Participation of Neighbouring Transition-metal in the Nucleophilic C–Si Cleavage of π-$C_5H_5(CO)_3MoCH_2SiMe_3$: Possible Formation of an Anionic Transition-metal Carbene Intermediate

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Summary The formation of π-$C_5H_5(CO)_3M^1Me$ (M^1 = Mo or W), under mild conditions from $[\pi$-$C_5H_5(CO)_3M^1]^-Na^+$ and $Me_3M^2CH_2I$ (M^2 = Si or Sn), is shown to proceed *via* attack of $[\pi$-$C_5H_5(CO)_3M^1]^-$ upon π-$C_5H_5(CO)_3M^1CH_2$-M^2Me_3; the effect of the transition-metal in labilising the C–M^2 bond is attributed to the stability of $[\pi$-C_5H_5-$(CO)_3M^1CH_2]^-$.

RECENTLY a new class of σ-alkyl transition-metal complex has been described in which the organic ligand (R^-) may be regarded as a carbanion in which one or more α-H atom(s) has been replaced by an organometallic or t-alkyl fragment.[1] Most widely studied have been the trimethylsilylmethyl derivatives ($R = Me_3SiCH_2$).[1,2] Such complexes often have high (compared with normal σ-alkyls) thermal and chemical stability, *e.g.*, in ZrR_4[1] and CrR_4.[2]

We now report experiments which arose initially from an attempted synthesis of π-$C_5H_5(CO)_3Mo$–CH_2SiMe_3. The corresponding Mo–Me derivative is among the more common metal σ-alkyls.

The reaction between $[\pi$-$C_5H_5(CO)_3Mo]^-Na^+$ and Me_3SiCH_2I in tetrahydrofuran gave π-$C_5H_5(CO)_3Mo$–Me as the principal product and only a trace (*ca.* 5%) of π-$C_5H_5(CO)_3$-Mo–CH_2SiMe_3. The reaction was 90% complete (i.r.) after 5·5 h at 20°. Repeating the same experiment, but now with $Me_3SiCHDI$, afforded isotopically pure[3] (n.m.r.) π-$C_5H_5(CO)_3Mo$–CH_2D; thus, a methyl migration pathway to π-$C_5H_5(CO)_3Mo$–Me from π-$C_5H_5(CO)_3Mo$–CH_2SiMe_3 was excluded. It was next shown that π-$C_5H_5(CO)_3Mo$–CH_2SiMe_3 was a precursor of π-$C_5H_5(CO)_3Mo$–Me in this system (see Scheme) in that the latter compound was formed from the former by its reaction with $[\pi$-$C_5H_5(CO)_3$-$Mo]^-Na^+$. Thus the components (1) and (2) of the reaction scheme below were established by independent experiments, while (3)[4] and) (4)[5] have precedents.

Reaction (2) is remarkable in that the C–Si bond is cleaved under exceedingly mild conditions. Normally the C–Si bond is very stable and attack by nucleophiles under forcing conditions is only possible when strongly electron-withdrawing groups are attached to carbon.[6] As it is established that the group π-$C_5H_5(CO)_3Mo$–CH_2– is strongly electron-releasing,[7] it is clear that a new mechanism must apply. We suggest that the large neighbouring-group effect exercised by the transition-metal moiety in reaction (2) is explained by the significantly greater thermodynamic stability of the anion $[\pi$-$C_5H_5(CO)_3Mo$–$CH_2]^-$ compared with $[H$–$CH_2]^-$. Such stabilisation could arise from extensive delocalisation of charge in $[\pi$-$C_5H_5(CO)_3Mo$–$CH_2]^-$; which thus has more the character of an anionic transition-metal carbene complex than of a carbanion. Complementary cationic carbene complexes have been invoked.[8,9]

The intervention of an anionic carbene complex may similarly account for the formation[8] in low yield of π-C_5H_5-$(CO)_3W$–CH_2Me from $[\pi$-$C_5H_5(CO)_3W]^-Na^+$ and MeCHClO-Me. Another consequence of our postulate is the prediction that the removal of an α-proton from other transition-metal σ-alkyls is relatively simple, *i.e.*, that the compounds have significant Brønsted acidity.

C–Si or C–Sn cleavage reactions under similarly mild reaction conditions have been observed *inter alia* in the following systems: $[\pi$-$C_5H_5(CO)_3W]^-Na^+/Me_3SiCH_2I$, $[\pi$-$C_5H_5(CO_3)Mo]^-Na^+/Me_3SnCH_2I$ and $[\pi$-$C_5H_5(CO)_2Fe]^-$-Na^+/Me_3SnCH_2I. Relative proportions in these reactions of the metal-CH_2MMe_3 (M = Si or Sn) and metal–Me products may in part be related to variations[10] in the nucleophilicities of the appropriate transition-metal anions.

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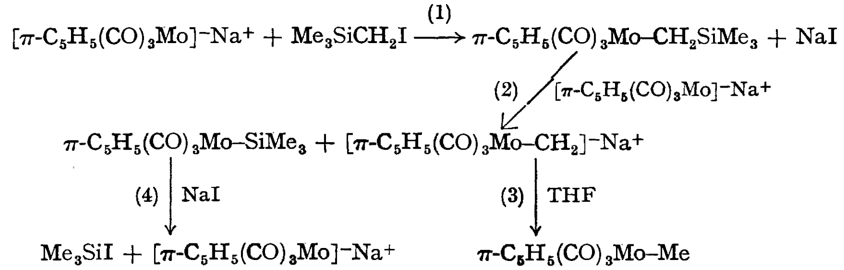

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