1,3-Organometallic Insertion Reactions with Trimethylsilyldiazomethane: Synthesis of (Trimethylsilyl)methylazo–Transition Metal Complexes

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Summary The reaction between π-$C_5H_5(OC)_3M$–H (M = Mo or W) and Me_3SiCHN_2 provides the first example of a 1,3-organometallic insertion and the products π-C_5H_5-$(OC)_2M{\cdot}N{=}N{\cdot}CH_2SiMe_3$ are the first stable alkylazo-compounds.

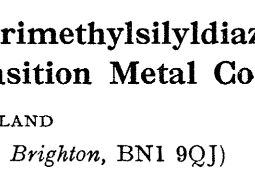
INSERTIONS (equation 1) are an important class of organometallic reactions.[1] They may be 1,1-(*e.g.*, A = CO), 1,2 (*e.g.*, A = $CH_2:CH_2$), or 1,4- (*e.g.*, A = $CH_2:CH{\cdot}CH:CH_2$) in character. We now report the first example (equation 2; M = Mo or W) of a 1,3-insertion.

$$\text{LM–X} + \text{A} \rightarrow \text{LM–A–X} \qquad (1)$$

$$\pi\text{-}C_5H_5(OC)_3M\text{–H} + Me_3Si\overset{-}{C}H{\cdot}N{=}\overset{+}{N} \xrightarrow{(-CO)} \pi\text{-}C_5H_5(OC)_2M{\cdot}N{=}N{\cdot}CH_2SiMe_3 \qquad (2)$$

(I)

It is possible that the reaction of diazomethane with a metal hydride [*e.g.*,[2] π-$C_5H_5(OC)_3W$–H + CH_2N_2 → π-$C_5H_5(OC)_3WCH_3$ (4%)] involves an initial 1,3-(rather than carbene-) insertion with subsequent nitrogen expulsion; by-products tend to be red oils and these may well be azo-compounds. Significant also are the following points. (i) The 1,3-dipolar character of the CN_2^{2-} ligand is evidently enhanced by the attachment to C of an organometallic group (see also ref. 3 regarding 1,3-cyclo-additions with dipolarophiles such as $MeO_2C{\cdot}C{:}C{\cdot}CO_2Me$); related ligands, such as N_3^-, may prove to be similarly stabilised. (ii) The isolation of stable *alkyl*azo-compounds (I) is unprecedented (phenylazo-derivatives of W^{II},[4] Mo^{II},[5] and Pt^{II} [6] are known) and suggests N=N π-electron delocalisation into the transition metal and/or the β-silicon *d*-orbitals. (iii) Compounds of type (I) may be useful precursors for synthesis of nitrogen complexes (*cf.* ref. 7).



(III)

With regard to (i), Me_3SnN_3 behaved (equation 3) as a pseudohalide rather than an azide (a side-reaction afforded the molybdenum azide); compound (II) is known.[8] Phenyl azide and molybdenum hydride did not react at 60°, while *p*-tosyl azide at −30° gave an, as yet, unidentified orange powder.

$$\pi\text{-}C_5H_5(OC)_3Mo\text{–H} + Me_3SnN_3 \rightarrow \pi\text{-}C_5H_5(OC)_3Mo\text{–}SnMe_3 + HN_3 \qquad (3)$$

(II)

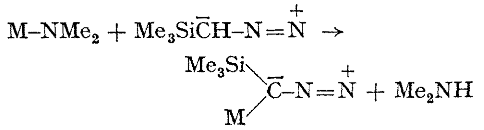
The structures of the alkylazo-compounds (I) were established spectroscopically (see Table). It is interesting that π-$C_5H_5(OC)_3W^-$ and diazoacetic ester undergo a different reaction from (2), providing compound (III).[9]

TABLE

Compound	Yield (%)	M.p.	ν (CO) (cm.$^{-1}$)[a]	ν(N_2) (cm.$^{-1}$)[a]	Appearance	$\lambda_{max.}$ (nm.) (ϵ)[b]
π-$C_5H_5(OC)_2W$–N=N–CH_2SiMe_3[c,d,e]	88	72°[d]	1899, 1979	1618, 1640	red cryst.	386(115), 471(31)
π-$C_5H_5(OC)(Ph_3P)W$–N=NCH_2SiMe_3[f]	26	139—141°	1820	overlaps with Ph	pink cryst.	
π-$C_5H_5(OC)_2Mo$–N=NCH_2SiMe_3[d,e,g]	84	63—64°	1908, 1982	1642	red cryst.	383(102), 459(28)

[a] Hexane solution; [b] cyclohexane solution; also strong absorptions 340—200 nm.; [c] n.m.r. chemical shifts (τ) in C_6H_6: 9·90 (Me_3), 6·78 (CH_2), 4·90 (C_5H_5); [d] prepared by reaction in Et_2O at 20°; [e] showed a parent molecular ion in mass spectrum; [f] prepared by reaction of π-$C_5H_5(OC)_2W$–N=NCH_2SiMe_3 and Ph_3P in C_6H_6 at 60° (8 hr.); [g] n.m.r. chemical shifts (τ) in C_6H_6: 9·86 (Me_3), 6·93 (CH_2), 4·76 (C_5H_5).

Attempted insertion reactions into M–M′ [π-$C_5H_5(OC)_3$-W–$SnMe_3/CH_2N_2$], M–R [π-$C_5H_5(OC)_3Mo$–Me/Me_3SiCHN_2], M–Cl [*trans*-$(Ph_3P)_2Ir(CO)Cl/Me_3SiCHN_2$], and M–$NR_2$ bonds proved unsuccessful. However, reactions of metal amides (equation 4) [M in (IV) = Me_3Sn, (b.p. 44—46°/0·5 mm., ν(N_2), 2022 cm.$^{-1}$) or $\frac{1}{2}(\pi$-$C_5H_5)_2Zr$ (pyrophoric solid); ν (N_2), 2050 cm.$^{-1}$] proved interesting. The zirconium compound may be the first transition-metal diazoalkane, but is still poorly characterised.



$$\text{M–NMe}_2 + \text{Me}_3\text{Si}\bar{\text{C}}\text{H–N}{=}\overset{+}{\text{N}} \rightarrow (\text{Me}_3\text{Si})(\text{M})\bar{\text{C}}\text{–N}{=}\overset{+}{\text{N}} + \text{Me}_2\text{NH} \qquad (4)$$

(IV)

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