# Organosilyl Derivatives of Zirconium, Molydenum, 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 discovered[3] $\pi\text{-}C_5H_5(CO)_3Mo\text{–}SiCl_3$. With the sole exception of this compound, no compounds of early transition metals were known.

$$(\pi\text{-}C_5H_5)_2ZrCl_2 + Ph_3SiLi \xrightarrow[-50^\circ]{\text{THF.}} (\pi\text{-}C_5H_5)_2ClZr\text{–}SiPh_3 + LiCl \quad (1)$$

$$\pi\text{-}C_5H_5(CO)_3M\text{–}H + Me_3Si\text{–}NMe_2 \xrightarrow[\substack{\text{(THF, 60°)}\\ \text{(2·5 hr.)}\\ \text{under CO}}]{(M{=}Mo \text{ or } W)} \pi\text{-}C_5H_5(CO)_3M\text{–}SiMe_3 + Me_2NH \quad (2)$$

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 ($\nu_{max}$, cm.$^{-1}$) |
|---|---|---|---|---|---|
| $(\pi\text{-}C_5H_5)_2ClZr\text{–}SiPh_3$ | Orange crystals (recrystallised from THF) | 175—178° [b] | 514[c] | $\tau$ = 3·71 (Cp)<br>$\tau$ = 2·56 (Ph)[f] | — |
| $\pi\text{-}C_5H_5(CO)_3Mo\text{–}SiMe_3$ | Yellow crystals | (~100°/0·005 mm.)[b] | 320[c] | $\tau$ = 4·80 (Cp)<br>$\tau$ = 9·94 (Me) | 1974, 1955, 1890[d] |
| $\pi\text{-}C_5H_5(CO)_3W\text{–}SiMe_3$ | Pale yellow | (~100°/0·005 mm.)[b] | 392[e] | $\tau$ = 4·56 (Cp)<br>$\tau$ = 9·86 (Me) | 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 $\nu$(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[e] Molecular-ion −14 [loss of 14 has been observed in other MeSi compounds (unpublished work)].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 $(\pi\text{-}C_5H_5)_2ZrCl_2$ by $Ph_3Si$ afforded a tarry product. When reaction (1) was explored further, using $(\pi\text{-}C_5H_5)_2TiCl_2$, a green-black product ($Ti^{III}$?) was obtained. Further evidence for the existence of a Zr–Si bond was provided by reaction (3).

$$(\pi\text{-}C_5H_5)_2ClZr\text{–}SiPh_3 + HCl(g) \xrightarrow[\text{Room temp.}]{\text{Benzene}} (\pi\text{-}C_5H_5)_2ZrCl_2 + Ph_3SiH \quad (3)$$

The metal hydride–metal amide reaction route[5] proved inapplicable for Zr–Si [using $Ph_3SiH$ and $(\pi\text{-}C_5H_5)_2Zr(NMe_2)_2$ (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]

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