Metal–Metal and Metal–Halogen Bond Cleavage by Lanthanide and Related Metals

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Summary Finely-divided lanthanide and other metals react with substrates such as $Mn(CO)_5Br$, h^3-$C_3H_5Fe(CO)_3I$, $[h^5$-$C_5H_5Mo(CO)_3]_2$, and h^5-$C_5H_5Cr(CO)_3HgCl$ in THF to yield reactive solutions which can be utilized as reagents for the synthesis of various organometallic compounds.

Our previous investigations[1] revealed that the metal sites in organolanthanides can act as Lewis acids towards bases such as bridging and terminal carbonyl ligands, terminal nitrosyl ligands, appropriate transition metals, and some C–C triple bonds. We now report that another synthetic route to compounds containing apparent lanthanide–transition metal bonds involves the reaction of finely-divided lanthanide metals with organometallic compounds possessing cleavable metal–metal or metal–halogen bonds. Thus, in a manner analogous to magnesium,[2] metals such as Y, Pr, Sm, Dy, Ho, Er, and Yb react with 0·1 M $Mn(CO)_5Br$ in THF under ambient conditions to produce red, air- and moisture-sensitive solutions. We tentatively formulate that these solutions contain the complexes "$[Mn(CO)_5]_x$-$LnBr_y$" (where x and y are integers such that $x + y = 2$ or 3 depending upon the lanthanide involved) which coexist with each other in a Grignard-type equilibrium.

The red solutions [which can also be generated in the case of Yb by reacting the metal with $Mn_2(CO)_{10}$ and $(CH_2Br)_2$ in refluxing THF for 24 h] are electrically conducting, but the extent of ionization is apparently slight since attempts to isolate any carbonyl anions with $[Ph_3P]_2NCl$ are unsuccessful. The solutions exhibit absorptions in the ν_{CO}-region of their i.r. spectra at 2045(s), 2000(vs), 1962(vs), 1950(sh), 1928(m), 1880(m), and 1855(m) cm^{-1} with the intensities of the higher frequency bands increasing upon dilution. The absence of a carbonyl absorption at a lower frequency rules out the possibility of a direct linkage between the lanthanides and a carbonyl oxygen atom of the $Mn(CO)_5$ species. Further, the u.v. spectrum of the Yb complex in THF shows a weak band at 10,250 cm^{-1} which can be assigned to a $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition[3] and is indicative of at least a part of the lanthanide being in a +3 oxidation state. Further evidence for this valence state is provided by the isolation of $[Mn(CO)_5]_2Ho(C_5H_7O_2)\cdot 2Et_2O$ after the corresponding red solution has been treated with an equimolar quantity of $NaC_5H_7O_2$ and worked up in Et_2O.

The Grignard-type solutions undergo a variety of other reactions. Treatment with an equimolar amount of Ph_3SnCl at room temperature affords $Ph_3SnMn(CO)_5$ in good yield. Methylation by MeI, on the other hand, requires refluxing overnight and the yield of $MeMn(CO)_5$ is low. Reaction with an equimolar quantity of PhCOCl at 65 °C for 2 h does not lead to the expected benzoyl derivative, $PhCOMn(CO)_5$, but instead the solvent is cleaved and the principal organic product obtained is $PhC(O)O(CH_2)_4Cl$ along with some $Mn_2(CO)_{10}$ which is usually a by-product in the described conversions. [The observed cleavage of the solvent is not without precedent in such reactions,[4,5] especially in view of the known acid character of the lanthanides.] Addition of bases such as 2,2′-bipyridyl (overnight), *o*-phenanthroline (overnight), and triphenylphosphine (20 min) at room temperature and in the absence of light produces the substituted carbonyl derivatives $Mn_2(CO)_8L_2$ (where L_2 = two monodentate ligands or one bidentate ligand) in fair yields. These experimental conditions are milder than those previously employed for the preparation of these complexes.[6] Finally, nitrosylation with *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide ("Diazald") proceeds smoothly at 10 °C and affords $Mn(CO)_4NO$. The red solutions do not, however, react with CO, H_2, C_5H_6, or simple olefins under ambient conditions.

In order to survey the extent of the bond cleavage reactions, we have also carried out preliminary studies utilizing lanthanides and other metals in conjunction with several organometallic substrates. For example, in the case of manganese, a red THF solution whose i.r. spectrum in the carbonyl region and reactivity are identical to that of the lanthanide systems can be prepared in any of the following ways: (a) Mn + $Mn(CO)_5Br$ (2—3 days, room temp.) (b) Mn + $Mn_2(CO)_{10}$ + $(CH_2Br)_2$ (overnight, reflux), (c) $MnCl_2$ + $Mn_2(CO)_{10}$ (2—3 days, reflux), and (d) $NaMn(CO)_5$ + $MnCl_2$ (overnight, room temp.) Further, i.r. spectroscopy indicates that Sn and Fe also afford some insertion products with $Mn(CO)_5Br$.

In a similar manner, h^3-$C_3H_5Fe(CO)_3I$ reacts very rapidly with Yb, Sm, Y, or Mn in THF to produce an air-sensitive mauve solution. The formation of this reactive species can be monitored by i.r. spectroscopy, and by comparison with a valid sample it appears that the mauve solution contains the equilibrium:[7]

$$2\ h^3\text{-}C_3H_5\dot{F}e(CO)_3 \rightleftharpoons [h^3\text{-}C_3H_5Fe(CO)_3]_2.$$

At room temperature, this solution instantly reacts with "Diazald" to give h^3-$C_3H_5Fe(CO)_2NO$ (55%) and with Ph_3P to give a green solid which is not h^3-$C_3H_5Fe(CO)_2[PPh_3]I$. [The exact nature of this latter compound remains to be ascertained.] In contrast, the metal carbonyl halides h^5-$C_5H_5Fe(CO)_2X$ [X = Cl or I] only form $[h_5$-C_5H_5Fe-

$(CO_2]_2$ and no Grignard-type product when treated with Yb or Sm.

The metal–metal bond in $[h^5\text{-}C_5H_5Mo(CO)_3]_2$ can be cleaved by Yb while refluxing in THF for 24 h either in the presence or absence of $(CH_2Br)_2$. Derivatives such as $h^5\text{-}C_5H_5Mo(CO)_3H$, $h^5\text{-}C_5H_5Mo(CO)_3I$, and $h^5\text{-}C_5H_5Mo(CO)_2NO$ are then obtained within minutes and in good yields upon reaction of the resultant brown solution at 25 °C with H_2O, I_2, or "Diazald" respectively.

It has been previously reported[2] that Mg undergoes metal exchange with Hg in RHgX [R = $Mn(CO)_5$ or $Co(CO)_4$] to form the corresponding "RMgX" reagents. Similarly, Yb instantly displaces Hg from $h^5\text{-}C_5H_5Cr(CO)_3HgCl$ in THF at room temperature. The brown-green solution thus formed contains at least two carbonyl-bearing compounds. One can be isolated and identified as $[h^5\text{-}C_5H_5Cr(CO)_3]_2$; the other is probably the reactive reagent $[h^5\text{-}C_5H_5Cr(CO)_3]_y\text{-}YbCl$ ($y = 1$ or 2) whose mull i.r. spectrum exhibits ν_{CO} at 2010(s), 1920(s), 1805(s), and 1670(s) thereby suggesting the presence of isocarbonyl linkages. Treatment of the Yb-containing entity with an equimolar quantity of Ph_3SnCl at 55 °C for 1 h yields the expected $Ph_3SnCr(CO)_3(h^5\text{-}C_5H_5)$. PhHgCl, on the other hand, reacts with Yb in THF at 25 °C to produce Ph_2Hg and no displacement is apparent.

Further studies concerning the reactions of organometallic compounds with metals and the considerable synthetic utility of the resultant complexes are currently in progress.

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[1] A. E. Crease and P. Legzdins, *J.C.S. Chem. Comm.*, 1972, 268; *J.C.S. Dalton*, 1973, 1501.
[2] J. M. Burlitch and S. W. Ulmer, *J. Organometallic Chem.*, 1969, **19**, P21.
[3] F. Calderazzo, R. Pappalardo, and S. Losi, *J. Inorg. Nuclear Chem.*, 1966, **28**, 987.
[4] M. S. Kharasch and O. Reinmuth, 'Grignard Reactions of Nonmetallic Substances,' Prentice-Hall, New York, 1954, ch. V.
[5] D. L. Manson and O. C. Musgrave, *J. Chem. Soc.*, 1963, 1011.
[6] W. Hieber and W. Schropp, jun., *Z. Naturforsch*, 1960, **15b**, 271; A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 1964, 634; W. Hieber, W. Beck, and G. Zeitler, *Angew. Chem.*, 1961, **73**, 364.
[7] H. D. Murdoch and E. A. C. Lucken, *Helv. Chim. Acta*, 1964, **47**, 1517.