Derivatives of Tricarbonylmetallates(−III) of Cobalt, Rhodium, and Iridium

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Summary Reduction of $[Co(CO)_4]^-$ or $[M(CO)_3]_4$ (M = Rh and Ir) with sodium in liquid ammonia, naphthalene–tetrahydrofuran, or hexamethylphosphoramide (only M = Rh and Ir) gives pyrophoric substances which provide the first main group 4 derivatives of $[M(CO)_3]^{3-}$ (M = Co, Rh, and Ir) in 20—90% yields.

RECENTLY, the first examples of noncluster binary metal carbonyl trianions, $[M(CO)_4]^{3-}$ (M = Mn and Re),[1] as well as a highly reduced vanadium carbonyl anion[2] have been prepared. We now report the synthesis of highly reduced cobalt, rhodium, and iridium carbonyls which have chemical and physical properties consistent with those expected for the previously unknown tricarbonylmetallate trianions, $[M(CO)_3]^{3-}$, of these metals.

Treatment of $Na[Co(CO)_4]$ with 3 equiv. of sodium metal in liquid ammonia at −78 °C provides after 8 h an exceedingly oxygen- and moisture-sensitive orange-red precipitate (I) which exhibits only two broad carbonyl stretching frequencies, at strikingly low energy [mineral oil mull, ν(CO): 1744m and 1600vs cm^{-1}]. Although attempts to obtain this material by reduction of $Na[Co(CO)_4]$ with sodium in hexamethylphosphoramide (HMPA) have been unsuccessful (no apparent reduction after 6—12 h at room temperature), analogous reductions by naphthalene–sodium in tetrahydrofuran (THF)[4] proceed slowly (40—48 h) to provide an insoluble brown solid whose i.r. spectrum (mull) in the carbonyl region and chemical reactions (*vide infra*) are identical to those of (I). Even after reduction for 2 days, substantial amounts of unchanged $Na[Co(CO)_4]$ remain in the THF. However, this naphthalene–sodium method is important in that it provides (I) free of strong base, in contrast to the product generated in liquid ammonia.†

New five-co-ordinate anionic complexes‡ were obtained in good yield (40—90%) based on $Co_2(CO)_8$ by the reaction of (I) with various main group 4 halides. For example, treatment of (I) with Ph_3ECl (E = Ge, Sn, or Pb) (⩾ 2 equiv.) provided colourless or yellow (E = Pb), air- and moisture-stable anions $[(Ph_3E)_2Co(CO)_3]^-$ isolated as their crystalline tetraethylammonium salts. These anions are analogous to the previously known cations $[(Ph_3Y)_2Co(CO)_3]^+$ (Y = P, As, or Sb).[3] I.r. solution spectra of $[Et_4N][(Ph_3E)_2Co(CO)_3]$ show only one band in the ν(CO) region (*e.g.*, E = Pb: 1915vs cm^{-1}, in THF) and are consistent with molecules of D_{3h} symmetry.

Reduction of $[M(CO)_3]_4$ (M = Rh and Ir) by sodium metal in liquid ammonia and naphthalene–THF proceeds more rapidly than that of $[Co(CO)_4]^-$; for example, within 1 h the blue colour of the sodium is completely discharged. Also, unlike $[Co(CO)_4]^-$, these tetrameric clusters are reduced by sodium in HMPA and sodium–αα′-bipyridyl in THF to provide very similar brown pyrophoric substances (II, M = Rh; III, M = Ir). These give mineral oil mull i.r. spectra in the carbonyl stretching frequency region which are nearly superimposable with that of (I) [(II), 1735m and 1598vs br; (III), 1744m and 1615vs br cm^{-1}]. By monitoring the reduction of $[M(CO)_3]_4$ in HMPA and THF by i.r. spectroscopy, it has been established that destruction of the cluster is essentially complete. Before (II) and (III) precipitate from solution, the soluble Rh and Ir carbonyls are almost completely in the form $[M(CO)_4]^-$. Previously, it has been established that $[M(CO)_4]^-$ (M = Rh[5] and Ir[6]) ions are formed in the reduction with sodium metal of $[M_4(CO)_{12}]$ in THF. Subsequent reduction of $[M(CO)_4]^-$ (M = Rh and Ir) provides (II) and (III).

Treatment of (II) and (III) with Ph_3ECl (E = Ge or Sn) (⩾ 2 equiv.) provides white to pale brown crystalline and air-stable $[Et_4N][(Ph_3E)_2M(CO)_3]$ (E = Ge or Sn; M = Rh or Ir) in 20—40% yields, based on $[M(CO)_3]_4$. I.r. spectra of these five-co-ordinate main group 4 complexes of Rh and Ir are very similar to those of the cobalt analogues which suggest that all these anions are isostructural [*e.g.*, ν(CO) in THF for E = Sn, M = Rh: 1937vs; E = Sn, M = Ir: 1923vs cm^{-1}].

Further characterization of (I)—(III) has been thwarted by their extreme air-sensitivity and insolubility in non-

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† $Na_3[M(CO)_4]$ (M = Mn and Re) (ref. 1) are also obtained in good yields from the Na–naphthalene reduction of $Na[M(CO)_5]$ in THF.

‡ Satisfactory analytical data were obtained for all new derivatives.

reactive solvents. The high yields of derivatives of $[Co(CO)_3]^{3-}$ obtained from (I) strongly suggest that this material is a monomeric carbonyl species. Also, since the i.r. spectra of (I)—(III) are nearly superimposable it is likely that these highly reduced carbonyls are homologous.

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