibly also that of the normal alkyl appearing as a high-field broadened doublet (δ −16.12). The PMe_3 groups give a complex multiplet probably due to the lack of symmetry in the molecule.

Unlike the ruthenium metallacycle (I), the ^1H n.m.r. spectrum of this complex is not temperature dependent. Cooling (−70 °C) merely results in broadening of the spectral lines while warming to 50 °C results in decomposition since re-cooling to 0 °C yields a greatly different and much more complex spectrum.

EXPERIMENTAL

Microanalyses were by Butterworth Microanalytical Consultancy Limited, Pascher, Bonn, and Imperial College laboratories. The spectrometers used were Perkin-Elmer R12 (^1H), Varian XL-100 (^{31}P, ^{13}C, Fourier transform), and Perkin-Elmer PE 457, 257 (i.r.) instruments.

All operations were carried out under oxygen-free nitrogen or *in vacuo* and all solvents were dried over sodium and distilled under nitrogen before use. The light petroleum used has b.p. 40—60 °C.

M.p.s were determined in sealed capillaries under nitrogen.

The magnetic moment of $Cr_2(CH_2SiMe_3)_4(PMe_3)_2$ was determined in solution by Evans' method, the chromium concentration being determined by plasma-arc emission spectroscopy.

(A) *Bis-μ-trimethylsilylmethyl-bis[trimethylphosphinebis(trimethylsilylmethyl)chromium*(II)](Cr–Cr).— Bis(trimethylsilylmethyl)magnesium (8.8 cm^3 of a 0.75M-diethyl ether solution) was added to a suspension of $Cr_2(O_2CMe)_4$ (0.56 g, 0.001 65 mol) in diethyl ether (40 cm^3) at 0 °C. The mixture was stirred for 5 h at 0 °C. The volatile material was removed under reduced pressure and the red-brown residue extracted with petroleum (50 cm^3) and filtered. The filtrate was concentrated to *ca.* 5 cm^3 and cooled (−20 °C) overnight. White crystalline material was removed from the deep red solution by filtration at 0 °C. Cooling (−20 °C) yielded after *ca.* 1 week, deep red *needles*. The compound can also be crystallised from diethyl ether; yield 0.3 g (30%). I.r. (petroleum solution, matched KBr cells), 1 276m, 1 236s, 1 115m, 935s, 865s, 837s, 815s, 735m, 706m, 691m, 672m, 565w, 508w, 458m, and 425w cm^{-1}. The compound decomposed at *ca.* 80—100 °C/10^{-2} mmHg to give a black air-sensitive solid. The compound also decomposes in solution when heated to *ca.* 50 °C in benzene. Mass spectra show that it does not cleanly eliminate $SiMe_4$ when heated (150 °C) under vacuum.

The compound is soluble in dichloromethane, chloroform, and pyridine, and survives for several days. It does not react with CO, H_2, ethylene or buta-1,3-diene in petroleum or toluene under ambient conditions. Prolonged treatment with CO (30 min) results in decomposition.

(B) *Bis[dimethylbis(trimethylphosphine)molybdenum]*(Mo–Mo); *Bis[dichlorobis(trimethylphosphine)molybdenum]*(Mo–Mo).—Dimethylmagnesium (7.0 cm^3 of a 0.75M-diethyl ether solution, 0.005 2 mol) was added to a suspension of $Mo_2(O_2CMe)_4$ (1.1 g, 0.002 6 mol) in diethyl ether (30 cm^3) and trimethylphosphine (1 cm^3). The colour gradually changed from red to green to deep blue as the acetate dissolved. After the mixture had been stirred for 6

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[10] J. Chatt and A. E. Underhill, *J. Chem. Soc.*, 1963, 2088; J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 2508.

[11] J. Chatt and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1836.

[12] H.-F. Klein and H. H. Karsch, *Chem. Ber.*, 1975, **108**, 944, 956.

h, the volatile material was removed under reduced pressure and the blue residue extracted into petroleum (60 cm^3). The solution was filtered, concentrated to *ca.* 25 cm^3, and cooled (−20 °C). The deep blue *crystals* were collected, washed with cold petroleum (2 × 1 cm^3), and dried *in vacuo*; yield 1.0 g (69%). I.r. (Nujol) 2 785w, 1 425m, 1 295m, 1 265m, 941s, 840w, 725m, 720m, and 667w cm^{-1}. The complex decomposed when heated in a sealed capillary (*ca.* 220 °C) and sublimed with decomposition at 120—130 °C/10^{-2} mmHg. It is stable in air in the solid state, soluble in most organic solvents, including chlorinated hydrocarbons and alcohols, without apparent decomposition.

The alkyl does not react with CO, H_2, CF_3CO_2H, and buta-1,3-diene at 1 atm pressure and room temperature, but it reacts with NO to yield a brown powder insoluble in toluene, ether, and tetrahydrofuran.

The compound reacts with concentrated hydrochloric acid in methanol to give *bis[dichlorobis(trimethylphosphine)-molybdenum]*(Mo–Mo), which has not previously been described although numerous analogues are known.[6]

To $Mo_2Me_4(PMe_3)_4$ (0.8 g) in methanol (15 cm^3) was added conc. HCl (0.5 cm^3 in 10 cm^3 MeOH). The blue precipitated crystals were collected after 2 h, washed with methanol and dried; yield, 0.9 g, *ca.* 100% (Found: C, 22.5; H, 6.1; Cl, 20.0; P, 18.0. $C_{12}H_{36}Cl_4Mo_2P_4$ requires C, 22.6; H, 5.6; Cl, 22.3; P, 19.4). ^{1}H N.m.r. ($CHCl_3$ with $SiMe_4$ internal reference): 2.43 (t, $^3J_{H,P}$ = 4 Hz); $^{31}P\{^1H\}$ n.m.r. [CH_2Cl_2 with [$^2H_6$]benzene (10%)] −9.80(s).

(C) *Bis[dimethylbis(dimethylphenylphosphine)molybdenum]*(Mo–Mo).—Dimethylmagnesium (9.3 cm^3 of a 0.55M-diethyl ether solution, 0.002 6 mol) was added to a suspension of $Mo_2(O_2CMe)_4$ (1.1 g, 0.002 6 mol) in diethyl ether (50 cm^3) and dimethylphenylphosphine (1 cm^3). The mixture was stirred at 0 °C for 5 h then evaporated to dryness and the residue extracted into toluene (45 cm^3), which was filtered and the filtrate concentrated to *ca.* 5 cm^3. Cooling of the latter (−20 °C) gave blue *crystals*; yield 1.6 g (75%), m.p. *ca.* 130 °C (decomp.). I.r. (Nujol) 3 080w, 3 050w, 2 790w, 1 538vw, 1 532vw, 1 435s, 1 285m, 1 270m, 1 100w, 1 070w, 1 205w, 935s, 900s, 860vw, 822m, 743s, 726m, 698s, and 675w cm^{-1}.

(D) *Bis-μ-acetato-bis[trimethylphosphine(trimethylsilylmethyl)molybdenum]*(Mo–Mo).— Bis(trimethylsilylmethyl)-magnesium (1.8 cm^3 of a 0.9M-diethyl ether solution, 0.001 6 mol) was added to $Mo_2(O_2CMe)_4$ (0.36 g, 0.000 84 mol) suspended in diethyl ether (40 cm^3) and trimethylphosphine (1 cm^3). The red suspension was stirred at 0 °C (1 h) and then at room temperature (4 h). The colour of the solution changed from red to deep maroon. After evaporation to dryness the blue residue was dissolved in light petroleum (30 cm^3), filtered, and concentrated to *ca.* 10 cm^3. Bright orange–red prisms were obtained after cooling of the solution (−20 °C). They were washed with cold petroleum (2 × 1 cm^3) and dried *in vacuo*. The compound does not react readily with CO (1 atm, 25 °C) in benzene solution; yield, 0.2 g (40%), m.p. 151—153 °C (decomp.). I.r. (Nujol), 1 425m, 1 355w, 1 345w, 1 295w, 1 280w, 1 245w, 1 235w, 940s, 905w, 870s, 850s, 835w, 815w, 735m, 710m, and 665m cm^{-1}. I.r. (Voltalef 3S B.D.H.) 2 940m, 2 900m, 2 860m, 1 510m, 1 430s, and 1 350m cm^{-1}.

(E) *μ-(Dimethylsilanediyl)dimethylene-bis(trimethylsilylmethyl)molybdiotris(trimethylphosphine)molybdenum.*— Bis(trimethylsilylmethyl)magnesium (4.0 cm^3 of a 0.9M-diethyl ether solution, 0.003 6 mol) was added to $Mo_2(O_2CMe)_4$, (0.36 g, 0.000 84 mol) suspended in diethyl ether (50 cm^3) and trimethylphosphine (1 cm^3). The red suspension was stirred (2 h) at 0 °C and then at room temperature (4 h). The colour of the solution gradually changed from red to deep maroon to blue. It was evaporated and the red residue was dissolved in petroleum (50 cm^3); the solution was filtered and concentrated to *ca.* 10 cm^3 to give red–brown *needles* on cooling (−20 °C); yield 0.45 g, (50%), m.p. 143—145 °C. I.r. (Nujol) 1 420m, 1 298m, 1 280m, 1 242s, 945s, 845s, 740m,br, 720m,br, 705m,br, and 670m,br cm^{-1}. The i.r. spectrum of (D) is virtually identical with that of (E) except for the strong band at 1 242 cm^{-1} in the latter.

The complex reacted with CO (1 atm, room temperature) in petroleum affording a solid (insoluble in petroleum, soluble in PhMe). The i.r. contained only terminal carbonyl absorptions and the ^{1}H n.m.r. showed only PMe_3 resonances and none due to Me_3SiCH_2. A red oil was produced with NO and the complex also reacted with CF_3CO_2H yielding a solution containing broad PMe_3 and Me_3SiCH_2 resonances in its ^{1}H n.m.r. spectrum. The i.r. spectrum (1 770 cm^{-1}, $CF_3CO_2^-$) revealed bridging and unidentate acetates (1 680, and 1 600 cm^{-1}).

Bis[tris(trimethylsilylmethyl)molybdenum](Mo–Mo).— This compound [13] was previously prepared from $MoCl_5$. Bis(trimethylsilylmethyl)magnesium (3.5 cm^3 of a 1.2M-diethyl ether solution, 0.004 2 mol) was added to $Mo_2(O_2CMe)_4$ (0.90 g, 0.004 2 mol) suspended in diethyl ether (50 cm^3). A brown–red solution was produced after the mixture had been stirred overnight. This was evaporated to dryness and extracted into petroleum (75 cm^3). The filtrate was concentrated to *ca.* 2 cm^3 and when cooled (− 20 °C) yielded orange-yellow *prisms* (*ca.* 0.2 g) which were shown to be $Mo_2(Me_3SiCH_2)_6$ by ^{1}H n.m.r. spectroscopy.

(F) *μ-(Dimethylsilanediyl)dimethylene-bis(trimethylsilylmethyl)molybdiotris(trimethyl phosphite)molybdenum.*— Bis(trimethylsilylmethyl)magnesium (5.6 cm^3 of a 1.0M-diethyl ether solution, 0.005 6 mol) was added to $Mo_2(O_2CMe)_4$ (1.2 g, 0.002 8 mol) suspended in diethyl ether (50 cm^3) and trimethyl phosphite (1.5 cm^3). The suspension was stirred for 12 h, evaporated to dryness, and the brown-red solid extracted into petroleum (50 cm^3). The solution was filtered and the filtrate was concentrated to *ca.* 10 cm^3 and cooled (−20 °C).

The large green *prisms* were collected, washed with cold petroleum (2 × 1 cm^3), and dried *in vacuo*; yield 1.0 g (43%), m.p. 122—124 °C (decomp.). I.r. (Nujol) 1 310w, 1 295m, 1 255s, 1 240s, 1 220m, 1 172s, 1 100s,sh, 1 030s,br, 970w, 920w, 895w, 830s,br, and 750s,br cm^{-1}.

(G) *Bis-μ-acetato-bis[2,2-dimethylpropyl(trimethylphosphine)molybdenum]*(Mo–Mo).— Bis(2,2-dimethylpropyl)magnesium (3.8 cm^3 of a 1.1M-diethyl ether solution, 0.004 2 mol) was added to $Mo_2(O_2CMe)_4$ (0.90 g, 0.002 1 mol) suspended in diethyl ether (50 cm^3) and trimethylphosphine (1 cm^3). The mixture was stirred for 1 h at 0 °C and then at room temperature for 3 h. The volatile material was removed under reduced pressure and the residue was extracted into petroleum (50 cm^3). The dark red-brown solution was filtered and the filtrate concentrated to *ca.* 10 cm^3. It was refiltered and cooled (−20 °C). The red *prisms* were collected, washed (2 × 2 cm^3 cold petroleum), and dried *in vacuo*; yield 0.7 g, (55%), m.p. *ca.* 140 °C (decomp.). I.r. (Nujol) 1 510m, 1 425s, 1 302w, 1 283m, 1 225m, 1 208w, 948s, 844w, 838w, 740m, 725m, and 668s cm^{-1}. Note:

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[13] W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533.

$Mo_2(O_2CMe)_4$ has absorptions at 1 510, 1 495, and 1 410 cm^{-1}.

The reaction of $Mo_2(O_2CMe)_4$ with 10 molar equivalents of $Mg(Bu^tCH_2)_2$ in the presence of PMe_3 yields a dark green petroleum-soluble oily material which could not be crystallised nor chromatographed (Al_2O_3, SiO_2 or cellulose) although it will sublime with decomposition (10^{-2} mmHg, 80—90 °C); we have not obtained the compound pure. The ^{1}H n.m.r. contains no resonances due to acetate.

(H) cis-*Dimethyltetrakis(trimethylphosphine)ruthenium*(II).—Dimethylmagnesium (3.6 cm^3 of a 0.65M-diethyl ether solution, 0.002 3 mol) was added to a suspension of $Ru_2(O_2CMe)_4Cl$ (0.44 g, 0.000 93 mol) in tetrahydrofuran (30 cm^3) and trimethylphosphine (1 cm^3). A homogeneous red solution was produced after the mixture had been stirred for 2 h. The volatile material was removed and the residue was extracted with petroleum (50 cm^3). After filtration the solution was concentrated to *ca.* 10 cm^3 and cooled (−20 °C) to give white prisms; yield 0.60 g, (74%), m.p. 200—210 °C (turns red at *ca.* 180 °C). I.r. (Nujol) 1 295s, 1 275s, 1 160w, 1 012w, 915s, 848s, 695s, and 655s cm^{-1}. The dialkyl is not fluxional since its ^{1}H n.m.r. spectrum does not vary from −80 to +80 °C. It will sublime at 100—120 °C *in vacuo*. It was obtained several years ago in these laboratories from *cis*-$RuCl_2(PMe_3)_4$ and methyl-lithium but never completely characterized.

(I) *(Dimethylsilanediyl)dimethylenetetrakis(trimethylphosphine)ruthenium*(II).— Bis(trimethylsilylmethyl)magnesium (2.0 cm^3 of a 1.0M-diethyl ether solution, 0.002 0 mol) was added to a suspension of $Ru_2(O_2CMe)_4Cl$ (0.30 g, 0.000 63 mol) in tetrahydrofuran (30 cm^3) and trimethylphosphine (1 cm^3). The solution was stirred for 1 h and then evaporated to dryness. The brown-red residue was extracted with petroleum (50 cm^3), the solution filtered and the filtrate concentrated to *ca.* 10 cm^3. Cooling (−20 °C) of the latter yielded pale yellow *needles*; yield, 0.50 g (80%), m.p. 150—151 °C. I.r. (Nujol) 1 300s, 1 280s, 1 235m, 1 220m, 1 020w, 965s, 935s, 875, 850s, 807s, 725m, 700s, and 657s cm^{-1}.

The reaction in the absence of PMe_3 results in reduction to metal and in diethyl ether there was no reaction after 1 week at room temperature.

(J) 2,2-*Dimethyldimethylenetetrakis(trimethylphosphine)ruthenium*(II).—Bis(2,2-dimethylpropyl)magnesium (1.4 cm^3 of a 1.0M-diethyl ether solution, 0.001 5 mol) was added to $Ru_2(O_2CMe)_4Cl$ (0.30 g, 0.000 63 mol) suspended in tetrahydrofuran (40 cm^3) and trimethylphosphine (1 cm^3) at 0 °C. The solution was warmed to room temperature and stirred for 30 min yielding a pale yellow clear solution. The volatile material was removed under reduced pressure and the residue extracted with toluene (20 cm^3) and filtered. The filtrate was concentrated to 10 cm^3 and cooled (−20 °C). The pale yellow *needles* were washed with cold petroleum (2 × 1 ml); yield 0.2 g (70%), m.p. 172—175 °C (decomp.). I.r. (Nujol) 1 440m, 1 417w, 1 365m, 1 300m, 1 280m, 960m, 940s, 855m, 715m, and 665m cm^{-1}.

The crystals of the compound are solvent dependent and lose crystallinity *in vacuo* or when dried under a stream of nitrogen. Low figures for carbon analysis may be due to ruthenium carbides being formed while the determinations were being made.

(K) fac-*Trimethyltris(trimethylphosphine)rhodium*.— Trimethylphosphine (1 cm^3) was added to a suspension of $Rh_2(O_2CMe)_4$ (0.45 g, 0.001 0 mol) in diethyl ether (50 cm^3) at 0 °C. The brown suspension was stirred for 15 min after which dimethylmagnesium (3.7 cm^3 of a 0.55M-diethyl ether solution, 0.002 0 mol) was added to it and the suspension stirred for 4 h (0 °C). The volatile material was removed under reduced pressure and the brown-yellow residue was extracted with petroleum (50 cm^3). The solution was filtered and concentrated to *ca.* 2 cm^3. Cooling (−20 °C) of the latter yielded yellow *needles*; yield, 0.60 g (40%), m.p. 106—108 °C. I.r. (Nujol) 1 420s, 1 330w, 1 295s, 1 280s, 1 260s, 1 162s, 1 090m,br, 1 015m,br, 935s,br, 870m, 860m, 845s, 800m, 772w, 745m, 740m, 715s, 670s, and 665s cm^{-1}.

The yellow complex did not sublime at 110 °C/10^{-2} mmHg.

(L) *(Dimethylsilanediyl)dimethylenetris(trimethylphosphine)trimethylsilylmethylrhodium*.—Trimethylphosphine (1 cm^3) was added to a suspension of $Rh_2(O_2CMe)_4$ (0.43 g, 0.000 97 mol) in diethyl ether at 0 °C.

Bis(trimethylsilylmethyl)magnesium (1.9 cm^3 of a 1.0M-diethyl ether solution, 0.001 9 mol) was added to the yellow-brown suspension which was stirred for 5 h (0 °C). The volatile material was removed under reduced pressure and the yellow residue was extracted with petroleum (50 cm^3). The solution was filtered, evaporated to *ca.* 5 cm^3, and cooled (−20 °C) to yield yellow *prisms*; yield 0.51 g (52%), m.p. 100—101 °C (decomp.). I.r. (Nujol) 1 420m, 1 298m, 1 280m, 1 242s, 945s, 845s, 740m,br, 720m,br, 705m,br, and 670m,br cm^{-1}.

We thank Dr. D. J. Cole-Hamilton for discussions, Dr. M. B. Hursthouse for permission to quote the results of structural determinations, Hercules Inc. for financial support, the S.R.C. for a studentship (R. A. J.), and Johnson Matthey Limited for the loan of ruthenium and rhodium.

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