Interaction of Magnesium Dialkyls with Binuclear Transition Metal Acetates: Crystal Structure of Bis(trimethylsilylmethyl)bis(trimethylphosphine) bis(μ-trimethylsilylmethyl)-dichromium(II)

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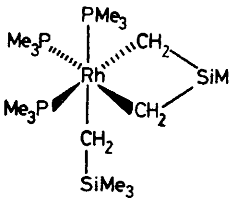
Summary Reaction between the dialkyl magnesium reagents MgR_2 (R = Me, CH_2SiMe_3, or CH_2CMe_3) and binuclear acetates of Cr, Mo, Re, Ru, and Rh containing metal–metal bonds gives either monomeric or binuclear species, the metal–metal bond being retained in the latter, and in some cases, loss of a hydrogen atom from a methyl group of the CH_2SiMe_3 ligand leading to the formation of a metallocycle $\overline{M{-}CH_2{\cdot}SiMe_2{\cdot}CH_2}$; the structure of the binuclear compound $Cr_2(CH_2SiMe_3)_4(PMe_3)_2$ has been determined by *X*-ray diffraction methods.

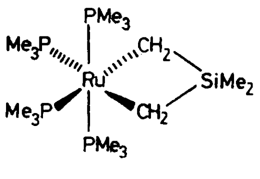
The interaction of alkylating agents with binuclear transition metal carboxylates containing multiple metal–metal bonds has, so far, given isolable products only for the reactions involving methyl-lithium and $Mo_2(O_2CMe)_4$ and

$Re_2Cl_2(O_2CMe)_4$. These give the lithium etherates of the anions $[Mo_2Me_8]^{4-}$ and $[Re_2Me_8]^{2-}$, respectively.[1]

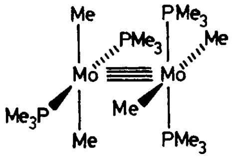
However, in the presence of trimethylphosphine, at 0 °C in ether or tetrahydrofuran, the acetates $Cr_2(O_2CMe)_4$, $Mo_2(O_2CMe)_4$, $Re_2Cl_2(O_2CMe)_4$, $Ru_2Cl(O_2CMe)_4$, and $Rh_2(O_2CMe)_4$ react with the dialkylmagnesium compounds R_2Mg ($R = Me$, CH_2SiMe_3, or CH_2CMe_3) to give neutral, isolatable, crystalline, trimethylphosphine-containing alkyls which are either monomeric, or dimeric with multiple metal–metal bonds.



(I)



(II)

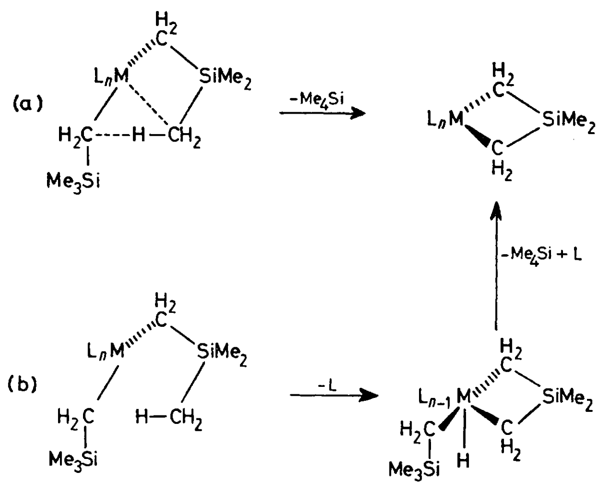


(III)

For R = Me, the rhodium and ruthenium acetates give *fac*-$RhMe_3(PMe_3)_3$† and *cis*-$RuMe_2(PMe_3)_4$, respectively. However, when $R = CH_2SiMe_3$, a metallocycle is formed [(I) and (II)]. This ring is similar to the phosphorometallocycles $M\text{-}CH_2{\cdot}PMe_2{\cdot}CH_2$[2] and the metallocyclobutanes in $(\pi\text{-}C_5H_5)_2W(CH_2{\cdot}CHR{\cdot}CH_2)$[3] and $PtCl_2py_2(CH_2{\cdot}CH_2{\cdot}CHPh)$.[4] The ring formation in our case doubtless occurs by loss of a γ-hydrogen from the methyl group of one metal-bonded CH_2SiMe_3 group, and transfer to a second alkyl group to give $SiMe_4$, by either of the paths indicated in the Scheme.

The other acetates give binuclear, metal–metal bonded species which, for R = Me, appear to be rather simple as in $Mo_2Me_4(PMe_3)_4$ (III). With $R = CH_2SiMe_3$ however, $Cr_2(O_2CMe)_4$ gives a dark red, pyrophoric crystalline material whose structure has been determined by single crystal *X*-ray diffraction methods.‡

Crystal data: $C_{44}H_{62}Cr_2Si_4P_2$, *M* 605, triclinic, $a = 16{\cdot}975(7)$, $b = 11{\cdot}396(6)$, $c = 10{\cdot}678(6)$ Å, $\alpha = 114{\cdot}87(7)$, $\beta = 91{\cdot}75(7)$, $\gamma = 84{\cdot}98(7)°$, $U = 1867$ Å^3, D_m not measured, $Z = 2$, $D_c = 1{\cdot}076$ g cm^{-3}, space group $P\bar{1}$, μ(Mo-K_α) 7·5 cm^{-1}. A total of 5951 unique, three-dimensional intensities were recorded using Mo-K_α radiation and a Nonius CAD4 diffractometer (ω-2θ scan, $1{\cdot}5 < \theta < 25°$), from a crystal sealed under nitrogen in a Lindemann capillary. The structure was solved using the automatic direct methods routine in the SHELX[5] program (Cr, P, Si positions developed *via* successive electron density syntheses and refined by blocked full-matrix least-squares. *R* is currently 0·030 (H isotropic, others anisotropic, unit weights, no absorption correction) for the 4345 significant $[I > 1{\cdot}5\sigma(I)]$ reflections.



SCHEME. Metallocycle formation by loss of γ-hydrogen by either (a) direct elimination of Me_4Si or (b) intermediate hydride formation *via* oxidative addition to the metal, followed by the reductive elimination of Me_4Si. The ligands, L, could be PR_3, acetate, or solvent molecules.

The molecular structure is shown in the Figure. It contains two bridging alkyl groups (*cf.* the manganese dialkyls[6]), arranged in a *cis* configuration with a dihedral

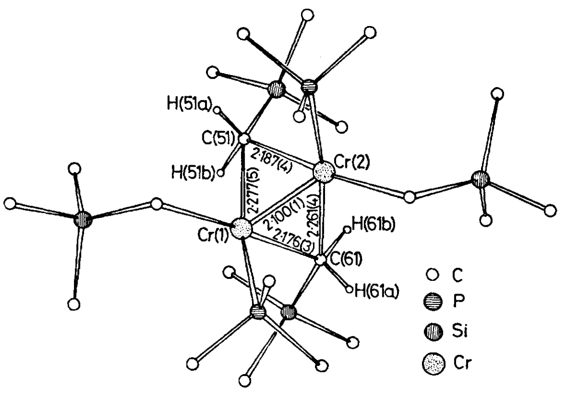


FIGURE. Structure of $Cr_2(CH_2SiMe_3)_4(PMe_3)_2$ viewed down an approximate molecular C_2 axis (bond lengths in Å). Average Cr–C and Cr–P distances for the monodentate ligands are 2·132 and 2·459 Å respectively.

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† Iridium analogues for PEt_3 and PEt_2Ph are known [J. Chatt and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1836] but attempts to obtain methyl compounds from $RhX_3(PR_3)_3$ failed (J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 2508; J. Chatt and A. E. Underhill, *J. Chem. Soc.*, 1963, 2088).

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

angle between the two (Cr–C–Cr) planes of 101°. The Cr–Cr distance of 2·100(1) Å is indicative of strong metal–metal bonding. Two other features of interest are the approximate C_2 symmetry of the molecule and the close approach (*ca.* 2·3 Å) of one hydrogen atom from each bridging CH_2 group [H(51b) and H(61b)] to one of the metal atoms. Both of these features might result from the packing requirements of the bulky ligands. The H · · · · · Cr contacts may also explain the slight asymmetry of the Cr–C bridge bonds (see Figure).

With $Mo_2(O_2CMe)_4$ and $Mg(CH_2SiMe_3)_2$, a red, petroleum-soluble, air-sensitive compound $Mo_2(CH_2SiMe_3)_3(PMe_3)_3$ is obtained. Using $Mg(CH_2CMe_3)_2$, however, moderately air-sensitive, red crystals of a compound that still contains the acetate, and of stoicheiometry $Mo_2(O_2CMe)_2(CH_2CMe_3)_2$-$PMe_3)_2$ are formed. The structures of these compounds are under investigation, but they have been characterised by ^1H, ^{31}P, and ^{13}C n.m.r. studies.

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[2] See *e.g.*, H. H. Karsch and H. Schmidtbauer, *Chem. Ber.*, 1974, **107**, 3684.

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