The Tetracarbonyl Trianions of Manganese and Rhenium, $M(CO)_4^{3-}$

By John E. Ellis* and Robert A. Faltynek

(*Department of Chemistry, University of Minnesota, Minneapolis, Minnesota* 55455)

Summary Alkali metal reduction of $M_2(CO)_{10}$ or $M(CO)_5^-$ (M = Mn and Re) in hexamethylphosphoramide provides the first non-cluster binary metal carbonyl trianions, $M(CO)_4^{3-}$, which are characterized by their spectral and chemical properties.

Hexamethylphosphoramide (HMPA) has been found recently to be an unusually effective medium for the generation of mononuclear metal carbonyl anions including $M(CO)_5^{2-}$ (M = Cr, Mo, W).[1] We now report on the synthesis in this medium of $M(CO)_4^{3-}$ (M = Mn and Re), the first examples of non-cluster binary metal carbonyl trianions.[2] $Re(CO)_4^{3-}$ is also the first compound containing rhenium in a formal −3 oxidation state.† The salts are formulated as $[Na(HMPA)_x]_3M(CO)_4$ (I) on the basis of their spectral and chemical properties and are produced in high yield by sodium metal reduction of the corresponding $M_2(CO)_{10}$ or $NaM(CO)_5$ compounds in HMPA at room temperature. They may be isolated as exceedingly air- and moisture-sensitive tan solids by treatment of the HMPA solutions with excess of light petroleum. Attempts to remove all co-ordinated HMPA from (I) or to prepare the trianions in other solvents, including liquid ammonia, have been unsuccessful. The i.r. spectrum of (I), (M = Mn) in HMPA (1805 w, 1670 vs, br cm^{-1}) is nearly identical to that of the rhenium analogue (1825, 1690 vs, br cm^{-1}) and strongly resembles those of other isoelectronic members, $Fe(CO)_4^{2-}$ to $Ni(CO)_4$, by virtue of its single strong absorption in the carbonyl stretching frequency region which is expected for a tetrahedral anion. The splitting of this band observed for (I) in HMPA (or as a mineral oil mull, which gives very similar spectra) is like splittings of corresponding bands for $NaCo(CO)_4$ in THF (1883 vs, 1861 m cm^{-1})[3] and $Na_2M'(CO)_4$ (M' = Fe, Ru, Os) in HMPA (*e.g.*, M' = Ru: 1778 w, 1734 vs cm^{-1}).[4] The latter species are conveniently generated in high yield by sodium metal reduction of $M'_3(CO)_{12}$ in HMPA.[4]

Treatment of HMPA solutions of (I) with Ph_3ECl (E = Ge, Sn, Pb) or Ph_3PAuCl provide colourless, air and moisture stable salts $(Ph_3E)_2M(CO)_4^-$, or gold, seven-co-ordinate molecular $(Ph_3PAu)_3M(CO)_4$, respectively, in yields up to 90% based on $M_2(CO)_{10}$.‡ I.r. spectra of isolated tetraethylammonium salts of the ionic derivatives are consistent with the formation of *cis*-$(Ph_3E)_2M(CO)_4^-$ (E = Sn, Pb) and

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† The only previously known compound in which manganese has a formal oxidation state of −3 is $Mn(NO)_3CO$, see F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Wiley, 1972, p. 845.

‡ Satisfactory analytical data were obtained for all new derivatives.

trans-$(Ph_3Ge)_2M(CO)_4^-$. For example, the mineral oil mull spectrum of $[Et_4N][(Ph_3Sn)_2Re(CO)_4]$ in the ν(CO) region shows four well resolved bands (2032 m, 1960 m, 1932 s, and 1910 vs cm^{-1}); in THF solution three absorptions are observed (2042 s, 1957 vs, and 1922 s cm^{-1}), one of which (1957 cm^{-1}) is rather broad and may consist of two unresolved bands. Corresponding spectra of the *cis*-substituted manganese derivatives show similar features but have absorptions at lower energy (*e.g.*, $[Et_4N][(Ph_3Sn)_2Mn(CO)_4]$ in THF; ν(CO) 2000 s, 1922 sh, and 1913 vs cm^{-1}). Similar three-band patterns of *cis*-disubstituted metal tetracarbonyls have been reported previously (*e.g.*, $Fe(CO)_4I_2$ in $CHCl_3$ and $Fe(CO)_4(AuPPh_3)_2$ in CCl_4).[5] I.r. spectral evidence indicates that reactions of (I) with Ph_3GeCl give mixtures of *cis*- and *trans*-isomers; however, thus far only the pure *trans*-$(Ph_3Ge)_2M(CO)_4^-$ have been isolated (as Et_4N^+ salts) in *ca.* 30% yields. These show a single strong absorption in THF in the ν(CO) region (Mn, 1906 cm^{-1}; Re, 1922 cm^{-1}). The apparent preference of the Ph_3Ge group to form *trans*-isomers in these reactions is not understood, particularly since steric factors have been found to be relatively unimportant in determining the stereochemistry of similar disubstituted neutral compounds of Fe, Ru, and Os.[6] Indeed, in contrast to our results, the isoelectronic $(Ph_3Sn)_2M'(CO)_4$ (M' = Ru, Os) have been isolated as *trans*-isomers, whilst, $(Ph_3Sn)_2Fe(CO)_4$ is of *cis*-configuration.[6,7] While $(Ph_3E)_2M(CO)_4^-$ are apparently unable to add a third Ph_3E^+ unit, neutral gold derivatives of stoicheiometry $(Ph_3PAu)_3M(CO)_4$ are readily formed. The ability of the triphenylphosphine gold unit to stabilize organotransition metal species in high co-ordination numbers relative to those of the triphenylmetal groups is well established (*e.g.*, $Ph_3PAuV(CO)_6$ is significantly more thermally and solvolytically stable than $Ph_3SnV(CO)_6$[8]) and particularly evident in these examples. Mineral oil mull spectra of $(Ph_3PAu)_3M(CO)_4$ are very similar, except the Re band positions occur at higher energy (Mn 1948 m, 1878 sh, 1871 vs, and 1860 vs cm^{-1}; Re, 1989 m, 1908 sh, 1901 vs, and 1878 s cm^{-1}).

Other chemical properties of (I) such as their behaviour on protonation and their suitability as transition metal carbyne precursors are under investigation. The high yields of many of the above derivatives are consistent with the presence of carbonyl trianions in (I) and rule out an alternative formulation involving species such as $M_2(CO)_8^{4-}$, which are believed to form on oxidation of the monomeric trianions. A possible alternative formulation of (I) involving $HM(CO)_4^{2-}$, which should have reactivity patterns similar to those of $M(CO)_4^{3-}$, is considered less likely in that the ^1H n.m.r. spectrum of (I) in $[^2H_{18}]$-HMPA was shown to have no signal due to a metal hydride. The extreme air sensitivity of (I) has prevented attempts to obtain conductivity data on these species.

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