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Preliminary communication

Polysilane derivatives of the transition metals
I. Synthesis of $(Me_3Si)_3SiMn(CO)_5$ and related compounds

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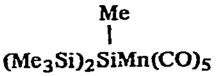
Although the preparations of some straight-chain polysilane derivatives of iron[1] and a similar compound of cobalt[2] have been reported, attempts to synthesise polysilane derivatives of other transition metals have been unsuccessful. Thus King *et al.*[1] were unable to isolate compounds containing silicon-transition metal bonds from salt elimination reactions of chloropentamethyldisilane with the anions $[M(CO)_5]^-$ (M = Mn,Re) and $[M(CO)_3C_5H_5]^-$ (M = Mo,W). We wish to report the preparation of a series of polysilane derivatives of manganese $(Me_3Si)_nSiMe_{3-n}Mn(CO)_5$ (n = 1-3) by the reaction of dimanganese decacarbonyl with the corresponding silane (eqn. 1)

$$2R_3SiH + Mn_2(CO)_{10} \xrightarrow[36\ h]{130^\circ,\ \text{sealed tube}} 2R_3SiMn(CO)_5 + H_2 \qquad (1)$$

$[R_3SiH = Me_3SiSiMe_2H^3, (Me_3Si)_2SiMeH^4, (Me_3Si)_3SiH^5]$

The products were isolated by preparative scale thin layer chromatography (elution with hexane from silica-gel plates) and siloxane impurities were removed by extraction with concentrated sulphuric acid at 0°. Vacuum sublimation gave the products, in ~ 20% yield, as white waxy crystals. The compounds were stable for long periods in an inert atmosphere but underwent slow hydrolysis on exposure to air.

TABLE 1

Compound	$\nu(CO)^a$ (cm^{-1})	Chemical shifts τ^b (ppm)
$Me_3SiMn(CO)_5$	2094 s 1993 vs	9.51^c
$Me_3SiSiMe_2Mn(CO)_5$	2092 m 1999 w (sh) 1993 vs	9.83 (Me_3Si) 9.54 (Me_2Si)
 $(Me_3Si)_2\overset{\overset{Me}{\vert}}{Si}Mn(CO)_5$	2091 m 1998 vw (sh) 1995 vs	9.78 (Me_3Si) 9.57 (MeSi)
$(Me_3Si)_3SiMn(CO)_5$	2091 m 1998 vs	9.75

^{a} Hexane solution. ^{b} 90% CS_2/10% C_6H_6 solution; TMS as internal standard. ^{c} 50% solution in cyclohexane[6].

Satisfactory analyses have been obtained for the compounds, and Table 1 shows the carbonyl absorption frequencies and proton NMR chemical shift data together with those for the corresponding monosilane derivative $Me_3SiMn(CO)_5$[6]. Work is now in progress on the preparation of polysilane derivatives of other transition metals, together with investigations of the effect of the presence of silicon atoms β to the transition metal atom on the physical and chemical properties of the silicon–metal bond.

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REFERENCES

1 R.B. King, K.H. Pannel, C.R. Bennett and M. Ishaq, *J. Organometal. Chem.*, 19 (1969) 327.
2 A.G. Mac Diarmid, unpublished results quoted in Ref. 1.
3 M. Kumada, M. Ishikawa and S. Maeda, *J. Organometal. Chem.*, 2 (1964) 478.
4 B.K. Nicholson and J. Simpson, unpublished work.
5 H. Gilman, J.M. Holmes and C.L. Smith, *Chem. Ind. (London)*, (1965) 848.
6 A.D. Berry and A.G. MacDiarmid, *Inorg. Nucl. Chem. Letters*, 5 (1969) 601.