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Preliminary communication

Oxidative cleavage of the metal-metal bond of bi- or poly-nuclear carbonyl complexes by cyclopentadienyl(trimethyl)stannane

E.W. ABEL, S.A. KEPPIE, M.F. LAPPERT, and S. MOORHOUSE

Department of Inorganic Chemistry, The University, Bristol (E.W.A. and S.M.), *and The School of Molecular Sciences, University of Sussex, Brighton, BN1 9QJ*(S.A.K. and M.F.L.), *(Great Britain)*

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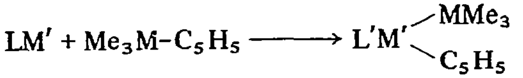
We wish to draw attention to the high reactivity of cyclopentadienyl(trimethyl)metallanes of the Group IVB elements $Me_3M-C_5H_5$ with respect to appropriate transition metal substrates. At present, there appear to be three classes of reaction. Those of Class (I) (oxidative addition) are reactions in which the Group IVB compound adds oxidatively to a single transition metal centre; they have been recognised previously[1], and illustration is provided by Eq. 1. Reactions of Class (II) (oxidative cleavage) are those in which the Me_3M and C_5H_5 fragments become attached to different metal sites; they form the essence of this communication, and illustration is provided by Eq. 2. While reactions of Classes (I) and (II) involve cleavage of the $M-C_5H_5$ bond, the integrity of the Group IVB molecule is maintained in reactions of Class (III); such ligand behaviour is particularly characteristic[2] of $Me_3SiC_5H_5$ (see Eq. 3). In Eqs. 1-3, M = Si, Ge, or Sn; M′ is a transition metal; and L, L′, and L″ represent the remaining ligands attached to M′.



$$LM' + Me_3M-C_5H_5 \longrightarrow L'M'\begin{matrix}\nearrow MMe_3\\ \searrow C_5H_5\end{matrix} \qquad (1)$$

$$LM'-M'L + Me_3M-C_5H_5 \longrightarrow L'M'-C_5H_5 + L''M'-MMe_3 \qquad (2)$$

$$LM' + Me_3M-C_5H_5 \longrightarrow \pi\text{-}Me_3MC_5H_4-M'L' \qquad (3)$$

Oxidative metal-metal bond cleavage is not a new reaction; for example, the halogens act in that sense, as in [3]: $Mn_2(CO)_{10} + Br_2 \rightarrow 2BrMn(CO)_5$. However, such organometallic oxidative addition is novel and provides a new[4] method for making compounds having metal-metal bonds, *e.g.* $L''M'-MMe_3$.
Representative examples are provided by (a) Eqs. 4 and 5, and (b) Table 1.

$$Mn_2(CO)_{10} + Me_3Sn-C_5H_5 \rightarrow \pi\text{-}C_5H_5Mn(CO)_3 + Me_3Sn-Mn(CO)_5 \qquad (4)$$

$$Co_2(CO)_8 + Me_3Sn-C_5H_5 \rightarrow \pi\text{-}C_5H_5Co(CO)_2 + Me_3Sn-Co(CO)_4 \qquad (5)$$

TABLE 1

REACTIONS WITH $Me_3SnC_5H_5$

Metal carbonyl	Reaction conditions[a]	Products	yield %
$Mn_2(CO)_{10}$	Reflux (4 h) in diglyme; ch. on Florisil (n-C_5H_{12})	π-$C_5H_5Mn(CO)_3$ $Me_3SnMn(CO)_5$	54 58
$Re_2(CO)_{10}$[b]	Reflux at 220°; ch. on Florisil (n-C_5H_{12})	π-$C_5H_5Re(CO)_3$ $Me_3SnRe(CO)_5$	41 38
$Fe_2(CO)_9$	Heat (2 h) in THF at 50°; ch. on Al_2O_3 (n-C_6H_{14})	$(\pi$-$C_5H_5)_2Fe$ $(Me_3Sn)_2Fe(CO)_4$ $[Me_2SnFe(CO)_4]_2$	c
$Fe_3(CO)_{12}$	Reflux (¼−4 h in THF; ch. on Al_2O_3 (n-C_6H_{14})	$(\pi$-$C_5H_5)_2Fe$ $[Me_2SnFe(CO)_4]_2$	c
$Co_2(CO)_8$	In THF or $(C_2H_5)_2O$ at 20°; ch. on Al_2O_3 or Florisil (n-C_5H_{12} or n-C_6H_{14})	π-$C_5H_5Co(CO)_2$ $Me_3SnCo(CO)_4$	46 41
$[\pi$-$C_5H_5(CO)_3Mo]_2$[d]	Reflux (3½ h) in diglyme	π-$C_5H_5(CO)_3MoSnMe_3$	
$[\pi$-$C_5H_5(CO)_2Fe]_2$	Reflux (3 h) in diglyme; ch. on Florisil (n-C_5H_{12})	$(\pi$-$C_5H_5)_2Fe$ π-$C_5H_5(CO)_2FeSnMe_3$	33 38
$[\pi$-$C_5H_5(CO)Ni]_2$	Reflux (1½ h) in diglyme; ch. on Florisil (n-C_5H_{12})	$(\pi$-$C_5H_5)_2Ni$ π-$C_5H_5(CO)NiSnMe_3$	26 15

[a] ch. = chromatographic separation; [b] π-$(Me_3SnC_5H_4)Re(CO)_3$ (44%) also isolated[2]; [c] Yields variable (see discussion); [d] Spectroscopic identification of reaction course, only.

Reactions were conducted in a nitrogen atmosphere, using degassed solvents, and were followed spectroscopically by observing the carbonyl stretching region (x 2.5 expansion) in the infrared region.

Product separation has often proved difficult; column chromatography or fractional sublimation were the usual procedures. The problem was sometimes circumvented by using the phenyl Group IVB compound $Ph_3Sn-C_5H_5$; in this case, more forcing reaction conditions were required but the reduced volatility of $L''M'-SnPh_3$ compared with $L''M'-SnMe_3$ was used to advantage. The conversions represented by Eq. (2) are undoubtedly (IR and NMR) essentially quantitative, but separation difficulties and the thermal sensitivity of products led to isolation of only quite small quantities of products in some cases. With $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and $[\pi$-$C_5H_5(CO)Ni]_2$ there was particularly serious product decomposition during work-up.

The reactions of the iron carbonyls [also $Fe(CO)_5$] are more complex. With $Fe_2(CO)_9$, the primary reaction path appeared to be (IR and NMR) that of Eq. 6. One important product decomposition route is that of Eq. 7[5].

$$Fe_2(CO)_9 + 2Me_3Sn-C_5H_5 \rightarrow (Me_3Sn)_2Fe(CO)_4 + (\pi\text{-}C_5H_5)_2Fe + 5CO \quad (6)$$

$$2(Me_3Sn)_2Fe(CO)_4 \rightarrow [Me_2SnFe(CO)_4]_2 + 2Me_4Sn \quad (7)$$

The relative reactivities of the transition metal substrates towards $Me_3SnC_5H_5$ appear to decrease in the series $Co_2(CO)_8 >> [\pi\text{-}C_5H_5(CO)Ni]_2 \sim$ Fe carbonyls $> [\pi\text{-}C_5H_5(CO)_2Fe]_2 > [\pi\text{-}C_5H_5(CO)_3Mo]_2 \sim Mn_2(CO)_{10} >> Re_2(CO)_{10}$.

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