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Photoinduced Substitution and Oxidative Addition Reactions of Pentacarbonylmanganese(−1) and Tetracarbonyl(triphenylphosphine)manganese(−1)

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Abstract: Photoinduced substitution and oxidative addition reactions of Mn(CO)₅⁻ and Mn(CO)₄PPh₃⁻ in tetrahydrofuran solutions are reported. Irradiation of Mn(CO)₅⁻ as the bis(triphenylphosphine)iminium salt results in chemistry reflecting the intermediacy of Mn(CO)₄⁻ or Mn(CO)₄(solvent)⁻. In the presence of PPh₃ or P(OMe)₃ the primary product is Mn(CO)₄-PPh₃⁻ or Mn(CO)₄(P(OMe)₃)⁻, respectively. This photosubstitution chemistry is efficient chemically and with respect to quanta of light absorbed. Near-UV quantum yields exceed 0.2 for the process (254, 313, 366 nm). The Mn(CO)₄(P(OMe)₃)⁻ appears to undergo further substitution upon irradiation, but the products were not characterized. However, Mn(CO)₄PPh₃⁻ undergoes photoreactions reflecting the loss of PPh₃, not CO, upon photoexcitation. Photolysis of Mn(CO)₅⁻ in the presence of HSiPh₃ or Ph₃SnSnPh₃ results in high chemical yields of the oxidative addition products *cis*-HMn(CO)₄SiPh₃⁻ and *cis*-Mn(CO)₄(SnPh₃)₂⁻, respectively. Irradiation of Mn(CO)₅⁻ as the Ph₄E⁺ salt (E = P, As) results in the formation of *cis*-PhMn(CO)₄EPh₃. Irradiation of Ph₃MeP[Mn(CO)₅] results in the formation of *cis*-PhMn(CO)₄PPh₂Me as the only oxidative addition product. Competition between oxidative addition of Ph₄P⁺ and substitution by PPh₃ suggests an important role for ion pairing in the oxidative addition of the cation.

Photoinduced substitution and oxidative addition reactions of metal carbonyls are numerous[2-4] and are important in the preparation of new derivatives and are likely important in photocatalyzed reactions of olefins.[4-9] We have undertaken a study directed toward the comparison of the reactivity of intermediates resulting from irradiation of neutral and anionic isoelectronic metal carbonyls. The hope is that a coordinatively unsaturated metal carbonyl anion will participate in unusual

Table I. Infrared Data for Relevant Complexes[a]

Complex	Bands, cm^{-1} (ϵ)
Fe(CO)$_4$PPh$_3$[b]	2054 (3500); 1978 (2300); 1942 (4900)
PPN[Mn(CO)$_5$]	1893 (5240); 1860 (7970)
Ph$_4$P[Mn(CO)$_5$]	1896 (5800); 1862 (8920)
Fe(CO)$_5$[b]	2025 (5470); 2000 (11 830)
PPN[Mn(CO)$_4$PPh$_3$]	1941 (3460); 1846 (1800); 1815 (6420)
Ph$_4$P[Mn(CO)$_4$PPh$_3$]	1940 (4230); 1846 (2370); 1815 (7920)
PPN[Mn(CO)$_4$P(OMe)$_3$]	1954 (2000); 1858 (2600); 1823 (7500)
PPN[Mn(CO)$_3$(P(OMe)$_3$)$_2$]	1788 (5400)
PPN[Mn(CO)$_4$(SnPh$_3$)$_2$]	1997 (3120); 1921 (sh, ~3100); 1908 (5280)
PPN[HMn(CO)$_4$(SiPh$_3$)]	2002 (1460); 1905 (5210); 1890 (3920)
PhMn(CO)$_4$PPh$_3$	2064 (2160); 1986 (2220); 1973 (3940); 1950 (2460)
PhMn(CO)$_4$AsPh$_3$	2060 (1510); 1975 (2700); 1967 (3900); 1951 (3350)
PhMn(CO)$_4$PPh$_2$Me	2063 (1230); 1988 (1380); 1969 (2370); 1947 (1650)
MeMn(CO)$_4$PPh$_3$	2056 (1800); 1974 (sh, ~3200); 1967 (4500); 1934 (2400)

[a] THF solutions at 298 K. [b] Reference 6b in isooctane.

oxidative addition reactions, owing to the increased electron density on the metal compared to a neutral electronic analogue.

Photoinduced dissociative loss of CO from mononuclear metal carbonyls is a common result,[2-4] and even certain metal carbonyl anions have been shown to undergo facile CO photosubstitution. The most well-studied[10-12] anions are M(CO)$_6^-$ (M = V, Nb, Ta), but it does appear that Mn(CO)$_5^-$ undergoes photosubstitution as well.[13] In this paper we wish to report a detailed study of the photochemistry of Mn(CO)$_5^-$. Aside from the usual photosubstitution and oxidative addition of neutral substrates, we find that certain cations can be oxidatively added to the photogenerated intermediates to yield neutral metal carbonyl products. This photochemistry has no precedent in studies of neutral metal carbonyls.

Results and Discussion

Photosubstitution of Mn(CO)$_5^-$ and Mn(CO)$_4$PPh$_3^-$. Except for the expected shift to lower energy,[14] the CO stretching absorptions for the anionic Mn(CO)$_{5-n}$(PPh$_3$)$_n^-$ (n = 0, 1) species are very similar to the neutral Fe electronic analogues (Table I). We adopt a ligand field assignment for the lowest absorption features (Table II) in these d^8 anionic systems, following the assignment for Fe(CO)$_5$.[15] Since the ligand field transitions terminate in the d$_{z2}$ (σ^*) orbital, the excited species should be more substitution labile than the ground electronic state.[16] We find that UV irradiation of either Mn(CO)$_5^-$ or Mn(CO)$_4$PPh$_3^-$ results in photosubstitution. For Mn(CO)$_5^-$ the primary photochemical step is apparently the reaction

$$\text{Mn(CO)}_5^- \xrightarrow{h\nu} \text{Mn(CO)}_4^- + \text{CO} \qquad (1)$$
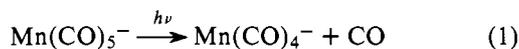
the dissociative loss of CO. In the presence of P(OMe)$_3$ or PPh$_3$ the Mn(CO)$_4$(P(OMe)$_3$)$^-$ or Mn(CO)$_4$PPh$_3^-$, respectively, species can be generated in good yield. The quantum yield for reaction 1 is high. Values of 0.31 (366 nm), 0.23 (313 nm), and 0.70 (254 nm) were obtained for the disappearance of Mn(CO)$_5^-$ as the bis(triphenylphosphine)iminium (PPN$^+$) salt in a degassed THF solution of 0.1 M P(OMe)$_3$. The error limits on these quantum yields are rather high (±25%), owing to the air sensitivity of the solutions of starting materials and

Table II. UV–Vis Data for Relevant Complexes

Complex	Bands, nm (ϵ)
Fe(CO)$_5$[a]	~280 (3800); ~250 (40 000)
PPN[Mn(CO)$_5$][b]	295 (5250)
Ph$_4$P[Mn(CO)$_5$][b]	291 (4700)
Ph$_4$P[Mn(CO)$_4$PPh$_3$][b]	306 (5020); 295 (sh, ~4700)

[a] Reference 15. [b] THF solutions, 298 K.

products. However, it is clear that Mn(CO)$_5^-$, with respect to the efficiency of CO loss, is like most, e.g., Fe(CO)$_5$, mononuclear metal carbonyls.[2-4]

Irradiation of PPN[Mn(CO)$_4$PPh$_3$] in the presence of PPh$_3$ in THF solution does not lead to any rapid chemical changes. Specifically, the generation of Mn(CO)$_3$(PPh$_3$)$_2^-$ is not found. This is in contrast to the photochemistry of the neutral analogue, Fe(CO)$_4$PPh$_3$, which gives Fe(CO)$_3$(PPh$_3$)$_2$ upon irradiation in the presence of PPh$_3$; Φ_{366nm} = 0.3.[17] Irradiation of Mn(CO)$_4$(PPh$_3$)$^-$ in the presence of P(OMe)$_3$ proceeds initially according to the reaction

$$\text{Mn(CO)}_4\text{PPh}_3^- \xrightarrow[\text{P(OMe)}_3]{h\nu} \text{Mn(CO)}_4\text{P(OMe)}_3^- + \text{PPh}_3 \qquad (2)$$
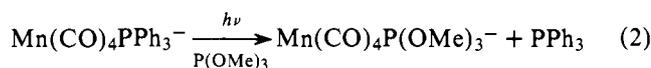
The quantum yields in degassed 0.1 M P(OMe)$_3$ THF solutions of the PPN$^+$ salt are fairly low: 0.01 (366 nm), 0.05 (313 nm), and 0.03 (254 nm) with errors of ±25%. The product Mn(CO)$_4$(P(OMe)$_3$)$^-$ is photosensitive in solution and infrared spectral changes are consistent with sequential CO substitution, but the products were not isolated. We tentatively ascribe an infrared band at 1788 cm^{-1} to *trans*-Mn-(CO)$_3$(P(OMe)$_3$)$_2^-$.

Photoinduced Oxidative Addition Reactions. Like Fe-(CO)$_5$,[18] we find that irradiation of Mn(CO)$_5^-$ in the presence of neutral oxidative addition substrates efficiently yields the expected products. For example, irradiation of either the Na$^+$ or PPN$^+$ salt of Mn(CO)$_5^-$ in THF solutions of HSiPh$_3$ or Ph$_3$SnSnPh$_3$ proceeds according to the reactions

$$\text{Mn(CO)}_5^- + \text{HSiPh}_3 \xrightarrow[\text{THF}]{h\nu} cis\text{-HMn(CO)}_4\text{(SiPh}_3)^- \qquad (3)$$

$$\text{Mn(CO)}_5^- + \text{Ph}_3\text{SnSnPh}_3 \xrightarrow[\text{THF}]{h\nu} cis\text{-Mn(CO)}_4\text{(SnPh}_3)_2^-$$

$$(4)$$
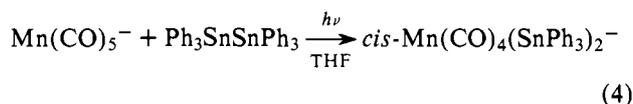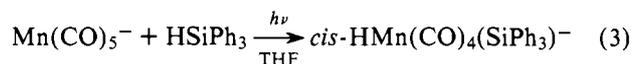
respectively. Figure 1 shows representative spectral changes accompanying reaction 3. The products have been identified by a combination of infrared spectra (Table I), elemental analyses, and comparison with authentic samples prepared by independent routes. The isoelectronic *cis*-HFe(CO)$_4$(SiPh$_3$) has been synthesized by irradiation of Fe(CO)$_5$ in the presence of HSiPh$_3$.[18] Infrared spectral changes upon irradiation of Mn(CO)$_5^-$ in the presence of HSi(CH$_2$Ph)$_3$ indicate the generation of *cis*-HMn(CO)$_4$(Si(CH$_2$Ph)$_3$), but this product was not isolated. Thus, for these reactions it appears that Fe(CO)$_5$ and Mn(CO)$_5^-$ are both viable precursors to intermediates which can oxidatively add certain neutral substrates.

Consistent with the fact that irradiation leads to loss of PPh$_3$, irradiation of Mn(CO)$_4$PPh$_3^-$ as the PPN salt in the presence of Ph$_3$SnSnPh$_3$ results in the generation of *cis*-Mn(CO)$_4$-(SnPh$_3$)$_2^-$. The infrared spectral changes accompanying this photoreaction are shown in Figure 2. Oxidative addition of HSiPh$_3$ can likely be induced as well, but the chemistry is complicated by the fact that Mn(CO)$_4$PPh$_3^-$ can apparently deprotonate HSiPh$_3$.

Irradiation of Mn(CO)$_5^-$ as the Ph$_4$E$^+$ (E = P, As) or Ph$_3$MeP$^+$ salt results in the formation of neutral tetracarbonyl
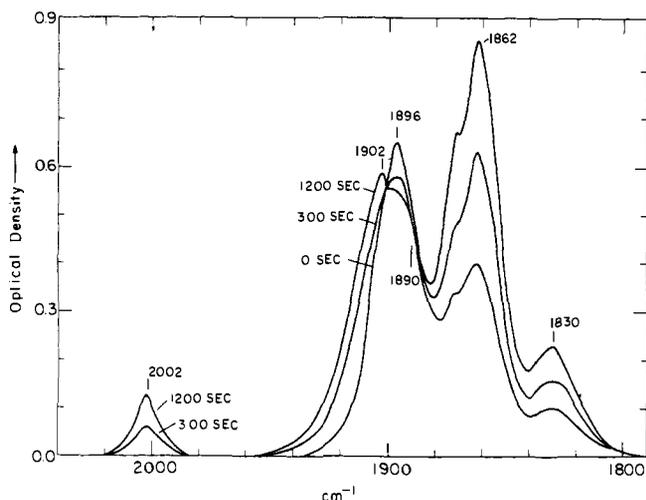
Figure 1. Spectral changes accompanying near-UV irradiation of 0.017 M Na[Mn(CO)₅] and 0.1 M HSiPh₃ in THF. Bands at 1896, 1862, and 1830 cm⁻¹ are for Mn(CO)₅⁻ and those at 2002, 1902, and 1890 cm⁻¹ are for the *cis*-HMn(CO)₄SiPh₃⁻ photoproduct. The irradiation shown was carried out in an infrared cell sealed under Ar.

Figure 2. Infrared spectral changes accompanying near-UV irradiation of 0.01 M PPN[Mn(CO)₄PPh₃] in the presence of 0.2 M Ph₃SnSnPh₃. Bands at 1941, 1846, and 1815 cm⁻¹ are starting material absorptions and those at 1997 and 1908 cm⁻¹ are associated with the oxidative addition product *cis*-Mn(CO)₄(SnPh₃)₂⁻. Irradiation carried out in an IR cell for times 0, 1, 2, 3, and 4 corresponding to 0, 120, 300, 600, and 1800 s, respectively. No thermal component for the reaction was detectable.

products arising from the oxidative addition of the cation. For the Ph₄E⁺ salts one such product is formed:

$$Mn(CO)_5^- + Ph_4E^+ \xrightarrow[THF]{h\nu} cis\text{-}PhMn(CO)_4EPh_3 + CO$$

(5)

$$E = P, As$$
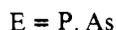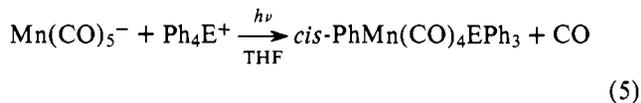
The initial chemical yield exceeds 80% based on Mn(CO)₅⁻ disappearance and 366 or 313 nm quantum yields are of the order of 0.1. For the Ph₃MeP⁺ salt we likewise observe only one product:

$$Mn(CO)_5^- + Ph_3MeP^+$$

$$\xrightarrow[THF]{h\nu} cis\text{-}PhMn(CO)_4PPh_2Me + CO \quad (6)$$
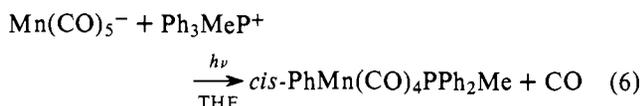
and the product is that resulting from oxidative addition of the phenyl carbon rather than the methyl carbon. The complex *cis*-MeMn(CO)₄PPh₃ was synthesized by a different route and is thermally stable. The initial infrared spectral changes accompanying reaction 6 are shown in Figure 3 and are consistent with only one product. The exclusive formation of one product may suggest that the carbon which is to be ultimately attached to the metal must be able to readily accept increased electron density in the transition state. In Ph₃MeP⁺ the phenyl carbon will do so more readily than the methyl carbon. Oxidative addition of other phosphonium salts does occur and the mechanistic details are under study. We emphasize that we use the term "oxidative addition" to refer to the stoichiometry[19] and not mechanism of the reaction.

Competition of Oxidative Addition and Substitution. Two sets of experiments have been carried out to examine the competition between oxidative addition and simple ligand substitution. In one series of experiments (Table III), Ph₄P[Mn(CO)₅] was irradiated in the presence of variable amounts of PPh₃. Both the oxidative addition product, *cis*-PhMn(CO)₄PPh₃, and the simple substitution product, Mn(CO)₄PPh₃⁻, are observed. The interesting finding is that even at 0.22 M PPh₃ the oxidative addition reaction proceeds to a healthy extent, and, indeed, there is relatively little quenching of the formation of *cis*-PhMn(CO)₄PPh₃. By way of contrast, a neutral oxidative addition substrate, Ph₃SnSnPh₃, competes with PPh₃ less effectively than Ph₄P⁺ under a comparable set of conditions (Table IV). At 0.25 M


Figure 3. Infrared spectral changes accompanying near-UV irradiation of 0.013 M Ph₃MeP[Mn(CO)₅]. Bands at 1896 and 1862 cm⁻¹ are associated with Mn(CO)₅⁻, and those at 2063, 1988, 1969, and 1947 cm⁻¹ are product, *cis*-PhMn(CO)₄PPh₂Me, bands. The other possible oxidative addition product, *cis*-MeMn(CO)₄PPh₃, has an absorption at 2056 cm⁻¹ which is not found in this photoreaction. Irradiation was carried out in an IR cell for times 0, 1, 2, 3, (0, 60, 120, and 300 s, respectively) and no thermal component of the reaction was found.

Table III. Irradiation of Ph₄P[Mn(CO)₅] in the Presence of PPh₃[a]

[PPh₃], M	Irradn time, s	% conver-sion[b]	% *cis*-PhMn(CO)₄-PPh₃[c]	% Mn(CO)₄-PPh₃⁻[c]
0.01	15	10	38	33
	30	17	35	38
	45	24	33	37
	60	30	31	37
0.06	15	11	30	28
	30	18	31	32
	45	25	29	33
	60	30	28	37
0.22	15	7	28	82
	30	14	31	71
	45	20	24	70
	60	26	21	65

[a] Irradiation at 298 K deoxygenated THF solutions of 0.01 M Ph₄P[Mn(CO)₅] with G. E. Black Light. Irradiation carried out in an infrared cell and analyses were by infrared. [b] Fraction of Mn(CO)₅⁻ consumed. [c] Yield based on amount of Mn(CO)₅⁻ consumed.

Table IV. Irradiation of PPN[Mn(CO)$_5$] in the Presence of Ph$_3$SnSnPh$_3$ and PPh$_3$[a]

[PPh$_3$]	Irradn time, s	% conversion[b]	% cis Mn(CO)$_4$-(SnPh$_3$)$_2^-$ [c]	% Mn(CO)$_4$-PPh$_3^-$ [c]
0.01	300	72	35	20
	600	90	34	17
0.07	300	75	20	56
	600	90	25	48
0.25	300	75	10	66
	600	90	11	59

[a] G. E. Black Light irradiation of a deoxygenated THF solution of 0.01 M PPN[Mn(CO)$_5$] and 0.01 M Ph$_3$SnSnPh$_3$. Irradiation was carried out in an infrared cell and analyses were by infrared. [b] Fraction of Mn(CO)$_5^-$ consumed. [c] Yield based on amount of Mn(CO)$_5^-$ consumed.

PPh$_3$ the oxidative addition of 0.01 M Ph$_3$SnSnPh$_3$ has been effectively diminished. One complicating feature, though, is that in doing the competition between Ph$_3$SnSnPh$_3$ we are using a different counterion for Mn(CO)$_5^-$. However, the relative constancy of the yield of *cis*-PhMn(CO)$_4$PPh$_3$ in Table III and the substantial attenuation of the yield of *cis*-Mn(CO)$_4$(SnPh$_3$)$_2^-$ in Table IV do seem to suggest an important role for ion pairing in the oxidative addition of the Ph$_4$P$^+$.

One additional qualitative experiment supports ion pairing in the addition of the cation. Generally, irradiation of the phosphonium or arsonium salts of Mn(CO)$_5^-$ was carried out in THF solvent, and irradiation to yield the neutral oxidative addition product is efficient. Irradiation of a CH$_3$CN solution of 0.01 M Ph$_3$MeP[Mn(CO)$_5$] in a closed vessel, however, yielded little or no oxidative addition. Little reaction of any kind was observed (~1% consumption of Mn(CO)$_5^-$ in 600 s). Repeat of the experiment in the presence of 0.09 M PPh$_3$ yielded >90% conversion to Mn(CO)$_4$PPh$_3^-$ in 600 s. Irradiation of Ph$_3$MeP[Mn(CO)$_5$] in a CH$_3$CN solution of HSiPh$_3$ does yield some of the expected oxidative addition product, although the reaction has a low quantum yield. In the absence of added nucleophile any photogenerated Mn(CO)$_4^-$ apparently back reacts with CO to regenerate Mn(CO)$_5^-$. Apparently, generation of Mn(CO)$_4^-$ ion paired to the phosphonium salt, presumably as in THF, more readily leads to oxidative addition. Ion pairing effects are likely an inescapable phenomenon in the chemistry of metal carbonyl anions.[20]

Experimental Section

All syntheses were carried out using standard Schlenk techniques under an argon atmosphere. Solvents were distilled from alkali metal ketyls where applicable, and saturated with argon before use. Neutral metal carbonyls and other reagent grade chemicals were purchased from commercial sources and used as received. Elemental analyses were obtained from Alfred Bernhardt Mikroanalytisches Laboratorium (West Germany) or Spang Microanalytical Laboratory (Ann Arbor, Mich.). Infrared solution spectra were recorded on a Perkin-Elmer Model 180 grating spectrophotometer in sealed NaCl cells. A Cary Model 17 spectrophotometer was used for electronic spectra, and a Varian Model T-60 instrument was used to record the NMR data.

Irradiations were carried out in Pyrex or Vycor Schlenk tubes with a medium-pressure 550-W mercury Hanovia lamp filtered for the 410–270-nm region (Corning filter no 7-54). The reaction vessel was positioned 5–10 cm from the source, and repeatedly evacuated to remove liberated CO. Short-term irradiations in NaCl infrared cells were done on a G. E. Black Light with output centered at 355 with a width at half-height of ~25 nm. Two 15-W lamps were used supplying ~10^{-6} einstein s^{-1} (cm^2)$^{-1}$ intensity in the experiments performed here. Appropriately filtered 550-W medium-pressure mercury Hanovia lamps were used to isolate the 366- and 313-nm regions for quantum yield determinations. A low-pressure mercury lamp (Ultra-Violet Products Model SCT-3) was used for the 254-nm studies. Light intensities were measured using ferrioxalate actinometry.[21]

Quantum Yield Determinations. Special precautions were employed in the quantum yield studies to ensure the integrity of dilute, air-sensitive solutions. Stock solutions were cannulated to a septum-sealed 10-mL buret that was previously flushed with argon for 1 h. Volumes accurate to ±0.02 mL were then recannulated into rigorously degassed receivers consisting of Pyrex or Vycor test tubes topped with three-way stopcocks. Finally, the complete assemblies were freeze–pump–thaw degassed four times on an oil diffusion pump. Solutions of Mn(CO)$_5^-$ and Mn(CO)$_4$PPh$_3^-$ salts thus prepared resisted decomposition for at least 24 h. Irradiations were at 313 or 366 nm at ~10^{-6}–10^{-7} einstein/min as determined by exposure of actinometers under the same conditions. Reactions of the carbonyls were monitored quantitatively by IR spectroscopy.

Competition Studies. To assess the importance of ion pairing in the photochemical reaction of R$_4$P[Mn(CO)$_5$] to give RMn(CO)$_4$PR$_3$, competition reactions were run between Ph$_4$P[Mn(CO)$_5$] and varying concentrations of PPh$_3$. Also, PPN[Mn(CO)$_5$] was photolyzed with an equal concentration of Ph$_3$SnSnPh$_3$ and varying concentrations of PPh$_3$. The reactants were dissolved in THF and irradiated in 0.1-mm NaCl infrared cells using the G. E. Black Light. Product distributions were determined spectroscopically by infrared.

Synthesis of Onium Salts of Mn(CO)$_5^-$. Dimanganese decarbonyl (generally 2.00 g) was reduced in 40 mL of tetrahydrofuran (THF) with 5 mL of 1% Na in Hg until the infrared showed only Na[Mn(CO)$_5$] (ca. 1 h). An equivalent of the appropriate onium halide was dissolved in a minimum of CH$_3$CN and cannulated into the mercury-free solution of Na[Mn(CO)$_5$]. Following 1 h of stirring at room temperature, the solution was filtered and evaporated to dryness, leaving a solid that was spectrally free of the sodium salt. Recrystallization in the dark from THF/isooctane provided bright yellow, crystalline samples of Ph$_4$P[Mn(CO)$_5$], Ph$_4$As[Mn(CO)$_5$], Ph$_3$MeP[Mn(CO)$_5$], and PPN[Mn(CO)$_5$]. All of the salts exhibited surprising air stability as solids, requiring around 2 h of atomspheric exposure before noticeably deteriorating. Solutions were universally air sensitive, however. With the exception of PPN[Mn(CO)$_5$], the onium salts were photosensitive in solution, giving rise to neutral tetracarbonyls described below.

Photochemistry of Onium Salts of Mn(CO)$_5^-$. Solutions of R$_4$P[Mn(CO)$_5$] (c 0.02–0.05 M) in THF were irradiated on the filtered Hanovia source until 50% conversion was realized (12–48 h). Longer irradiations resulted in secondary photoreactions of the products. The solids remaining after THF evaporation were extracted with 3× 20 mL of benzene. Following filtration and evaporation of the extracts, the crude neutral products were recrystallized from dichloromethane/isooctane to yield the tetracarbonyls RMn(CO)$_4$PR$_3$ (Table I). The compounds were stable indefinitely under argon in the solid state, but they slowly deteriorated in air. All formed bright yellow, moderately air sensitive solutions in the standard organic solvents. They were marginally soluble in alkanes and insoluble in water. Solutions absorbed strongly below 400 nm and the compounds formed unidentified carbonyl species when irradiated in this region.

Related neutral tetracarbonyls of manganese have been reported, and their infrared spectra and physical properties agree well with those of the compounds described here.[22] We have also synthesized PhMn(CO)$_4$PPh$_3$, PhMn(CO)$_4$AsPh$_3$, and PhMn(CO)$_4$PPh$_2$Me, via the thermal reaction of PhMn(CO)$_5$ and the appropriate pnicogen ligand.

PhMn(CO)$_4$PPh$_3$. Anal. Calcd for C$_{28}$H$_{20}$MnO$_4$P: C, 66.41; H, 3.98; P, 6.12. Found: C, 66.42; H, 3.96; P, 6.04. Mp 114–116 °C dec.

PhMn(CO)$_4$AsPh$_3$. Anal. Calcd for C$_{28}$H$_{20}$AsMnO$_4$: C, 61.11; H, 3.66. Found: C, 61.12; H, 3.71. Mp 130–133 °C dec.

PhMn(CO)$_4$PPh$_2$Me. Anal. Calcd for C$_{23}$H$_{18}$MnO$_4$P: C, 62.18; H, 4.08. Found: C, 62.39; H, 4.18. Mp ~10 °C (an oil at room temperature).

Photochemistry of Mn(CO)$_5^-$ and Group IV Substrates. Prolonged near-UV irradiation of either Na[Mn(CO)$_5$] or PPN[Mn(CO)$_5$] in THF failed to initiate new product formation. Both salts, however, were cleanly converted to substituted tetracarbonyl anions when solutions were irradiated on the filtered Hanovia source in THF for 12

h with either HSiPh$_3$ or Ph$_3$SnSnPh$_3$. Chemical yields of PPN$^+$ salts approached 100%.

The products PPN[HMn(CO)$_4$SiPh$_3$] and PPN[(Ph$_3$Sn)$_2$-Mn(CO)$_4$] were isolated directly in the photolysis vessel following irradiation of 0.1 M solutions of PPN[Mn(CO)$_5$] in THF with a fivefold excess of the appropriate substrate. Following trituration with 3 × 20 mL of benzene to remove excess neutral compounds, the white solids were recrystallized from acetone/diethyl ether, resulting in highly crystalline, air-stable salts (Table I). Neither compound exhibited near-UV absorption bands at longer wavelengths than the PPN$^+$ band at 275 nm.

The hydride complex exhibited a high-field NMR signal at τ 18.24 in acetone-d_6, further confirming its identity. It is isoelectronic to the neutral HFe(CO)$_4$SiPh$_3$ described earlier, also prepared via oxidative addition of the silane across an unsaturated metal carbonyl.[18] The triphenylstannyl compound has been recently synthesized as the Et$_4$N$^+$ salt from the reaction of "superreduced" [Mn(CO)$_4$]$^{3-}$ and Ph$_3$SnCl.[23]

PPN[HMn(CO)$_4$SiPh$_3$]. Anal. Calcd for C$_{58}$H$_{46}$MnNO$_4$P$_2$Si: C, 72.12; H, 4.80; Mn, 5.69; P, 6.41; Si, 2.91. Found: C, 72.18; H, 4.72; Mn, 5.48; P, 6.30; Si, 2.75. Mp 147–150 °C dec.

PPN[(Ph$_3$Sn)$_2$Mn(CO)$_4$]. Anal. Calcd for C$_{76}$H$_{60}$MnNO$_4$P$_2$Sn$_2$: C, 64.94; H, 4.30; P, 4.41. Found: C, 64.69; H, 4.35; P, 4.61. Mp decomposition above 210 °C.

Synthesis of Na[Mn(CO)$_4$PPh$_3$]. The literature procedure describing reduction of Mn$_2$(CO)$_8$(PPh$_3$)$_2$ with Na/Hg in THF did not give clean solutions of Na[Mn(CO)$_4$PPh$_3$] in our hands. Furthermore, metathesis of the crude Na$^+$ salt thus prepared led to intractable, rather than crystalline, samples of the Ph$_4$P$^+$ and PPN$^+$ salts. It was recently reported that good yields of Mn(CO)$_4$P(C$_6$H$_{11}$)$_3$$^-$ were obtained from the photolysis of the phosphine and Mn(CO)$_5$$^-$ in THF,[13] and we have further confirmed the utility of the method by producing Na[Mn(CO)$_4$PPh$_3$] in this manner.

A 0.1 M solution of freshly prepared Na[Mn(CO)$_5$] in THF was photolyzed for 36 h on the filtered Hanovia lamp in the presence of a threefold excess of PPh$_3$. Yellow crystals of Na[Mn(CO)$_4$PPh$_3$] were found precipitated at this time. The yield was increased to 60% by concentrating the 80-mL solution to ca. 10 mL and cannulating off the remainder. The very pure but highly air sensitive sodium salt was washed with 3 × 5 mL of ice-cold THF and 3 × 20 mL of pentane. Metathesis in CH$_3$CN with PPNCl or Ph$_4$PBr produced respectively deep yellow and orange-red crystals of the less air sensitive onium salts, suitably pure for quantum yield and competition studies.

Ph$_4$P[Mn(CO)$_4$PPh$_3$]. Anal. Calcd for C$_{46}$H$_{35}$MnO$_4$P$_2$: C, 71.88; H, 4.59; P, 8.06. Found: C, 71.79; H, 4.67; P, 8.23.

References and Notes

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