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# Preparation, Characterisation and X-ray Photoelectron Spectroscopic (XPS) Studies on Neutral and Cationic Dinitrosyl Complexes of Manganese(I)

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*Novel cationic dinitrosyl compounds of general formula* $[Mn(NO)_2L_3]BF_4$ *[*$L = PMe_2Ph, P(OMe)_2Ph$ *and* $P(OMe)_3$*] have been prepared from the corresponding* $[MnCl(NO)_2L_2]$ *species and have been characterised using i.r. and* $^1H$ *n.m.r. spectroscopy. Reaction of the cationic complexes with* tert*-butyl isocyanide resulted in replacement of one tertiary phosphorus ligand only. An XPS study failed to reveal any significant correlation between the N(1s) binding energies and the i.r. stretching frequencies for the closely related range of compounds studied. Certain short-comings, inherent in the XPS technique, when studying electronic effects in coordination compounds, are discussed.*

## Introduction

By comparison with neutral transition metal nitrosyl complexes, the number of known cationic species is relatively small [1]. This is particularly true of manganese, for which the only known cationic nitrosyls are derivatives of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(NO)]PF_6$ [2–9] and the complex $[Mn(CO)(NO)\{P(OMe)_3\}_4](PF_6)_2$ [10]. We have recently shown [11] that a convenient route to cationic manganese(I) carbonyl complexes is obtained by halogen abstraction reactions of the series of compounds $[MnBr(CO)_{5-x}L_x]$ ($x = 1$–$3$; L = tertiary phosphorus ligand), using the silver salt of a suitable counterion, *e.g.* $AgPF_6$. This method has now been extended to the preparation of new cationic dinitrosyl complexes of manganese, using as precursors the readily obtainable neutral halide species $[MnX(NO)_2L_2]$ (X = Cl or Br; L = tertiary phosphorus ligand). Current interest in the structure and electronic bonding features of the nitrosyl ligands has led to the collection of a substantial amount of X-ray diffraction and infra-red absorption data [12, 13], more recently augmented by X-ray photoelectron spectroscopic measurements [14–16]. We have extended these studies by examining the closely related $[MnX(NO)_2L_2]$ and $[Mn(NO)_2L_3]^+$ species using XPS and attempted to correlate the measured N(1s) and P(2p) binding energies with other spectroscopic data.

## Experimental

### Starting Materials

All reactions were performed under an inert atmosphere. The carbonyl precursors $[MnCl(CO)_3L_2]$ [$L = PMe_2Ph, PPh_3, P(OPh)_3, P(OMe)_3$ and $P(OMe)_2Ph$] were prepared by refluxing an ethanolic solution of $[MnCl(CO)_5]$ with 2.1 molar equivalents of the respective ligand, and were isolated as was described previously [17]. All other reagents were obtained commercially and were not further purified.

### Preparation of Complexes

All physical data for the compounds prepared are presented in Table I.

*$[MnCl(NO)_2(PMe_2Ph)_2]$* A strong stream of nitric oxide was passed through a refluxing solution of $[MnCl(CO)_3(PMe_2Ph)_2]$ (1.0 g, 2.2 mmol) in benzene (60 ml), previously flushed with nitrogen. After 4 h the deep red solution was cooled and again flushed with nitrogen before exposure to the atmosphere. Removal of solvent under reduced pressure gave a red oil which was crystallised from a mixture of ether and hexane to give the required compound as brick-red prisms (yield 0.49 g, 52%).

Similarly prepared from the respective tricarbonyl halide precursors were:

$[MnCl(NO)_2(PPh_3)_2]$, crystallised from dichloromethane–methanol mixtures as copper plates in 75% yield;

$[MnCl(NO)_2\{P(OMe)_3\}_2]$, crystallised from ether–hexane mixtures as red prisms in 58% yield;

$[MnCl(NO)_2\{P(OMe)_2Ph\}_2]$, crystallised from hot ethanol as orange prisms in 63% yield;

$[MnBr(NO)_2\{P(OMe)_2Ph\}_2]$, crystallised from dichloromethane–cyclohexane mixtures as red prisms in 57% yield;

and the known [18] complex $[MnCl(NO)_2\{P(OPh)_3\}_2]$ as orange needles in 71% yield.

*$[Mn(NO)_2(PMe_2Ph)_3]BF_4$* To a solution of $[MnCl(NO)_2(PMe_2Ph)_2]$ (1.0 g, 2.3 mmol) in degassed acetone (20 ml) at room temperature was added silver tetrafluoroborate (0.45 g, 2.3 mmol). A heavy precipitate of silver chloride was formed almost immediately and after 5 min was filtered off.

TABLE I. Physical Data for Neutral and Cationic Manganese Dinitrosyl Complexes.

| Compound | M.P. (°C) | Conductivity[a] ($\Omega^{-1}$ cm$^2$ mol$^{-1}$) | Analysis: Found(Calc) (%) | | | | $\nu$(CNR) and $\nu$(NO)[b] (cm$^{-1}$) | $^1$H n.m.r. data[c] ($\tau$) (J/Hz) |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | Cl | | |
| $[\mathrm{MnCl(NO)_2(PPh_3)_2}]$ | 178–181[d] | 0.23 | 64.0<br>(64.05) | 4.35<br>(4.5) | 4.15<br>(4.15) | 5.65<br>(5.25) | 1712, 1664 | n.m. |
| $[\mathrm{MnCl(NO)_2(PMe_2Ph)_2}]$ | 120–2 | 0.16 | 45.2<br>(45.05) | 5.2<br>(5.2) | 6.8<br>(6.55) | 8.15<br>(8.3) | 1706, 1660 | 8.14(dt) (J* = 10.2) |
| $[\mathrm{MnCl(NO)_2\{P(OMe)_3\}_2}]$ | 91–3 | 0.30 | 18.25<br>(18.1) | 4.5<br>(4.55) | 7.25<br>(7.05) | 8.45<br>(8.9) | 1737, 1682 | 6.22(dt) (J* = 11.8) |
| $[\mathrm{MnCl(NO)_2\{P(OMe)_2Ph\}_2}]$ | 136–7 | 0.34 | 39.2<br>(39.15) | 4.6<br>(4.5) | 5.95<br>(5.7) | 7.2<br>(7.25) | 1723, 1674 | 6.26(dt) (J* = 12.0) |
| $[\mathrm{MnBr(NO)_2\{P(OMe)_2Ph\}_2}]$ | 143–7 | 0.21 | 35.95<br>(35.9) | 4.25<br>(4.15) | 5.05<br>(5.25) | | 1729, 1678 | 6.30(dt) (J* = 12.0) |
| $[\mathrm{Mn(NO)_2(PMe_2Ph)_3}]\mathrm{BF_4}$ | 146–9[d] | 147 | 46.55<br>(46.8) | 5.4<br>(5.4) | 4.35<br>(4.55) | | 1731, 1687 | 8.16(dt) (J* = 9.4), 8.78(d) ($J_{\mathrm{P-H}}$ = 8.0) |
| $[\mathrm{Mn(NO)_2\{P(OMe)_3\}_3}]\mathrm{BF_4}$ | 132–4[d] | 137 | 18.95<br>(18.85) | 4.8<br>(4.75) | 5.05<br>(4.9) | | 1772, 1722 | 6.10(dt) (J* = 11.2), 6.18(d) ($J_{\mathrm{P-H}}$ = 11.7) |
| $[\mathrm{Mn(NO)_2\{P(OMe)_2Ph\}_3}]\mathrm{BF_4}$ | 153–5[d] | 139 | 40.25<br>(40.45) | 4.8<br>(4.65) | 3.65<br>(3.9) | | 1760, 1712 | 6.31(dt) (J* = 11.8), 6.83(d) ($J_{\mathrm{P-H}}$ = 11.4) |
| $[\mathrm{Mn(CNC_4H_9)(NO)_2(PMe_2Ph)_2}]\mathrm{BF_4}$ | 164–7 | 150 | 44.85<br>(44.95) | 5.75<br>(5.55) | 7.55<br>(7.5) | | 2204, 1744, 1699 | 7.93(dt) (J* = 10.0) 8.75(s) |
| $[\mathrm{Mn(CNC_4H_9)(NO)_2\{P(OMe)_2Ph\}_2}]\mathrm{BF_4}$ | 153–7[d] | 141 | 40.55<br>(40.35) | 4.9<br>(5.0) | 6.85<br>(6.75) | | 2193, 1762, 1719 | 6.08(dt) (J* = 12.2), 8.55(s) |

[a] Measured in acetone solution. [b] Measured in dichloromethane solution. [c] Measured in acetone-$d_6$ solution. s = singlet, d = doublet, dt = distorted triplet, J* = separation of outer peaks. [d] With decomposition.

To the filtrate was added a solution of dimethylphenylphosphine (0.39 g, 2.8 mmol) in acetone (10 ml). Solvent was removed under reduced pressure and the resulting red oil was left to stand under methanol (2 ml) at 0 °C. The solid which slowly separated was recrystallised from dichloromethane–methanol mixtures as red prisms of the required product (yield 0.82 g, 57%).

*$[Mn(NO)_2\{P(OMe)_3\}_3]BF_4$* Silver tetrafluoroborate (0.49 g, 2.5 mmol) was added to a solution of $[MnCl(NO)_2\{P(OMe)_3\}_2]$ (1.0 g, 2.5 mmol) in acetone (25 ml) containing trimethylphosphite (0.37 g, 3.0 mmol) at room temperature. After 2 h the heavy silver chloride precipitate was filtered off and solvent removed under reduced pressure to give a yellow oil which was taken up in ethanol (5 ml). Dropwise addition of ether gave the required product as golden needles of analytical purity (yield 1.28 g, 89%).

$[Mn(NO)_2\{P(OMe)_2Ph\}_3]BF_4$ was similarly prepared from $[MnCl(NO)_2\{P(OMe)_2Ph\}_2]$ and dimethoxyphenylphosphine, and crystallised from dichloromethane–ether mixtures as orange prisms in 74% yield.

*$[Mn(CNC_4H_9)(NO)_2(PMe_2PH)_2]BF_4$* To a solution of $[Mn(NO)_2(PMe_2Ph)_3]BF_4$ (0.40 g, 0.65 mmol) in chloroform (25 ml) at room temperature was added *tert*-butyl isocyanide (0.10 g, 1.2 mmol). The colour rapidly changed from deep red to pale orange and the solution was refluxed for 1 h. Removal of the solvent under reduced pressure gave an oil which was crystallised from a mixture of ethanol and hexane to give the required product as yellow plates (yield 0.30 g, 82%).

$[Mn(CNC_4H_9)(NO)_2\{P(OMe)_2Ph\}_2]BF_4$ was similarly prepared from $[Mn(NO)_2\{P(OMe)_2Ph\}_3]BF_4$, as red plates in 93% yield.

### *Apparatus*

Melting points were obtained on a Kofler hot-stage apparatus and conductivities on a Van Waters and Rogers model 31 conductivity bridge. Infra-red spectra were recorded using a Perkin Elmer model 457 grating spectrophotometer and $^1H$ n.m.r. spectra with a Varian HA-100 instrument. Elemental analyses were performed in this laboratory.

### *X-Ray Photoelectron Spectroscopy*

Thin layers of the compounds were placed on a copper sample holder by evaporation of dichloromethane solutions. They were then immediately transferred to the source region of an AEI ES 200B Photoelectron Spectrometer *via* an intermediate pumping stage; the resulting base pressure was $\sim 5 \times 10^{-8}$ τ after the sample holder had been cooled to −150 °C with a liquid nitrogen feed-through. Al(Kα) [1487 eV] and Mg(Kα) [1254 eV] radiation was used for excitation and the measured binding energies were calculated with respect to the C(1s) level, present in all samples, which was assumed to have a binding energy of 284.0 eV. Results are presented in Table II.

**TABLE II. N(1s) and P(2p) Binding Energies for Neutral and Cationic Manganese Dinitrosyl Complexes.**

| $[MnX(NO)_2L_2]$ | | N(1s) (eV)[a] | P(2p) (eV)[a] |
|---|---|---|---|
| L | X | | |
| $PPh_3$ | Cl | 400.1 | 131.4 |
| $PMe_2Ph$ | Cl | 400.2 | 130.4 |
| $P(OPh)_3$ | Cl | 400.8 | 130.8 |
| $P(OMe)_2Ph$ | Cl | 400.6 | 131.2 |
| $P(OMe)_2Ph$ | Br | 400.2 | 131.2 |
| $P(OMe)_3$ | Cl | 401.1 | 132.4 |
| $[Mn(NO)_2L_3]^+Y^-$ | | | |
| L | $Y^-$ | | |
| $PMe_2Ph$ | $BF_4^-$ | 400.0 | 130.6 |
| $P(OMe)_2Ph$ | $BF_4^-$ | 400.2 | 131.4 |
| $P(OMe)_3$ | $BF_4^-$ | 400.2 | 132.2 |

[a] All values quoted ± 0.2 eV.

## Results and Discussion

### *Preparation of Neutral Complexes*

The neutral dinitrosyl complexes $[MnCl(NO)_2L_2]$ were prepared for a representative series of ligands [L = $PPh_3$, $PMe_2Ph$, $P(OMe)_3$, $P(OMe)_2Ph$ and $P(OPh)_3$ [18]] by passing nitric oxide through a refluxing benzene solution of the respective tricarbonyl species $[MnCl(CO)_3L_2]$. The reaction solutions were thoroughly flushed with nitrogen both before and after nitrosylation, in order to prevent oxidation of nitric oxide to the considerably more reactive nitrogen dioxide [19]. Traces of $NO_2$ in the solutions caused preferential, single electron oxidation reactions of the tricarbonyl compounds to occur, giving the respective paramagnetic cations $[MnCl(CO)_3L_2]^+$ which we have described previously [10] and which could be recognised by their deep colouration and characteristic infra-red carbonyl stretching frequencies. An alternative preparative route to a number of the $[MnCl(NO)_2L_2]$ complexes was *via* nitrosylation of the respective dicarbonyl species $[MnCl(CO)_2L_3]$*. Under comparable conditions, reaction times were

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*These complexes could be prepared by a procedure analogous to that described for the known [17] $[MnBr(CO)_2L_3]$ complexes.

significantly shorter than those for the tricarbonyls (an average of 30 min compared to 5 h) and this effect can be attributed [19] to the greater steric crowding in the $[MnCl(CO)_2L_3]$ complexes, which promotes ligand dissociation. Despite the shorter reaction times, this preparative route is not recommended, as the displaced tertiary phosphorus ligand in the reaction solution makes product isolation more difficult.

The complexes $[MnCl(NO)_2L_2]$ and $[MnBr(NO)_2\{P(OMe)_2Ph\}_2]$ were isolated as reasonably air stable orange to red crystals, which required an inert atmosphere for extended storage. They are analogous to the range of iodide complexes prepared previously [18]. Of the three possible halides, we consider the chloride complexes to be the most convenient precursors to the cationic dinitrosyl species, as the bromide complexes tend to be too soluble in organic solvents and the precursor to the iodides, $[MnI(CO)_5]$, is not as readily prepared as $[MnX(CO)_5]$ (X = Cl or Br).

$[MnCl(NO)_2\{P(OMe)_2Ph\}_2]$ has been shown [20] crystallographically to possess a trigonal bipyramidal geometry, containing *trans* phosphonite groups in the axial positions and nitrosyl groups which are not completely linear, with Mn–N–O angles of 165 and 166°. The $^1$H n.m.r. spectrum of the complex exhibits a distorted triplet for the magnetically equivalent phosphonite methyl groups. This spectral pattern is observed for the ligand methyl groups throughout the series (see Table I) and although a *trans* ligand arrangement is not unequivocally indicated, we suggest that all the $[MnX(NO)_2L_2]$ complexes are isostructural, as steric crowding within the molecule is minimised in this configuration [21]. In the infra-red spectra of the $[MnCl(NO)_2L_2]$ complexes, the frequencies of the nitrosyl bands can be correlated with the $\pi$-acceptor properties of the ligands (L) [22] and the gradual shift to lower frequencies for the series $P(OPh)_3 > P(OMe)_3 > P(OMe)_2Ph > PPh_3 > PMe_2Ph$ establishes this as the order of decreasing $\pi$-acceptor capability (see Table I; $[MnCl(NO)_2\{P(OPh)_3\}_2]$ $\nu_{NO}$ [22] = 1751, 1699 cm$^{-1}$). Comparison of $[MnX(NO)_2\{P(OMe)_2Ph\}_2]$ (X = Cl or Br) however, shows the opposite order of $\nu_{NO}$ that would be predicted on simple electronegativity arguments. This has been observed previously [22] and was attributed to a greater $\pi$-acceptor ability for a bromide ligand compared to chloride, which overrules the electronegativity effect.

### Preparation of Cationic Complexes

Treatment of acetone solutions of $[MnCl(NO)_2L_2]$ [L = $PPh_3$, $PMe_2Ph$, $P(OMe)_2Ph$, $P(OMe)_3$ and $P(OPh)_3$] with silver tetrafluoroborate in the presence of one molar equivalent of the respective ligand, has given a limited series of cationic dinitrosyl complexes $[Mn(NO)_2L_3]BF_4$. The ease of reaction could be correlated with the steric requirements of the ligand L. Thus with $P(OMe)_3$ and $P(OMe)_2Ph$ the reaction proceeded readily and the dinitrosyl cations were isolated in high yield. With $PMe_2Ph$ this preparative procedure resulted in extensive decomposition. $[Mn(NO)_2(PMe_2Ph)_3]BF_4$ could, however, be isolated by first treating $[MnCl(NO)_2(PMe_2Ph)_2]$ with silver tetrafluoroborate in degassed acetone, followed by removal of the silver chloride precipitate and reaction of the solvated cation with $PMe_2Ph$. With the larger ligands $PPh_3$ and $P(OPh)_3$, green solutions were obtained from which no $[Mn(NO)_2L_3]BF_4$ species could be isolated by either method. The complexes $[Mn(NO)_2L_3]BF_4$, [L = $PMe_2Ph$, $P(OMe)_2Ph$ and $P(OMe)_3$] were substantially less stable than their neutral precursors, both in solutions and in the solid state, and required storage under nitrogen.

The replacement of the halide ligand in $[MnCl(NO)_2L_2]$ with a tertiary phosphorus ligand results in a decreased electron density on the metal. This is observed in the infra-red spectra as an overall shift of $\nu_{NO}$ to higher frequencies for the cationic species (see Table I). In addition to this shift, the relationship between the ligand $\pi$-acceptor properties and $\nu_{NO}$ established for the neutral dinitrosyl complexes, is duplicated in the cationic derivatives. The decrease of electron density on the metal can also be expected to favour a retention of the trigonal bipyramidal ligand arrangement observed for the neutral precursors [21]. This is confirmed by the $^1$H n.m.r. ligand methyl resonances for the complexes $[Mn(NO)_2L_3]BF_4$ [L = $PMe_2Ph$, $P(OMe)_2Ph$ and $P(OMe)_3$] which appear in each case as a distorted triplet for the two strongly coupled *trans* axial ligands and a doublet for the unique equatorial ligand (see Table I).

The cationic complexes $[Mn(NO)_2L_3]BF_4$ [L = $PMe_2PH$, $P(OMe)_2Ph$ and $P(OMe)_3$] reacted further in refluxing chloroform solution with an excess of *tert*-butyl isocyanide to give replacement of one tertiary phosphorus ligand. $[Mn(CNC_4H_9)(NO)_2L_2]BF_4$ [L = $PMe_2Ph$ and $P(OMe)_2Ph$] were thus isolated and fully characterised. In the $^1$H n.m.r. spectra, the phosphorus methyl resonance appeared as a distorted triplet in each case, suggesting that the equatorial ligand had been displaced and that these complexes had the same ligand configuration as the neutral $[MnX(NO)_2L_2]$ species. Reaction of the $[Mn(NO)_2L_3]BF_4$ complexes with carbon monoxide under similar conditions did not effect ligand replacement.

### X-Ray Photoelectron Spectroscopy Measurements

The measured N(1s) and P(2p) binding energies for the series of complexes $[MnCl(NO)_2L_2]$ [L = $PPh_3$, $PMe_2Ph$, $P(OPh)_3$ and $P(OMe)_3$], $[MnX(NO)_2\{P(OMe)_2Ph\}_2]$ (X = Cl and Br) and $[Mn(NO)_2L_3]BF_4$ [L = $PMe_2Ph$, $P(OMe)_2Ph$ and $P(OMe)_3$] are presented in Table II. The results indicate that within the closely related range of compounds studied here, the N(1s) binding energies are fairly insensitive to the electronic effects of the different tertiary phosphorus ligands, although the variations within the series of neutral compounds allow some comment. Thus the higher N(1s) binding energies for $[MnCl(NO)_2L_2]$ [L = $P(OMe)_3$ and $P(OPh)_3$] reflect the stronger electron withdrawing properties of the phosphite ligands compared to those of the phosphines $PMe_2Ph$ and $PPh_3$ in the same series. It is also possible to correlate the N(1s) values observed for $[MnX(NO)_2\{P(OMe)_2Ph\}_2]$ (X = Cl and Br) with the electronegativity of the halide ligands. With the exception of the $PPh_3$ and $P(OPh)_3$ compounds, the P(2p) binding energies follow the expected trend throughout the series.

The small binding energy shifts of N(1s) levels in this limited series is not surprising when the results are compared with previous data [14], where the total span in the N(1s) levels for 29 different nitrosyl complexes of the VIB, VIIB and VIII transition metal groups was only 3.7 eV.

In addition it should be noted that the interpretation of bulk electronic properties of coordination compounds, based on XPS data, could be erroneous and may lead to unreliable results. The following observations lead to this conclusion: (a) it is by now well established that the sampling depth for XPS is $< 100$ Å [23], *i.e.* surface impurities, undetected by conventional analytical methods, can lead to errors of interpretation; (b) there is a growing body of evidence to suggest that photo-reduction during XPS measurements [24, 25] occurs in many instances; (c) the high vacuum necessarily present in the photoelectron spectrometer can lead to the loss of a coordinating ligand from the sample surface. Although firm evidence for this was lacking in the present study, preliminary XPS measurements on some platinum and palladium complexes [26], $[PtX_2L_3]$ and $[PdX_2L_3]$ (X = halide, L = tertiary phosphine), in these laboratories [27] suggested that free tertiary phosphines were readily evolved even at a sample temperature of −175 °C.

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