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Preliminary communication

μ-Methylene transition metal binuclear compounds: complexes with $Me_3SiCH_2^-$ and related ligands

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We wish to draw attention to an important class of ligands R^-, which promises significantly to extend the scope of σ-alkyl complexes and hence of organometallic compounds. These may formally be regarded as carbanions in which one or more α-H atom(s) have been replaced by an organometallic or t-alkyl fragment. Attention to date has concentrated upon transition metal complexes LMR having as ligand(s) the groups Me_3SiCH_2, $Me_2PhSiCH_2$, $(Me_3Si)_2CH$, $(Me_3Si)_3C$, $(Me_3Si)Ph_2C$, Me_3SnCH_2, Me_3CCH_2, and Me_2PhCCH_2.

Satisfactory analyses and spectra have been obtained for the compounds shown in Table 1. Less complete data are available for *inter alia* $Ti(CH_2SiMe_3)_4$, $Zr(CH_2SiMe_3)_4$, $Zr(CH_2SiMe_2Ph)_4$, $(\pi\text{-}C_5H_5)_2Nb(CH_2SiMe_3)_2$, $(Ph_3P)_3RhCH_2SiMe_3$, $\pi\text{-}C_5H_5(Ph_3P)NiCH_2SiMe_3$, and $Ni(CPh_2SiMe_3)_2$. Some results have been described at a conference in East Germany[1], and in a patent application[2]. An unexpectedly large neighbouring group effect of the transition metal moiety LM in the complexes $LM{-}CH_2{-}M'Me_3$ [$LM = \pi\text{-}C_5H_5(CO)_3Mo$, $\pi\text{-}C_5H_5(CO)_3W$, or $\pi\text{-}C_5H_5(CO)_2Fe$; and M = Si or Sn] has been discovered[3], as demonstrated by the ease of nucleophilic cleavage of the $CH_2{-}M'$ bond; an effect which is very sensitive to changes in LM or M′.

The compounds shown in Table 1 were prepared by the salt elimination procedure,

TABLE 1

Compound	Yield (%)	Appearance	M.p. (°C)
$(\pi\text{-}C_5H_5)_2Ti(CH_2SiMe_3)_2$ [a]	60	golden needles	[b]
$(\pi\text{-}C_5H_5)_2Zr(CH_2SiMe_3)_2$ [a]	70	white needles	96–97
$(\pi\text{-}C_5H_5)_2Hf(CH_2SiMe_3)_2$ [a]	50	white needles	83
$\pi\text{-}C_5H_5(CO)_3MoCH_2SiMe_3$ [c,d]	3	(yellow liquid)	–
$\pi\text{-}C_5H_5(CO)_3WCH_2SiMe_3$ [c,d]	55	yellow crystals	32
$\pi\text{-}C_5H_5(CO)_3WCH_2SiMe_2Ph$ [d]	40	yellow needles	47–49
$\pi\text{-}C_5H_5(CO)_2FeCH_2SnMe_3$ [d,e]	60	yellow needles	29–30

[a] Using Me_3SiCH_2Li. [b] Compound did not melt (sealed tube under argon) up to 300° but gradually darkened to a black solid. ^{1}H NMR in $CDCl_3$ ($CHCl_3$ as standard), τ 3.89 ($\pi\text{-}C_5H_5$), τ 9.11 (CH_2), τ 10.06 (Me_3Si). [c] See ref. 3. [d] Using Me_3SiCH_2I, $PhMe_2SiCH_2I$, or Me_3SnCH_2I. [e] The Si analogue has been reported[14].

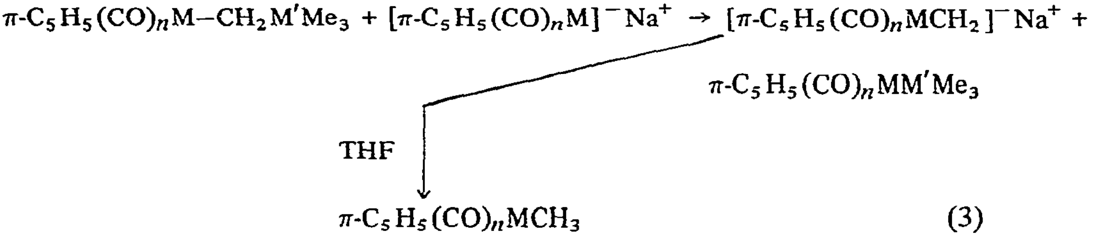
as illustrated by Eqs. (1) and (2). The transition metal anion procedure was necessarily inapplicable to the Group IVA derivatives. The yields (see Table 1) for reactions of Eq. (2) depend on the relative importance (a function of M, M′, and n) of the competing reactions of Eq. (3)[3].

$$(\pi\text{-}C_5H_5)_2MCl_2 + 2LiCH_2SiMe_3 \xrightarrow{Et_2O,\ 0^\circ} (\pi\text{-}C_5H_5)_2M(CH_2SiMe_3)_2 + 2LiCl \quad (1)$$

(M = Ti, Zr, or Hf)

$$[\pi\text{-}C_5H_5(CO)_nM]^-Na^+ + Me_3M'CH_2I \xrightarrow[\text{(see also ref. 3)}]{THF,\ 20^\circ} \pi\text{-}C_5H_5(CO)_nM\text{-}CH_2M'Me_3 + NaI \quad (2)$$

(M = Mo or W, M′ = Si, n = 3; or M = Fe, M′ = Sn, n = 2)



$$\pi\text{-}C_5H_5(CO)_nM\text{–}CH_2M'Me_3 + [\pi\text{-}C_5H_5(CO)_nM]^-Na^+ \rightarrow [\pi\text{-}C_5H_5(CO)_nMCH_2]^-Na^+ + \pi\text{-}C_5H_5(CO)_nMM'Me_3$$
$$[\pi\text{-}C_5H_5(CO)_nMCH_2]^-Na^+ \xrightarrow{THF} \pi\text{-}C_5H_5(CO)_nMCH_3 \quad (3)$$

The thermal stability of these compounds seems, in all cases, to be equal to or greater than that of the corresponding methyl compounds, and greater than that of higher alkyl homologues. For example, it has been noted[4] that $(\pi\text{-}C_5H_5)_2TiMe_2$ can spontaneously decompose upon attempted sublimation at 40° and even at 20° often decomposes to a black material within a few days[5], whereas the corresponding $(\pi\text{-}C_5H_5)_2Ti(CH_2SiMe_3)_2$ appears to be stable indefinitely at 20°. Also $\pi\text{-}C_5H_5(CO)_2FePr\text{-}i$ and $\pi\text{-}C_5H_5(CO)_3WPr\text{-}i$ decompose at or below 60° and attempted preparation of $\pi\text{-}C_5H_5(CO)_2FeBu\text{-}t$ gave only the corresponding hydride and isobutene[6], whereas $\pi\text{-}C_5H_5(CO)_3WCH_2SiMe_3$ was distilled in vacuo without appreciable loss. A β-hydrogen abstraction decomposition pathway has been shown to be the major decomposition route not only for the complexes $\pi\text{-}C_5H_5(CO)_2FeR$ and $\pi\text{-}C_5H_5(CO)_3MR$ (M = Mo or W, R = alkyl but not methyl) but also very recently for the analogous $(\pi\text{-}C_5H_5)_2TiPh_2$ complex[7].

The new ligands R^- appear to us to be of interest for the following reasons.

(a) σ-Alkyl (C_nH_{2n+1}, $n > 1$) transition metal complexes are often unstable because, with derivatives other than methyl, a β-hydrogen abstraction pathway (*e.g.* an olefin-producing elimination reaction) is available; this is not the case for LMR.

(b) Trimethylsilyl substitution at nitrogen has provided interesting transition metal chemistry: *e.g.* transition metal dimethylamides $M(NMe_2)_n$, in contrast to $M[N(SiMe_3)_2]_n$ analogues[8], are often polymeric or unstable; $Fe[N(SiMe_3)_2]_3$ is the first authenticated three-coordinate transition metal complex[9]. Since $N(SiMe_3)_2$ is isoelectronic and pseudo-isostructural with $CH(SiMe_3)_2$, Me_3Si substitution at the α-C promises similar rewards.

(c) Groups such as Me_3SiCH_2, when attached to carbon, are powerfully electron-releasing[10]. Their electronic effect upon a transition metal centre is of interest, especially when considered serially [*e.g.* in $LM{-}CH_2{-}SiMe_3$, $LM{-}CH(SiMe_3)_2$, and $LMC(SiMe_3)_3$; $LMCH_2SiMe_3$ and $LM'CH_2SiMe_3$; and $LMCH_2SiMe_3$, $LMCH_2GeMe_3$, and $LMCH_2SnMe_3$]; quantitative studies are in hand.

(d) Groups such as Me_3SiCH_2 may be electronically related to $PhCH_2$ from the standpoint of radical or carbanion stabilisation; *e.g.* the radical $(Me_3Si)_3C^{\cdot}$, which may be generated from $Hg[C(SiMe_3)_3]_2$, is relatively long-lived[11], comparable with but less stable than $Ph_3C^{\cdot}$. Such stabilisation, in addition to (a), may account for some recent developments in the chemistry of benzyl[12] and trityl[13] transition metal complexes.

(e) Ligands such as Me_3SiCH_2 are likely to confer solubility in non-polar media upon metal complexes. This may have a bearing on spectroscopic studies and on their use in homogeneous catalysis.

Consistent with (a)–(e) is the enhanced (for σ-alkyl complexes) thermal and chemical stability of the transition metal complexes LMR (*e.g.* $R = Me_3SiCH_2$). Additionally, it appears that unusual (for σ-alkyls) oxidation states (*e.g.* Nb^{IV}) or coordination numbers (*e.g.* the NiR_2 complex), and complexes free from "stabilising" ligands such as π-C_5H_5, CO, and Ph_3P (*e.g.* the ZrR_4 complexes) become accessible.

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