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**Preliminary communication**

# THE SYNTHESIS AND SPECTRAL PROPERTIES OF MANGANESE PENTACARBONYL PHOSPHINE AND PHOSPHITE CATION DERIVATIVES AND RELATED COMPLEXES

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## Summary

The preparations of a variety of monosubstituted manganese carbonyl cationic species of the form $[Mn(CO)_5L][PF_6]$ are reported. Infrared spectral (including C-*K* force constant calculations) and reactivity properties of these derivatives are discussed as well.

Although there are numerous reports of preparations of Group VIB $M(CO)_5L$ species (L = Group VA Lewis base) as well as of the $[V(CO)_5L]^-$ anions, there is surprisingly little in the literature on the preparation of the isoelectronic $[Mn(CO)_5L]^+$ cations. For studies defining the nature and magnitude of the effects on the carbonyl ligand of subtle changes in electronic and steric properties in substituted metal carbonyl complexes, we have developed preparative methods for a variety of $[Mn(CO)_5L]^+$ derivatives. In addition, we wish to report our initial studies on the spectral and reactivity properties of these species.

Kruck and Hofler [1] have previously prepared mono- and di-substituted cationic manganese carbonyl derivatives according to the following high pressure synthesis:

$$Mn(CO)_{5-n}L_nCl + AlCl_3 \xrightarrow[CO]{250\ atm.} [Mn(CO)_{6-n}L_n][AlCl_4] \qquad (1)$$

where $L = PPh_3$, $P(cyclo\text{-}C_6H_{11})_3$ and *o*-phenanthroline. We report here the preparation of a variety of analogous monosubstituted complexes under mild conditions employing the following two procedures:

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$$[LMn(CO)_4]_2 \xrightarrow{Na/Hg} Na^+[LMn(CO)_4]^- \xrightarrow{EtO_2CCl} \xrightarrow[\text{or } BF_3]{HBF_4} [LMn(CO)_5][BF_4] + EtOH + NaCl \qquad (2)$$

$$[Mn(CO)_5(CH_3CN)][PF_6] + L \rightarrow [Mn(CO)_5L][PF_6] + CH_3CN \qquad (3)$$

$[LMn(CO)_4]_2$ complexes were prepared from $Mn_2(CO)_{10}$ according to the thermal procedure of Basolo and Wawersik [2], using 1-butanol as solvent. The reduction of the substituted dimeric products was readily effected in THF by Na/Hg amalgam. Subsequent treatment with ethyl chloroformate followed by addition of $BF_3$ or $HBF_4$ led to the $[LMn(CO)_5][BF_4]$ complexes as crystalline products. The complexes where L = $PPh_3$, $PMe_2Ph$, and $P(OPh)_3$ were prepared by procedure 2 in purified yield of about 18% based on the starting material $Mn_2(CO)_{10}$.

In order to provide a more versatile and effective synthesis of these complexes we have investigated the preparation of $Mn(CO)_5L^+$ derivatives employing reaction (3). $[Mn(CO)_5(CH_3CN)][PF_6]$ was prepared in large quantities using $Mn_2(CO)_{10}$ and $NOPF_6$ in acetonitrile [3–6]. Recrystallized product was obtained in greater than 61% yield from acetone—$Et_2O$ as a white powder (m.p. 160° dec.). $[Mn(CO)_5PMe_2Ph][PF_6]$ was obtained by heating a suspension of $[Mn(CO)_5(CH_3CN)][PF_6]$ with dimethylphenylphosphine in chloroform for 10 h at 60°. The product was obtained as white microcrystals in 83% yield (m.p. 149–151° dec.). $[Mn(CO)_5(NC_5H_5)][PF_6]$ was prepared in a similar manner from $[Mn(CO)_5(CH_3CN)][PF_6]$ and pyridine at room temperature following a 15 h reaction period. The purified product was obtained in 81% yield as light yellow needles upon recrystallization from acetone—$Et_2O$ (m.p. ~150° dec.). Mono-ligated manganese pentacarbonyl cations containing triphenylphosphine, tri-*p*-tolylphosphine and 1,2-bis(diphenylphosphino)-ethane were obtained from prolonged room temperature reactions (18–24 h) of $[Mn(CO)_5(CH_3CN)][PF_6]$ with the corresponding phosphines in acetone solution. $[Mn(CO)_5PPh_3][PF_6]$ was isolated as a white solid (m.p. 214° dec.) in 93% yield; $[Mn(CO)_5P(p\text{-}MeC_6H_4)_3][PF_6]$ and $[Mn(CO)_5(\text{diphos})][PF_6]$ were isolated as light yellow solids in 53% (m.p. 163° dec.) and 41% (m.p. 208° dec.) yields, respectively.

Complexes which resulted from loss of carbon monoxide ligands were also prepared. For example, $[Mn(CO)_3(NC_5H_5)_2(CH_3CN)][PF_6]$* [5] was prepared from $[Mn(CO)_5(CH_3CN)][PF_6]$ and excess pyridine in acetonitrile at room temperature over a 48 h reaction period in 43% yield (m.p. 168° dec.); whereas, $[Mn(CO)_3(NC_5H_5)_3][PF_6]$ was obtained by a rapid room temperature reaction of $[Mn(CO)_5(CH_3CN)][PF_6]$ with pyridine in the absence of solvent. The product was recrystallized from acetone—$Et_2O$ to give yellow microcrystals in 64% yield (m.p. 163°). In addition, the tris-acetonitrile complex, $[Mn(CO)_3(CH_3CN)_3][PF_6]$ [5], was obtained in 91% yield from $[Mn(CO)_5(CH_3CN)][PF_6]$ in $CH_3CN$ at 50° for 5 h (m.p. 130° dec., $\nu$(CO) 2063.0 vs, 1973.7 vs).

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*This complex was found to readily exchange $CH_3CN$ ligand with $CH_3CN$ solvent molecules as indicated by NMR studies with $CD_3CN$.

$[Mn(CO)_5PR_3][PF_6]$ species were found to rapidly react with primary amines to form carbamoyl compounds [7]. For example, $[Mn(CO)_5PMe_2Ph][PF_6]$ was observed to react with $C_6H_{11}NH_2$ or $CH_3NH_2$ in $CH_2Cl_2$ to form the yellow neutral carbamoyl complexes, $Mn(CO)_4[PMe_2Ph]C(=O)NHC_6H_{11}$ and $Mn(CO)_4[PMe_2Ph]C(=O)NHCH_3$. These complexes appear to be primarily the *cis* isomers as indicated by the four band $\nu$(CO) pattern*.

The infrared spectra in the $\nu$(CO) region (Table 1) show the expected three band pattern for a $Mn(CO)_5L^+$ species which is of $C_{4v}$ symmetry with respect to the metal pentacarbonyl moiety ($2A_1 + E$). We report in Table 2 Cotton—Kraihanzel force constants [8] calculated for the CO stretching vibrations in these $Mn(CO)_5L^+$ derivatives. As noted in Table 2, the $Mn(CO)_5L^+$ derivatives (where L = phosphine or phosphite) exhibit $k_1$ and $k_2$ values which are very similar to each other, however smaller than the value in the parent hexacarbonyl cation, with $k_1$ being greater than $k_2$ for the triphenylphosphite derivative. The $k_1$ values for the phosphine and phosphite derivatives are considerably larger than the corresponding value in acetonitrile and pyridine derivatives. At the same time the acetonitrile and pyridine

TABLE 1

INFRARED SPECTRA IN THE $\nu$(CO) REGION FOR $Mn(CO)_5L^+$ AND RELATED SPECIES

| Compound[a] | $\nu$(CO) (cm$^{-1}$)[b] | | |
|---|---|---|---|
| | $A_1^2$ | $A_1^1$ | $E$ |
| $Mn(CO)_5P(OPh)_3^+$[c] | 2153.5w | 2083.5m | 2063.5vs |
| $Mn(CO)_5PPh_3^+$ | 2141.8 | 2063 (sh) | 2052.0 |
| $Mn(CO)_5P(p\text{-}MeC_6H_4)_3^+$ | 2141.5 | 2062 (sh) | 2051.5 |
| $Mn(CO)_5PMe_2Ph^+$ | 2141.8 | 2062 (sh) | 2050.3 |
| $Mn(CO)_5(diphos)^+$ | 2140.6 | 2062 (sh) | 2050.1 |
| $Mn(CO)_5(NC_5H_5)^+$ | 2153.5 | 2041.8 | 2063.3 |
| $Mn(CO)_5(CH_3CN)^+$ | 2161.3 | 2047.3 | 2073.5 |
| $Mn(CO)_3(NC_5H_5)_2(CH_3CN)^+$ | | 2048.0vs | 1955.3vs |
| $Mn(CO)_3(NC_5H_5)_3^+$ | | 2041.0vs | 1947.0vs |

[a] All compounds existed as the $PF_6^-$ salt. [b] Frequencies determined in $CH_3CN$ and are accurate to ± 1 cm$^{-1}$, except for shoulder (± 3 cm$^{-1}$). [c] All compounds prepared in this study gave satisfactory elemental analysis.

TABLE 2

FORCE CONSTANTS FOR THE CO STRETCHING VIBRATIONS IN $Mn(CO)_5L^+$ AND RELATED SPECIES[a]

| Compound[b] | $k_1$ | $k_2$ | $k_i$[c] |
|---|---|---|---|
| $Mn(CO)_6^+$ | 18.13 | 18.13 | $0.22_0$ |
| $Mn(CO)_5P(OPh)_3^+$ | 17.74 | 17.65 | $0.22_2$ |
| $Mn(CO)_5PPh_3^+$ | 17.37 | 17.46 | $0.22_4$ |
| $Mn(CO)_5P(p\text{-}MeC_6H_4)_3^+$ | 17.35 | 17.45 | $0.22_5$ |
| $Mn(CO)_5PMe_2Ph^+$ | 17.36 | 17.44 | $0.22_8$ |
| $Mn(CO)_5(diphos)^+$ | 17.36 | 17.43 | $0.22_6$ |
| $Mn(CO)_5(NC_5H_5)^+$ | 16.97 | 17.67 | $0.23_5$ |
| $Mn(CO)_5(CH_3CN)^+$ | 17.05 | 17.83 | $0.23_1$ |

[a] Calculated from frequency data determined in $CH_3CN$. [b] All compounds existed as the $PF_6^-$ salt. [c] $k_i = k_c = k_c' = 1/2\, k_t$ [8].

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* There may, however, be small quantities of the *trans* isomers present. The stereochemical course of this reaction as a function of the amine and the substituted L ligand on the $Mn(CO)_5^+$ moiety is being further studied in our laboratory.

complexes have $k_2$ significantly greater than $k_1$, the order observed in all other neutral $Mn(CO)_5L$ derivatives as well as isoelectronic Group VIB derivatives.

These results are therefore somewhat unexpected based on our usual ideas concerning the bonding in $M(CO)_5L$ derivatives and the effect of bonding on the CO stretching force constants [9]. It may very well be that direct donation of electron density into the $\pi^\star$ orbitals of the equatorial CO ligands by the phosphines or phosphite ligands in $Mn(CO)_5L^+$ is responsible for the lowering of $k_2$ relative to $k_1$ [10,11].

Further work in progress in our laboratories on these newly acquired $[Mn(CO)_5L]^+$ species involves a mechanistic study of their formation from $[Mn(CO)_5(CH_3CN)]^+$, more detailed infrared and Raman studies* (including $\nu$(CO) infrared intensity measurements), and additional studies of their reactivity with a variety of nucleophilic reagents.

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* Far-infrared and Raman studies of these complexes are being carried out by Professors G.R. Dobson (North Texas State) and R.A. Levenson (Texas A & M).