941. *Trinitrosylcarbonylmanganese.**

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The preparations of trinitrosylcarbonylmanganese and triphenylphosphinetrinitrosylmanganese are reported. The infrared spectra and physical properties of the compounds are given, and factors which may influence the relative stability of the nitrosyl carbonyls of manganese are discussed.

NITRIC OXIDE, in forming complexes with transition elements, in the majority of cases, may formally be considered to donate three electrons, *i.e.*, to co-ordinate essentially as the nitrosonium ion.[1] Therefore, in the formation of a nitrosyl-carbonyl complex from

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[1] Addison and Lewis, *Quart. Rev.*, 1955, **9**, 115; Lewis, *Sci. Prog.*, 1959, **47**, 187, 506.

a carbonyl, two nitric oxide groups replace three carbon monoxide molecules. In the case of manganese carbonyl, $Mn_2(CO)_{10}$, there are two possible monomeric nitrosyl derivatives, in which the inert-gas configuration of the metal is still maintained, *viz.*, $Mn(NO)(CO)_4$ and $Mn(NO)_3(CO)$. The latter is a member of the pseudo-nickel carbonyl series $Ni(CO)_4$, $Co(NO)(CO)_3$, $Fe(NO)_2(CO)_2$, $Mn(CO)(NO)_3$, $Cr(NO)_4$, and the former would be the first nitrosyl derivative of a pseudo-iron carbonyl series. In the pseudo-nickel carbonyl series, the iron and cobalt nitrosyl carbonyls have been known for a considerable time. We report here the preparation of the manganese analogue of this series.

Discussion.—We attempted to prepare the nitrosylcarbonylmanganese by direct reaction of nitric oxide with manganese carbonyl in the solid state and in solution in inert solvents. Nitric oxide was also heated with manganese carbonyl in sealed tubes (2 atm.) to 50°. In no case was any nitrosyl of manganese detected. Nitric oxide and nitrosyl chloride were also treated with sodium pentacarbonylmanganese in tetrahydrofuran: although sodium chloride was precipitated, no nitrosyl-carbonyl of manganese was detected in either the solution or the solid obtained on evaporation. However, reaction of nitric oxide with pentacarbonylmanganese iodide or bis(tetracarbonylmanganese iodide) yielded a green vapour that condensed in a carbon dioxide trap to a green solid. This compound was purified by fractional distillation, to give a green solid, m. p. 27°.

The green solid gave analyses corresponding to $Mn(NO)_3CO$, and it is the manganese member of the pseudo-nickel carbonyl series. As with the corresponding nitrosyls of iron and cobalt, the compound is very readily oxidized by air, the rate of oxidation increasing in the series $Co < Fe < Mn$.

The infrared spectrum of the compound, in cyclohexane, shows strong bands at 2088, 1823, and 1734 $cm.^{-1}$. The complex would be expected to have essentially a tetrahedral structure involving sp^3 hybrid bonds, and such a molecule with C_{3v} symmetry would give rise to one infrared-active carbon monoxide stretching frequency and two infrared-active nitric oxide stretching frequencies. The nitric oxide stretching frequencies at 1823 and 1734 $cm.^{-1}$ are very similar to those observed in the compounds $Fe(NO)_3Cl$ (1826, 1763 $cm.^{-1}$) [2] and $Fe(NO^+)_3(NO^-)$ (1810, 1730 $cm.^{-1}$).[3]

The yield of product from the above reactions was very low, and it was not possible to carry out molecular-weight and magnetic measurements on the complex; however, the compound was shown to be a non-conductor in nitrobenzene solution, and in order to establish the general nature of the manganese nitrosyl compound more closely we have prepared the triphenylphosphine derivative. Malatesta and Araneo [4] noted that in the case of the nitrosyl carbonyls of iron and cobalt, one and sometimes two of the carbon monoxide groups can be replaced by triphenylphosphine and other Group V donor ligands, to give compounds appreciably more stable than the parent compounds. Triphenylphosphine reacted with the trinitrosylcarbonylmanganese in benzene with the evolution of carbon monoxide, and dark green crystals were isolated from the solution which analysis showed to be $Mn(NO)_3PPh_3$. The same compound was also prepared by reaction of nitric oxide with triphenylphosphinetetracarbonylmanganese in *p*-xylene at 100°. The complex was monomeric in benzene, a non-electrolyte in nitrobenzene, and diamagnetic, agreeing with the formulation of the parent nitrosylcarbonyl as a monomer with an inert-gas configuration, $Mn(NO)_3(CO)$. The phosphine–nitrosyl complex showed two infrared-active NO stretching frequencies, as required for a pseudo-tetrahedral molecule, at 1781 and 1688 $cm.^{-1}$. The lowering of the frequencies from those observed in the carbonyl-nitrosyl, is similar to that observed in the nitrosylcarbonyl cobalt substituted compounds, where the NO stretching frequency is lowered from 1832 for the parent compound to 1750—

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* For preliminary note, see *Proc. Chem. Soc.*, 1960, 81.

[2] Hieber and Jahn, *Z. Naturforsch.*, 1958, **13**b, 196.

[3] Griffith, Lewis, and Wilkinson, *J.*, 1958, 3993.

[4] Malatesta and Araneo, *J.*, 1957, 3803.

1760 cm.$^{-1}$ for the phosphorus-, arsenic-, and antimony-substituted complexes.[5] This lowering may be associated with the decrease in the π-bonding capacity of the metal–Group V donor systems, compared with carbon monoxide, with the resultant increase in the π-bonding between the metal and the nitrogen of the nitrosyl group.

Manganese is the first carbonyl studied where it is possible to have more than one monomeric neutral nitrosylcarbonyl derivative. If the nitrosyl-carbonyls followed the same stability sequence as found with the hydrides, $HCo(CO)_4$, $H_2Fe(CO)_4$, $HMn(CO)_5$,[6] we would have expected the mononitrosyl-carbonyl $Mn(CO)_4NO$ to be a stable species. However, recent work on the hydrides implies that the hydrogen is embedded in a *d*-orbital of the metal,[7] whereas the stability of nitrosyls seems closely associated with the π-bonding capacity of the metal–nitrogen system. In the mononitrosyl compound, if the NO group is considered to contribute three electrons, the manganese may be considered to have a formal valency of (—I), whereas in the trinitrosylcarbonyl the formal valency would be (—III). The degree of π-bonding in a metal–nitrogen bond will depend on (i) the stereochemistry of the metal, (ii) the electronegativity of the metal, and (iii) the π-bonding capacity of the other ligands present.

These effects may be considered for members of the pseudo-nickel carbonyl series. In this case the stereochemistry of the complexes is the same, but the formal charges, and hence the electronegativity, of the metal varies, being Ni(0), Co(—I), Fe(—II), Mn(—III). The CO and NO infrared stretching frequencies of these compounds are given in the Table.

Compound	$Ni(CO)_4$ [1]	$Co(CO)_3(NO)$ [1]	$Fe(CO)_2(NO)_2$ [2]	$Mn(CO)(NO)_3$ [2]
CO stretching frequency (cm.$^{-1}$)	2128 (Raman)	2047	2083	2088
	2057	2011	2034	
NO stretching frequency (cm.$^{-1}$)		1822	1810	1823
			1766	1734
Force const. (10^5 dynes/cm.)				
CO	17·4	16·5	17·1	17·6
NO	—	14·6	14·1	13·7
CO–M–CO	0·3	0·2	0·4	
CO–M–NO		0·3	0·2	0·3
NO–M–NO			0·3	0·5

[1] See Cotton, " Modern Co-ordination Chemistry," Interscience Publ. Inc., New York, 1960, p. 335. [2] Measured in dilute solution of cyclohexane.

Only approximate values of the force constants are listed, as these were computed from only the CO and NO stretching frequencies. In the case of nickel carbonyl the calculated constants agree favourably with those of Jones,[8] $K_{CO} = 17{\cdot}3 \times 10^5$ dyne/cm. and $K_{CO\cdot NiCO} = 0{\cdot}23 \times 10^5$ dyne/cm., which were determined from more complete data. It appears from these results that there is no major change in the CO and NO force constants in the complexes. However, the force constant for the NO group seems slightly lower than for the CO group. In the nitrosyl carbonyls, the NO force constant appears to decrease with increasing number of NO groups, while the CO force constant appears to increase as the number of NO groups increases. In this series of compounds we are varying both the electronegativity of the metal and the nature of the groups present, and the decrease in the electronegativity of the metal may be offset by the increase in the number of nitric oxide groups in the complex, which from these data appears to be a slightly better π-bonding ligand than carbon monoxide.

In the case of the complexes $K_2[Fe(CN)_5NO]$, $K_3[Mn(CN)_5NO]$, and $K_5[V(CN)_5NO]$ both the stereochemistry of the metal ion and the nature and number of the groups present remain constant. In this case we may then consider only the effect of the electronegativity of the metal. The formal valencies of the metals in these compounds are Fe(II), Mn(I),

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[5] Lewis, Irving, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.

[6] Moeller, " Inorganic Chemistry," John Wiley and Sons, New York, 1952, p. 705.

[7] Cotton, *J. Amer. Chem. Soc.*, 1958, **80**, 4425; Bishop, Down, Emtage, Richards, and Wilkinson, *J.*, 1959, 2484.

[8] Jones, *J. Chem. Phys.*, 1958, **28**, 1215.

and V(—I). If the NO stretching frequency is taken as indicative of the degree of π-bonding in the metal–nitrogen bond, then, as the stretching frequencies [5,9] are 1937, 1730, and 1575 cm.$^{-1}$ for the series of compounds, the degree of π-bonding increases in the expected order of decreasing electronegativity of the metal, Fe < Mn < V.

On the basis of electronegativity arguments, we would thus expect trinitrosylcarbonylmanganese to be more stable than nitrosyltetracarbonylmanganese. This, of course, assumes that the major factor in governing the stability is π-bonding. Any decrease in the electronegativity of the metal, although favouring π-bonding, will tend to reduce the σ-bond strength of the metal–ligand bond. In the case of nitric oxide and carbon monoxide, it is probable, however, that π-bonding is more important than σ-bonding; but in a consideration of metal–nitrosyl complexes containing other groups where σ-bonding may be important, the stability may follow a different pattern of behaviour.

The two possible nitrosyl-carbonyl complexes of manganese also differ in their stereochemistry; if it is assumed that the orbital energies do not differ significantly in the various stereochemical arrangements, then this will influence the π-bonding in the metal ligand bonds. Thus for the mononitrosyl, $Mn(CO)_4NO$, there would be five groups competing for the four available filled *d*-orbitals, whereas in the tetrahedral trinitrosylcarbonylmanganese there would be four groups competing for five filled *d*-orbitals (see refs. 10, 11). If we assume that the NO and the CO group have similar orders of π-bonding capacity, there would obviously be a greater π-bond contribution for each group in the trinitrosylcarbonylmanganese. Thus from both electronegativity and stereochemical considerations we would expect the contribution of π-bonding to be higher in the trinitrosyl- than the mononitrosylcarbonyl-manganese. We have attempted to prepare derivatives of the mononitrosylcarbonylmanganese, by reactions such as that of nitric oxide with tricarbonyl-(*o*-phenylenebisdimethylarsine)manganese; no replacement of carbon monoxide occurred up to the decomposition temperature of the complex. However, it is difficult to differentiate in such cases between thermodynamic stability and kinetic reactivity.

EXPERIMENTAL

Trinitrosylcarbonylmanganese.—Nitric oxide was allowed to react with pentacarbonylmanganese iodide (1 g.) or bis(tetracarbonylmanganese iodide) (1 g.) at 90—100° under nitrogen. A rapid reaction ensued, with production of a white solid suspended in a green vapour. The white solid separated immediately outside the reaction zone. The green vapour was condensed in a carbon dioxide–acetone trap, and was purified by vacuum-distillation into a second trap (yield 20—30 mg.). The green crystalline product melted without decomposition at 27° (Found: Mn, 30·8; N, 23·5. $CMnN_3O_4$ requires Mn, 31·8; N, 24·3%); thermal decomposition occurs *in vacuo* at 60°. It is rapidly oxidized by air, and is decomposed by water.

Triphenylphosphinetrinitrosylcarbonylmanganese.—(*a*) Triphenylphosphine (40 mg.) was dissolved in benzene, and trinitrosylcarbonylmanganese (20 mg.) added. The solution was stored at room temperature for 24 hr., a slow evolution of carbon monoxide occurring; methanol (3 ml.) was added, and the solution concentrated under vacuum until green crystals separated. The compound (15 mg.) recrystallized from methanol. All initial operations were carried out in nitrogen, but the recrystallization was carried out in air.

(*b*) Triphenylphosphinetetracarbonylmanganese was prepared by Hieber and Freyer's method.[12] The triphenylphosphinetetracarbonyl (0·2 g.) was dissolved in *p*-xylene (20 ml.), the solution heated under reflux to 100°, and a stream of nitric oxide passed through the solution for 2 hr. The colour gradually changed from orange to brown-green. The solution was cooled to room temperature, filtered, and evaporated in a vacuum. The residue was extracted with methanol (4 × 5 ml.), and the extracts were concentrated under a vacuum, to yield green crystals, which were recrystallized from methanol (yield 0·1 g.).

The crystals are stable in air, and melt at 119° (decomp.). The *compound* is diamagnetic,

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[9] Griffith, Lewis, and Wilkinson, *J.*, 1959, 1632.

[10] Cotton and Goodgame, *J. Amer. Chem. Soc.*, in the press.

[11] Kimball, *J. Chem. Phys.*, 1940, **8**, 188.

[12] Hieber and Freyer, *Chem. Ber.*, 1959, **92**, 1765.

and a non-conductor in nitrobenzene (a 0·001M-solution gave an equivalent conductance of 0·1 ohm^{-1}) [Found: Mn, 13·4; N, 9·9; P, 7·0%; *M* (in benzene, isopiestic), 396. $C_{18}H_{15}MnN_3O_3P$ requires Mn, 13·5; N, 10·3; P, 7·6%; *M*, 407].

Infrared Spectra.—These were recorded on a Grubb–Parsons G.S.2A double-beam spectrometer.

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