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NOTE

ORGANONITROGEN DERIVATIVES OF METAL CARBONYLS
V*. SOME PYRROLYL DERIVATIVES OF MANGANESE CARBONYL

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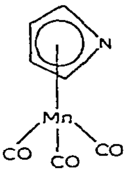
Within the last decade the chemistry of the π-cyclopentadienylmetal carbonyls has received much attention. On the other hand, the reported chemistry of the π-pyrrolylmetal carbonyls is limited to two brief reports[2,3] on the manganese compound $C_4H_4NMn(CO)_3$ (I). This note reports an improved preparation, additional spectroscopic properties, and new derivatives of this manganese complex, (I).



(I)

EXPERIMENTAL

A nitrogen atmosphere was routinely provided for the following operations: (*a*) Carrying out reactions; (*b*) Admitting to evacuated vessels; (*c*) Handling filtered solutions of organometallic derivatives. Decacarbonyldimanganese was prepared by carbonylation of $CH_3C_5H_4Mn(CO)_3$[4].

Preparation of π-pyrrolyltricarbonylmanganese

A mixture of 10.0 g (25.6 mmoles) of $Mn_2(CO)_{10}$, 2.8 ml (2.7 g, 40.5 mmoles) of pyrrole, and 80 ml of n-octane was boiled under reflux for 15 h. After cooling to room temperature, solvent was removed at 50°/0.2 mm. A concentrated hexane solution of the oily residue was chromatographed on a 2 × 60 cm alumina column. The chromatogram was developed with hexane. The fast moving yellow band was eluted with hexane. Evaporation of the eluate from this band gave 0.3 g (3% recovery) of unreacted $Mn_2(CO)_{10}$. A second more slowly moving yellow band which contained the desired

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[*] For part IV see ref. 1.
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$C_4H_4NMn(CO)_3$ was eluted with a 1/4 mixture of dichloromethane and hexane and finally purified by sublimation at 40°/0.7 mm to give 6.25 g (30.5 mmoles, 59.5% yield) of yellow $C_4H_4NMn(CO)_3$, m.p. 41° (lit.[3] m.p. 41°).

The previously described procedure[3] for the preparation of $C_4H_4NMn(CO)_3$ was reported to give only 1.4 g of $C_4H_4NMn(CO)_3$ from 3.9 g of $Mn_2(CO)_{10}$ corresponding to a 33% yield (rather than the 66% given).

Reactions of π-pyrrolyltricarbonylmanganese with the triphenyl derivatives $(C_6H_5)_3E$ (E=P, As, or Sb)

A mixture of 0.75 g (3.66 mmoles) of $C_4H_4NMn(CO)_3$, 4.2 mmoles of the $(C_6H_5)_3E$ (E = P, As, or Sb) derivative, and ~50 ml of hexane was exposed for 10 h to the ultraviolet irradiation from a 450 watt mercury lamp placed ~10 cm from the reaction vessel. The reaction mixture was then treated with 10 ml of dichloromethane and chromatographed on a 2 × 40 cm column of deactivated alumina made up in hexane. A yellow band of unreacted $C_4H_4NMn(CO)_3$ was first eluted with 1/5 dichloromethane/hexane. A more slowly moving yellow band of the $C_4H_4NMn(CO)_2$-$E(C_6H_5)_3$ derivative was then eluted with 1/4 dichloromethane/hexane. Evaporation of this eluate at ~25°/40 mm followed by recrystallization from a mixture of dichloromethane and hexane gave a 3 to 4% yield of the $C_4H_4NMn(CO)_2E(C_6H_5)_3$ derivative (Table 1). Attempts to prepare the $C_4H_4NMn(CO)_2E(C_6H_5)_3$ derivatives by the method of Barbeau[5] failed presumably owing to the instability of the intermediate tetrahydrofuran adduct $C_4H_4NMn(CO)_2OC_4H_8$.

Other reactions of π-pyrrolyltricarbonylmanganese

Attempts were made to prepare the $[C_4H_4NMn(CO)_2NO]^+$ cation by reaction of $C_4H_4NMn(CO)_3$ with the following nitrosylating agents: (*a*) A mixture of potassium nitrite and hydrochloric acid in boiling aqueous ethanol as in the reported preparation[6] of $[C_5H_5Mn(CO)_2NO]^+$; (*b*) A dichloromethane suspension of nitrosonium hydrogen sulfate ("nitrosyl sulfuric acid") as in the reported preparation[7] of $[C_5H_5Re(CO)_2NO]^+$. In both cases neither the cation $[C_4H_4NMn(CO)_2NO]^+$

TABLE 1

SOME YELLOW π-PYRROLYL DERIVATIVES OF MANGANESE CARBONYL

Compound	M.p.	Analyses, found (calcd.) (%)[b]				Proton NMR chemical shift, τ[c]		
		C	H	O	N	C_6H_5	α-H	β-H
$C_4H_4NMn(CO)_3$[a]	41°						3.93	4.79
$C_4H_4NMn(CO)_2P(C_6H_5)_3$	175–177°	65.4 (65.7)	4.3 (4.4)	7.3 (7.3)	3.2 (3.2)	2.64	4.49	5.13
$C_4H_4NMn(CO)_2As(C_6H_5)_3$	170–171°	58.9 (59.7)	3.7 (4.0)	6.4 (6.6)	3.0 (2.9)	2.63	4.40	5.10
$C_4H_4NMn(CO)_2Sb(C_6H_5)_3$	156–157°	54.2 (54.4)	3.5 (3.6)	6.2 (6.0)	2.7 (2.6)	2.60	4.19	4.99

[a] For the original preparation of this compound see refs. 2 and 3. [b] These analyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. [c] These spectra were taken in $CDCl_3$ solution and recorded on a Varian HA-100 NMR Spectrometer at 100 MHz. No fine structure was observed.

nor unreacted $C_4H_4NMn(CO)_3$ could be obtained from the reaction mixture.

Attempts to prepare $C_4H_4NMn(CO)_2(C_2R_2)$ ($R = CF_3$ and C_6H_5) derivatives by ultraviolet irradiation of $C_4H_4NMn(CO)_3$ with the corresponding acetylene $RC{\equiv}CR$ ($R = CF_3$ or C_6H_5) led only to decomposition of the starting material without isolation of any of the desired product.

DISCUSSION

The infrared spectrum of the π-cyclopentadienyl derivative $C_5H_5Mn(CO)_3$, even under the optimum conditions (cyclohexane solution, grating optics[8]) exhibits two $\nu(CO)$ frequencies (A_1+E) as expected for C_{3v} symmetry with a cylindrically symmetric manganese–π-cyclopentadienyl bond. However, under similar conditions the infrared spectrum of the π-pyrrolyl derivative $C_4H_4NMn(CO)_3$ exhibits three $\nu(CO)$ frequencies ($2A'+A''$) in accord with the lower C_s symmetry which arises from the fact that manganese–π-pyrrolyl bond is no longer cylindrically symmetrical as a consequence of asymmetry introduced by the nitrogen atom. The heteroatom thus has a noticeable effect on the $\nu(CO)$ infrared frequencies. A similar heteroatom effect has been noted in the infrared spectra of arenechromium tricarbonyls[9]: the benzene complex $C_6H_6Cr(CO)_3$ exhibits two $\nu(CO)$ frequencies whereas the less symmetrical thiophene complex $C_4H_4SCr(CO)_3$ exhibits three $\nu(CO)$ frequencies.

The infrared spectra of the $C_4H_4NMn(CO)_2E(C_6H_5)_3$ ($E = P$, As, or Sb) derivatives exhibit the expected two $\nu(CO)$ frequencies. A comparison of the positions of infrared $\nu(CO)$ frequencies in analogous π-pyrrolyl derivatives $C_4H_4NMn(CO)_2$-$E(C_6H_5)_3$ and π-cyclopentadienyl derivatives $C_5H_5Mn(CO)_2E(C_6H_5)_3$ (Table 2) show that corresponding $\nu(CO)$ frequencies are 10–25 cm^{-1} higher in the π-pyrrolyl derivatives than in the corresponding π-cyclopentadienyl derivatives. The thereby

TABLE 2

A COMPARISON OF $\nu(CO)$ FREQUENCIES OF ANALOGOUS π-CYCLOPENTADIENYL- AND π-PYRROLYLMANGANESE CARBONYL DERIVATIVES[a]

Compound	Medium	$\nu(CO)$ (cm^{-1})
$QMn(CO)_3$		
$Q = \pi\text{-}C_5H_5$	Cyclohexane	2018 (s), 1953 (vs)
$Q = \pi\text{-}C_4H_4N$	Cyclohexane	2032 (s), 1974 (vs), 1964 (vs)
$QMn(CO)_2P(C_6H_5)_3$		
$Q = \pi\text{-}C_5H_5$[b]	Nujol mull	1930 (s), 1861 (s)
$Q = \pi\text{-}C_4H_4N$	Nujol mull	1940 (s), 1870 (s)
$QMn(CO)_2As(C_6H_5)_3$		
$Q = \pi\text{-}C_5H_5$[b]	Nujol mull	1916 (s), 1854 (s)
$Q = \pi\text{-}C_4H_4N$	Nujol mull	1941 (s), 1870 (s)
$QMn(CO)_2Sb(C_6H_5)_3$		
$Q = \pi\text{-}C_5H_5$[b]	Nujol mull	1917 (s), 1857 (s)
$Q = \pi\text{-}C_4H_4N$	Nujol mull	1941 (s), 1871 (s)

[a] These spectra were taken on a Perkin–Elmer Model 257 Spectrometer with grating optics. [b] Data from ref. 5.

indicated higher carbon–oxygen bond order in the π-pyrrolyl derivatives indicates a lower metal–carbon bond order and hence less retrodative d_π–p_π^* bonding from filled metal d orbitals to the empty CO π^* antibonding orbitals in the π-pyrrolyl derivatives than in the π-cyclopentadienyl derivatives. The reduced retrodative bonding from the metal atom to the carbonyl groups in the π-pyrrolyl derivatives relative to the analogous π-cyclopentadienylmetal carbonyl derivatives indicates less negative charge on the metal atom in the π-pyrrolyl derivatives. This indicates that the π-pyrrolyl ring is either a poorer σ- or π-donor or a better δ-acceptor* than the π-cyclopentadienyl ring.

A recent study[10] demonstrates a high negative correlation between the π-C_5H_5 chemical shifts and the ν(CO) infrared frequencies in cyclopentadienylmetal carbonyls showing that increases in the π-C_5H_5 chemical shifts like decreases in the ν(CO) infrared carbonyl stretching frequencies can be used to indicate an increased negative charge on the metal atom arising either from increased forward bonding or decreased retrodative bonding. In this connection the π-C_5H_5 chemical shift decreases from τ 5.95 in ferrocene ($C_5H_5FeC_5H_5$) to τ 5.85 in the π-pyrrolyl derivative azaferrocene ($C_5H_5FeC_4H_4N$)[11] again indicating that π-pyrrolyl derivatives have less negative charge on the metal atom than analogous π-cyclopentadienyl derivatives.

The π-C_4H_4N rings in the manganese compounds studied in this paper exhibit the expected two NMR resonances of equal relative intensities corresponding to the two non-equivalent pairs of protons on carbon atoms in α- and β-positions relative to the nitrogen heteroatom. The chemical shifts increase in the following sequence:

$C_4H_4NMn(CO)_3$ (least) $<$ $C_4H_4NMn(CO)_2E(C_6H_5)_3$ $<$ $C_5H_5FeC_4H_4N$ (greatest).

This increase in chemical shifts of the π-pyrrolyl protons upon replacing the strongly π-accepting carbonyl groups with other weaker π-acceptors is consistent with the similar trends in the positions of π-cyclopentadienyl NMR resonances in cyclopentadienylmetal carbonyl derivatives[10].

Some of the chemical reactions of $C_4H_4NMn(CO)_3$ studied in this work indicate instability of the metal–π-pyrrolyl bond relative to the metal–π-cyclopentadienyl bond. The reactions of $C_4H_4NMn(CO)_3$ with the $(C_6H_5)_3E$ (E = P, As, or Sb) ligands gave only 3 to 4% yields of the analogous $C_4H_4NMn(CO)_2E(C_6H_5)_3$ derivatives owing to side reactions which led to complete decomposition. Attempts to prepare the $C_4H_4NMn(CO)_2E(C_6H_5)_3$ derivatives through an intermediate tetrahydrofuran complex $C_4H_4NMn(CO)_2OC_4H_8$ were completely unsuccessful apparently owing to insufficient stability of the tetrahydrofuran derivative. The analogous tetrahydrofuran complex with a π-cyclopentadienyl ligand, although rather unstable, is sufficiently stable to serve as an intermediate for the preparation of $C_5H_5Mn(CO)_2$-$E(C_6H_5)_3$ (E = P, As, or Sb) derivatives in ~80% yield[5]. The inability to prepare the cation $[C_4H_4NMn(CO)_2NO]^+$ by nitrosation of $C_4H_4NMn(CO)_3$ may not be a true indicator of the instability of the manganese–π-pyrrolyl bond but instead may be a further example of the previously observed[3] reactivity of the π-pyrrolyl nitrogen atom towards electrophilic reagents, in this case the NO^+ cation.

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* The metal–π-pyrrolyl bond is assumed to have forward σ and π components and retrodative components similar to the metal–π-cyclopentadienyl bond depicted in ref. 10.

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