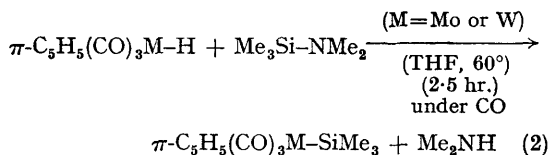
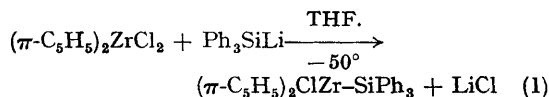


Organosilyl Derivatives of Zirconium, Molybdenum, and Tungsten

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THE first compound containing a silicon to transition-metal covalent bond was reported by Piper, Lemal, and Wilkinson in 1956.¹ There have since appeared twenty other publications, mostly during the last three years (see ref. 2, for the latest Papers). Derivatives of Mn, Re, Fe, Co, Rh, Ir, Ni, and Pt are known, together with the recently discovered³ $\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo-SiCl}_3$. With the sole exception of this compound, no compounds of early transition metals were known.



TABLE

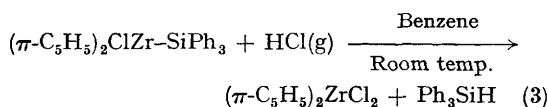
Characterisation of organosilyl transition-metal derivatives

Compound	Appearance	M.p. (Sublimation)	Highest peak in mass spectrum ^a	¹ H n.m.r. signals	I.r. characteristic (ν_{max} , cm.^{-1})
$(\pi\text{-C}_5\text{H}_5)_2\text{Zr-SiPh}_3$	Orange crystals (recrystallised from THF)	175—178 ^b	514 ^c	$\left\{ \begin{array}{l} \tau = 3.71 \text{ (Cp)} \\ \tau = 2.56 \text{ (Ph)}^f \end{array} \right.$	—
$\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo-SiMe}_3$	Yellow crystals	($\sim 100^\circ/0.005 \text{ mm.}$) ^b	320 ^c	$\left\{ \begin{array}{l} \tau = 4.80 \text{ (Cp)} \\ \tau = 9.94 \text{ (Me)} \end{array} \right.$	1974, 1955, 1890 ^d
$\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{W-SiMe}_3$	Pale yellow	($\sim 100^\circ/0.005 \text{ mm.}$) ^b	392 ^e	$\left\{ \begin{array}{l} \tau = 4.56 \text{ (Cp)} \\ \tau = 9.86 \text{ (Me)} \end{array} \right.$	2027, 1935, 1898 ^d

^a We thank Dr. M. R. Litzow for these data.^b With some decomposition.^c Molecular ion.^d All strong peaks, due to $\nu(\text{CO})$ (Nujol mulls).^e Molecular-ion -14 [loss of 14 has been observed in other MeSi compounds (unpublished work)].^f Approximate centre of a multiplet.

We now report the synthesis (see equations) and characterisation (see Table) of derivatives of Zr^{IV} (significant as an example of a d^0 and high-oxidation-state system), Mo^{II} , and W^{II} , all of which are air-sensitive. It has been inferred (see, *e.g.*, ref. 4) that the stability of metal-silicon compounds decreases from right to left in a transition series, and with increasing oxidation state of the transition metal.

An attempt to replace the second chlorine atom of $(\pi\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ by Ph_3Si afforded a tarry product. When reaction (1) was explored further, using $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2$, a green-black product (Ti^{III} ?) was obtained. Further evidence for the existence of a Zr-Si bond was provided by reaction (3).



The metal hydride-metal amide reaction route⁵ proved inapplicable for Zr-Si [using Ph_3SiH and $(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{NMe}_2)_2$ (see ref. 6)]; there was no reaction at 125° .

Reaction (2) is of interest not only for providing the new metal-silicon compounds, but also because (a) the more usual route [analogous to equation (1)] previously proved inapplicable for trisubstituted silyl compounds,³ and (b) the Me_3Si derivatives are usually less stable than Cl_3Si .³

*(Received, August 31st, 1967; Com. 936.)*¹ T. S. Piper, D. Lemal, and G. Wilkinson, *Naturwiss.*, 1956, **43**, 129.² R. N. Haszeldine, R. V. Parish, and D. J. Parry, *J. Organometallic Chem.*, 1967, **9**, P13; J. Chatt, C. Eaborn, S. Ibekwa, and P. N. Kupoor, *Chem. Comm.*, 1967, 869.³ W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1967, **89**, 2773.⁴ H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 1401.⁵ D. J. Cardin and M. F. Lappert, *Chem. Comm.*, 1966, 506.⁶ G. Chandra, T. A. George, and M. F. Lappert, *Chem. Comm.*, 1967, 116.