Transition-metal Nitrosyl Compounds. Part VIII.[1] The Preparation and Properties of Some Cationic Nitrosyl Complexes of Zerovalent Ruthenium and Osmium

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Cationic nitrosyl complexes of the type $[M(CO)_2(NO)L_2]Y$ (M = Ru or Os; L = PPh_3 or PCy_3; Y = BPh_4 or PF_6) have been prepared and their properties are discussed. Carbonyl and phosphine substitutions led to isolation of the species $[M(CO)(NO)L_3]^+$ [M = Ru, L_3 = $(PPh_3)_3$ or (PPh_3)dppe; M = Os, L_3 = $(PPh_3)_3$, $(PMePh_2)_3$, (PPh_3)dppe, or $(PPh_3)_2P(OMe)_3$] and $[M(NO)(dppe)_2]^+$ (M = Ru or Os). The reaction of $M(CO)(NO)(PPh_3)_2Cl$ with $AgPF_6$ in CH_2Cl_2/acetone followed by the addition of ligands (CO, PPh_3, or dppe) provides an alternate route to the cations $[M(CO)_2NO(PPh_3)_2]^+$ and $[M(CO)(NO)L_3]^+$. The cations $[M(CO)_2(NO)L_2]^+$ are oxidized by chlorine to produce *cis*- $M(CO)_2L_2Cl_2$ (M = Ru or Os) and $M(NO)L_2Cl_3$ (M = Ru); they react with halide ion (X^-) to give $M(CO)(NO)L_2X$ and with OMe^- to produce $M(CO)(NO)L_2(CO_2Me)$ (M = Os, L = PPh_3). Reduction of $[Os(CO)NO(PPh_3)_3]^+$ with BH_4^- yields the hydride $OsH(CO)NO(PPh_3)_2$. Possible structures for these complexes are discussed.

THE isolation and characterization of the iron-nitrosyl cations $[Fe(CO)_2NOL_2]^+$, $[Fe(CO)(NO)L_3]^+$, and $[Fe(NO)(dppe)_2]^+$ (where L = tertiary phosphine, dppe = 1,2-bisdiphenylphosphinoethane) were reported recently and their probable structures discussed.[1] Here we describe the preparation and some reactions of the corresponding ruthenium and osmium species. A preliminary account of this work [2] has been given and more recently others [3] have reported the results of an *X*-ray structural analysis of the salt $[Os(CO)_2(NO)(PPh_3)_2]$-ClO_4,CH_2Cl_2.

In Part VII [1] of this series treatment of the complexes $Fe(CO)_3L_2$ with $NOPF_6$ in benzene–methanol was reported to provide a convenient route to the cationic nitrosyl complexes $[Fe(CO)_2(NO)L_2]PF_6$. We now report that in contrast to this previous observation the reaction of analogous ruthenium and osmium derivatives $M(CO)_3(PPh_3)_2$ (M = Ru or Os) leads not to the expected cations $[M(CO)_2(NO)(PPh_3)_2]^+$ but rather to cationic hydrido-species $[MH(CO)_3(PPh_3)_2]^+$. This reaction must involve the initial formation of HPF_6 as follows:

$$NOPF_6 + MeOH \longrightarrow HPF_6 + MeONO$$

The ready formation of these hydrido-cations is in accord with the improved basic character of the $M(CO)_3(PPh_3)_2$ (M = Ru or Os) complexes as has been previously discussed.[2] The protonated species were also obtained as white crystalline salts by treatment of the tricarbonyl complexes with strong acids HX (X = PF_6, ClO_4, or BF_4) in ether. The hydrido-ions $[MH(CO)_3(PPh_3)_2]^+$ where M = Fe [4] or Os [5] have been reported previously.

As a consequence of this preferential formation of metal hydrides an alternative route to the required cations was sought. The use of different solvents such as methyl cyanide was of no value since although a reaction undoubtedly occurred nitrosyl derivatives were not produced. The observation that the trimeric systems $Ru_3(CO)_9L_3$ are readily cleaved by carbon monoxide under moderate pressure to produce the monomeric derivatives $Ru(CO)_4L$ led us to consider the possibility of generating nitrosyl cations by the cleavage of such trimers with NO^+. With $Ru_3(CO)_9(PPh_3)_3$ such a cleavage does take place and treatment of this trimer with $NOPF_6$ in methanol led to moderate yields of $[Ru(CO)_2(NO)(PPh_3)_2]PF_6$. A feature of this reaction is the generation of the bistriphenylphosphine cation rather than the expected tricarbonyl species $[Ru(CO)_3(NO)(PPh_3)]^+$. Related behaviour has been noted previously.[6] Thus, treatment of $Fe(CO)_4PPh_3$ with NOCl leads not to the expected tricarbonyl cation $[Fe(CO)_3(NO)(PPh_3)]^+$ but rather the dicarbonyl species $[Fe(CO)_2NO(PPh_3)_2]^+$. Similarly the nickel cation $[Ni(CO)(NO)(PPh_3)_2]^+$ which is produced from the reaction of $Ni(CO)_2(PPh_3)_2$ with $NOPF_6$ in toluene–methanol rapidly undergoes a disproportionation reaction in solution to yield $[Ni(NO)(PPh_3)_3]^+$.[7] In contrast the isoelectronic carbonyl complexes $Fe(CO)_4(PPh_3)$ and $Ni(CO)_2(PPh_3)_2$ do not undergo disproportionation and tend to resist further substitution. Presumably the presence of the formal positive charge together with the strong electron-withdrawing ability of the nitrosyl group in complex cations such as $[M(CO)_3(NO)(PPh_3)]^+$ labilizes the co-ordinated CO groups leading both to ease of substitution (see below and ref. 1) and also to disproportionation reactions.

The corresponding reaction of $Os_3(CO)_9(PPh_3)_3$ with $NOPF_6$ in benzene–methanol does not lead to nitrosyl derivatives, and in methyl cyanide both the ruthenium and osmium clusters give cationic carbonyl species. A more general route to the nitrosyl cations was therefore sought. Laing and Roper have reported that the hydridocarbonyl species $MHCl(CO)(PPh_3)_3$ (M = Ru [8] or Os [9]) undergo reaction with *N*-methyl-*N*-nitrosotoluene-4-sulphonamide (MNTS) in hot ethanol to produce the nitrosyl derivatives $M(CO)(NO)(PPh_3)_2Cl$. In these com-

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[1] Part VII, B. F. G. Johnson and J. A. Segal, *J.C.S. Dalton*, 1972, 1268.

[2] B. F. G. Johnson and J. A. Segal, *J. Organometallic Chem.*, 1971, **31**, C79.

[3] G. R. Clark, K. R. Grundy, W. R. Roper, J. M. Waters, K. R. Whittle, *J.C.S. Chem. Comm.*, 1972, 119.

[4] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 3653.

[5] K. R. Laing and W. R. Roper, *J. Chem. Soc.* (*A*), 1969, 1889.

[6] G. R. Crooks and B. F. G. Johnson, *J. Chem. Soc.* (*A*), 1968, 1238.

[7] S. Bhaduri, N. G. Connolly, and B. F. G. Johnson, *J. Organometallic Chem.*, 1972, **40**, C36.

[8] K. R. Laing and W. R. Roper, *J. Chem. Soc.* (*A*), 1970, 2149.

[9] K. R. Laing and W. R. Roper, *Chem. Comm.*, 1968, 1556.

plexes the chloride ion is labile and may be displaced by carbon monoxide in the presence of either sodium tetraphenylborate or sodium hexafluorophosphate to yield the required cations:

$$\mathrm{M(CO)NOL_2Cl + NaY \xrightarrow{CO/CH_2Cl_2} [M(CO)_2(NO)L_2]Y + NaCl}$$

$$[\mathrm{M = Ru\ or\ Os;\ L = PPh_3\ or\ PCy_3\ (Cy = cyclohexyl);\ Y = BPh_4\ or\ PF_6}]$$

Analogous derivatives containing the PCy_3 ligand were obtained similarly. The preparation of the complex M = Ru, L = PCy_3 necessitated the prior formation of the new hydrido-species $RuHCl(CO)(PCy_3)_2$ (see Experimental section). The salts produced by this route may be crystallized from dichloromethane and, when $Y = PF_6^-$ dichloromethane adducts $[M(CO)_2(NO)L_2]PF_6,CH_2Cl_2$ are formed.

The complexes are very reactive and are relatively unstable in solution. They decompose readily with gas evolution in several solvents which possess nucleophilic properties, *e.g.* MeCN, and in chloroform chlorination occurs. The lower stability of the ruthenium cations is indicated by their rapid decomposition in acetone and in neutral or basic alcohols, behaviour which is not observed with the osmium analogues. They are however stable and insoluble in acidified (HPF_6) alcohols and may be handled in a few solvents previously saturated with carbon monoxide. Characterization of the complexes follows from their i.r. data, microanalytical results (see Table), and conductivity measurements which correspond to values expected for 1 : 1 electrolytes in nitrobenzene. One NO and two CO stretching frequencies are observed in the i.r. spectra of these complexes, evidence consistent with the trigonal bipyramidal structure found[3] for $[Os(CO)_2(NO)(PPh_3)_2]^+$ and the neutral analogue $Mn(CO)_2(NO)(PPh_3)_2$.[10]

Colour, microanalytical, and i.r. spectroscopic data * (1500—2100 cm^{-1}) for the nitrosyl complexes

Compound	Colour	Found (%) C	H	N	P	Required (%) C	H	N	P	ν(CO)	ν(NO)
$[Ru(CO)_2(NO)(PPh_3)_2]BPh_4$	Cream	72·0	5·0	1·3	5·8	72·2	4·9	1·4	6·0	2065s, 2014vs	1765vs
$[Ru(CO)_2(NO)(PPh_3)_2]PF_6,CH_2Cl_2$ [a]	Orange	49·9	3·4	1·9	9·7	49·8	3·4	1·5	9·9		
$[Ru(CO)_2(NO)PCy_3)_2]BPh_4$	Cream	69·6	8·0	1·1	5·7	69·8	8·1	1·3	5·8	2043s, 1990vs	1736vs
$[Ru(CO)(NO)(PPh_3)_3]BPh_4$	Buff-yellow	74·8	5·1	1·1	7·1	75·0	5·2	1·1	7·3	1973s	1724vs
$[Ru(CO)(NO)(PPh_3)_3]PF_6$	Buff-yellow	60·3	4·2	1·4	11·1	60·6	4·2	1·2	11·4		
$[Ru(CO)(NO)(PPh_3)(dppe)]PF_6$	Brown	56·3	4·2	1·4	12·6	56·0	4·1	1·5	12·8	1983s	1728vs
$[Ru(NO)(dppe)_2]BPh_4,Me_2CO$	Red	72·5	5·5	0·9	9·8	72·7	5·7	1·1	9·5		1673vs †
$Ru(CO)(NO)(PCy_3)_2Cl$ [b]	Yellow	58·9	8·7	1·8	8·1	58·8	8·8	1·9	8·2	1920vs †	1580vs †
$[Os(CO)_2(NO)(PPh_3)_2]BPh_4$	Pink-cream	66·3	4·8	1·3	5·3	66·5	4·5	1·3	5·5	2055s, 1998vs	1748vs
$[Os(CO)_2(NO)(PPh_3)_2]PF_6,CH_2Cl_2$ [c]	Orange	45·3	3·2	1·1	9·0	45·5	3·1	1·4	9·0		
$[Os(CO)_2(NO)(PCy_3)_2]BPh_4$	Pink-cream	64·3	7·6	1·1	5·4	64·4	7·5	1·2	5·4	2034s, 1974vs	1721vs
$[Os(CO)(NO)(PPh_3)_3]BPh_4$	Light brown	70·0	4·8	1·0	6·7	70·1	4·8	1·0	6·9	1960s	1711vs
$[Os(CO)(NO)(PPh_3)_3]PF_6$	Light brown	55·9	4·1	1·1	10·5	56·0	3·8	1·2	10·5		
$[Os(CO)(NO)(PMePh_2)_3]BPh_4$	Orange-brown	66·1	5·2	1·1	8·0	65·8	5·1	1·2	8·0	1956s	1711vs
$[Os(CO)(NO)(PPh_3)_2P(OMe)_3]BPh_4$	Beige	63·4	5·1	1·0	7·4	63·2	4·9	1·2	7·6	1975s	1717vs
$[Os(CO)(NO)(PPh_3)(dppe)]BPh_4$	Light brown	67·7	4·9	1·1	7·6	67·5	4·8	1·1	7·6	1970s	1715vs
$[Os(CO)(NO)(PPh_3)(dppe)]PF_6$	Pink-brown	51·2	3·8	1·4	11·6	51·3	3·7	1·3	11·8		
$[Os(NO)(dppe)_2]BPh_4,Me_2CO$	Red	68·3	5·4	0·9	8·9	68·1	5·4	1·0	8·9		1671vs †
$Os(CO)(NO)(PCy_3)_2Cl$ [d]	Yellow	52·2	7·7	1·8	7·1	52·6	7·9	1·7	7·3	1905vs †	1555vs †
$Os(CO)(NO)(PPh_3)_2I$	Brown	49·1	3·6	1·7	6·8	49·4	3·4	1·6	6·9	1912vs †	1655vs †
$Os(CO)(NO)(PPh_3)_2CO_2CH_3$	Light brown	56·4	3·9	1·6	7·2	56·3	4·0	1·7	7·4	1911vs †, 1622s †‡ 1609s †‡	1648vs †
$OsH(CO)(NO)(PPh_3)_2$	Brown	57·6	4·2	1·7	7·8	57·4	4·0	1·8	8·0	1895vs †	1630vs †

Chlorine analyses (%). Found (Required) [a] 7 5(7·5); [b] 4·6(4·7); [c] 6·6(6·9); [d] 4·0(4·2).

dppe = 1,2-Bisdiphenylphosphinoethane.

* All measurements in CH_2Cl_2 solution unless stated otherwise. † Nujol mull. ‡ ν(CO) in CO_2Me function.

Unlike the isoelectronic complexes $Ru(CO)_3L_2$ and $Os(CO)_3L_2$ which resist substitution, further replacement of the carbonyl groups in the cationic complexes will occur on reaction with tertiary phosphine ligands. Thus, one of the carbonyl groups in the cation $[Os(CO)_2(NO)(PPh_3)_2^+$ is displaced by triphenylphosphine in hot acetone giving $[Os(CO)(NO)(PPh_3)_3]^+$. A similar reaction with the more basic phosphine $PMePh_2$ proceeds considerably faster and results not only in carbonyl substitution but also in replacement of the two triphenylphosphine ligands forming $[Os(CO)(NO)(PMePh_2)_3]^+$. A comparatively fast reaction also occurs with $P(OMe)_3$, without PPh_3 displacement, to produce $[Os(CO)(NO)(PPh_3)_2P(OMe)_3]^+$. Although $[Ru(CO)_2(NO)(PPh_3)_2]Y$ (Y = PF_6 or BPh_4) is unstable in acetone solution if dissolved in an acetone solution of triphenylphosphine then rapid substitution takes place leading to the isolation of $[Ru(CO)(NO)(PPh_3)_3]^+$. In these systems however, complete substitution of the carbonyl groups by mono tertiary phosphines was not observed and as is generally found with nitric oxide complexes displacement of the NO group does not occur. For the ruthenium cation $[Ru(CO)_2(NO)(PPh_3)_2]^+$ complete substitution of the CO groups was achieved by employing the chelating phosphine 1,2-bisdiphenylphosphinoethane (dppe) in hot acetone. The initial product of this reaction is $[Ru(CO)(NO)(PPh_3)dppe]^+$ but in the presence of an

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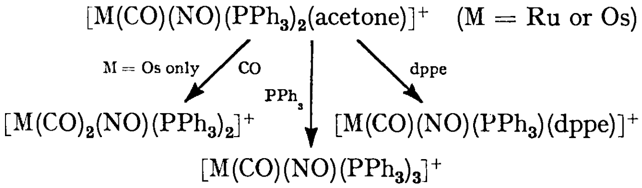
[10] J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 1575.

excess of dppe further reaction occurs and the cation $[Ru(NO)(dppe)_2]^+$ may be obtained. A similar reaction of $[Os(CO)_2(NO)(PPh_3)_2]^+$ leads only to the formation of $[Os(CO)(NO)(PPh_3)dppe]^+$. Further substitution is effected, however, in higher boiling solvents such as isobutyl methyl ketone provided that a large excess of dppe is also employed. By this method $[Os(NO)(dppe)_2]^+$ is obtained in good yield.

$$[M(CO)_2(NO)(PPh_3)_2]^+ \xrightarrow[\text{acetone}]{\text{dppe}} [M(CO)(NO)(PPh_3)(dppe)]^+ \xrightarrow{\text{dppe}} [M(NO)(dppe)_2]^+$$
$$(M = Ru \text{ or } Os)$$

In each case (M = Ru or Os) the salts $[M(NO)(dppe)_2]BPh_4$ were isolated as their acetone adducts as evidenced by their ^1H n.m.r. spectra which exhibited the expected $(CH_3)_2CO$ resonance in the correct intensity ratio. Under certain reaction conditions it is also possible to obtain dppe bridged dimers of the type previously observed with iron;[1] these products were not investigated further.

A more convenient route to certain of these cations has been employed. Treatment of $M(CO)(NO)(PPh_3)_2Cl$ (M = Ru or Os) with $AgPF_6$ in dichloromethane/acetone produces highly reactive yellow systems tentatively formulated as $[M(CO)(NO)(PPh_3)_2(acetone)]^+$ which readily react with additional ligands (L) to produce



trisubstituted derivatives. Attempts to isolate the intermediate acetone complex were not successful.

Recent *X*-ray crystal-structure determinations of the osmium complex[3] $[Os(CO)_2(NO)(PPh_3)_2]ClO_4,CH_2Cl_2$ and of the ruthenium complex[11] $[Ru(NO)(dppe)_2]BPh_4$, acetone indicate that both species possess essentially trigonal bipyramidal geometries (possibly a little more distortion exists in the dppe complex). Both structures also involve an essentially linearly bonded nitrosyl ligand located in the plane of the trigonal bipyramid. We suggest that this essential stereochemistry is maintained in all the species reported here * although the presence of three triphenylphosphine groups in $[M(CO)(NO)(PPh_3)_3]^+$ and of two dppe groups in $[Os(NO)(dppe)_2]^+$ will probably lead to greater distortion.

The reactions of the $[M(CO)_2(NO)L_2]^+$ cations have been examined and where possible compared with those observed for the iron system. As expected, these formally zerovalent d^8 metal complexes easily undergo oxidative reactions with halogens; behaviour in contrast to the iron species where only slow decomposition occurs. However, rather surprisingly, the ruthenium and osmium cations behave differently from one another. Thus, whereas reaction of $[Ru(CO)_2(NO)L_2]^+$ with chlorine produces predominantly $Ru(NO)L_2Cl_3$ together with a little *cis*-$Ru(CO)_2L_2Cl_2$ the corresponding reaction of $[Os(CO)_2(NO)L_2]^+$ produces the *cis*-dicarbonyl complex as the sole product. The formation of *cis*-$Ru(CO)_2L_2Cl_2$ in these reactions is unexpected in view of the considerable stability normally attributed to the derivatives of the $Ru(NO)^{3+}$ unit,[12] indeed the removal of co-ordinated NO is considered to be one of the major problems encountered in ruthenium chemistry.[13] The apparent ease by which NO is removed from the osmium system is less surprising and is consistent with the view that the M–NO bond strength decreases in going from ruthenium to osmium. For the ruthenium system i.r. evidence suggests that the initial product of the chlorine oxidation is $Ru(CO)(NO)L_2Cl$ which then reacts further to give $Ru(NO)L_2Cl_3$. Addition of hydrochloric acid to $[Os(CO)_2(NO)L_2]^+$ results in the formation of the previously reported[14] compound $Os(CO)(HNO)(PPh_3)_2Cl_2$.

For the reasons outlined earlier[1] the reaction of the cations with various nucleophiles was also investigated. Addition of halide ion (as Bu_4NX) to $[M(CO)_2(NO)L_2]^+$ in dichloromethane leads to attack at the metal centre giving the corresponding neutral halide $M(CO)(NO)L_2X$ (X = Cl or I). Chloride attack on $[Ru(CO)_2(NO)L_2]^+$ occurs so readily that it has proven to be a major problem in the isolation of this cation. In the presence of air the osmium cation $[Os(CO)_2(NO)(PPh_3)_2]^+$ reacts to give the carbonato-species $Os(CO_3)(NO)(PPh_3)_2Cl$ *via* the reaction sequence:

$$[Os(CO)_2(NO)(PPh_3)_2]^+ \xrightarrow{X^-} Os(CO)(NO)(PPh_3)_2X \xrightarrow{O_2} Os(CO_3)(NO)(PPh_3)_2X$$

Reaction with I^- in air proceeds similarly but more slowly. With methoxide ion reaction occurs at a co-ordinated carbonyl rather than the nitrosyl group and leads to the formation of the neutral carboxy-derivative

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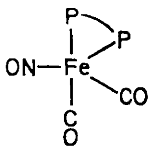
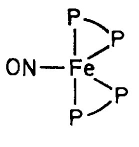
* In view of the crystal structures referred to above we now consider that the proposed geometries, presented in Part VII of this series,[1] for the species $[Fe(CO)_2(NO)(dppe)]PF_6$ (1) and $[Fe(NO)(dppe)_2]PF_6$ (2) should be revised as below. The change



(1)



(2)

in the relative intensity of the ν(CO) absorptions in going from $[Fe(CO)_2NO(PPh_3)_2]PF_6$ to $[Fe(CO)_2NO(dppe)]PF_6$ is easily explained using structure (1) above and it seems unlikely that any considerable stereochemical change of the type TBP to SP should occur amongst the complexes reported since the nitrosyl moiety in all these species is considered to be linearly bonded.

[11] C. G. Pierpont, A. Pucci, R. Eisenberg, *J. Amer. Chem. Soc.*, 1971, **93**, 3050.

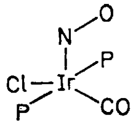
[12] W. P. Griffith, 'The Chemistry of the Rarer Platinum Metals,' Interscience, London, 1967, p. 174.

[13] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience, London, 1966, p. 995.

[14] K. R. Grundy, C. A. Reed, and W. R. Roper, *Chem. Comm.*, 1970, 1501.

$Os(CO)(NO)(PPh_3)_2(CO_2Me)$. In the ruthenium system i.r. evidence has been obtained for the formation of the corresponding carboxy-derivative at low temperatures but decomposition occurs readily under ambient conditions and no stable complex was isolated. This behaviour is in marked contrast to that shown by the analogous iron systems.[1] The osmium carboxyl exhibits a singlet at τ 7·27 in [^{1}H] n.m.r. spectrum (C_5D_5N) which is attributable to the OCH_3 protons and in the i.r. spectrum absorptions are seen at *ca.* 1615 cm^{-1} (νC=O) and *ca.* 1030 cm^{-1} (νC–O). As observed with the corresponding iron complex treatment with HPF_6 regenerates the cationic nitrosyl complex in virtually quantitative yield.

Although the BH_4^- reduction of $[Os(CO)_2(NO)(PPh_3)_2]^+$ does not give one simple derivative, a similar reaction with $[Os(CO)(NO)(PPh_3)_3]^+$ in tetrahydrofuran solution leads smoothly to the neutral hydrido-species $OsH(CO)(NO)(PPh_3)_2$.[3] At ambient temperatures the [^{1}H] n.m.r. spectrum (CD_2Cl_2) of this complex displayed a triplet upfield of Me_4Si. The multiplicity of this resonance must result from ^{31}P coupling, but it is possible that the observed signal is the product of an averaging effect caused by some rapidly exchanging system. Measurements at temperatures down to −80 °C provided no evidence of exchange broadening. These results suggest that the non-rigid behaviour of the complex $IrH(CO)_2(PPh_3)_2$ which exists in two rapidly interchanging forms,[15] does not extend to the isoelectronic osmium species. Several structures for this complex can be conceived on the basis of a trigonal bipyramidal arrangement[16] but analogy with the related cation $[IrCl(CO)(NO)(PPh_3)_2]^+$ [17] [see (A)] might *possibly* suggest a square-based pyramidal structure with a bent nitrosyl group.



(A)

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 grating instrument and ^{1}H n.m.r. spectra on a Perkin-Elmer R12 or a Varian Associates XL100 spectrometer at 60 or 100 MHz respectively. Mass spectra were recorded on an AEI MS12 spectrometer and microanalytical data (see Table) were determined by the Microanalytical Department of this Laboratory. The hydrides $MHCl(CO)(PPh_3)_3$ (M = Ru [8] or Os [9]) were prepared by previously reported methods and *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (MNTS) was obtained from B.D.H. Ltd. All reactions were carried out under an atmosphere of dry oxygen-free nitrogen.

Chlorohydridocarbonylbis(tricyclohexylphosphine)ruthenium(II).—A solution of ruthenium trichloride hydrate (0·54 g) and tricyclohexylphosphine (4·0 g) in 2-methoxyethanol (25 ml) was stirred under reflux for 48 h. The mixture was cooled and filtered to give an air-sensitive yellow solid (1·40 g) which was washed with pentane and dried *in vacuo* (Found: C, 61·1; H, 9·3; P, 8·3. $C_{37}H_{67}ClOP_2Ru$ requires C, 61·2; H, 9·3; P, 8·5%). I.r. spectrum (Nujol) ν(CO), 1907vs cm^{-1}. A parent ion is seen in the mass spectrum with *m*/*e*, 726 (^{35}Cl, ^{102}Ru) and the ^{1}H n.m.r. spectrum (CD_2Cl_2) shows a triplet at τ 34·6 (J_{PH}, 17·5 Hz).

The analogous osmium complex[18] was prepared similarly.

Chlorocarbonylnitrosylbis(tricyclohexylphosphine)ruthenium(0).—A suspension of $RuHCl(CO)(PCy_3)_2$ (0·120 g) and MNTS (0·055 g) in ethanol (4 ml) was stirred under reflux for 1 h. The solution was cooled and the yellow precipitate (0·105 g) was filtered off and washed with ethanol (2 × 2 ml). Two recrystallizations from dichloromethane–ethanol gave yellow crystals of the analytically pure material. This complex may also be purified by chromatography.

Chlorocarbonylnitrosylbis(tricyclohexylphosphine)osmuim(0) was prepared similarly.

Dicarbonylnitrosylbis(triphenylphosphine)osmium(0) *Tetraphenylborate.*—A suspension of $OsHCl(CO)(PPh_3)_3$ (1·04 g) and MNTS (0·34 g) in ethanol (30 ml) was stirred under reflux for 3 h. The resulting brown suspension was filtered off and taken up in dichloromethane (40 ml) with gentle warming to give a red solution. Sodium tetraphenylborate (0·34 g) in ethanol (3 ml) was added to this vigorously stirred solution which at the same time was saturated with carbon monoxide. The solution gradually became lighter in colour and somewhat cloudy as sodium chloride was precipitated. While maintaining carbon monoxide saturation as long as sodium chloride was present, the solution was filtered through Kieselguhr; the product crystallized upon addition of ethanol or ether. Filtration gave pink-white crystals (0·88 g) which could be recrystallized from dichloromethane and ethanol or ether under an atmosphere of carbon monoxide.

A similar preparation using $NaPF_6$ instead of $NaBPh_4$ gave *dicarbonylnitrosylbis(triphenylphosphine)osmium*(0) *hexafluorophosphate* as the dichloromethane solvate.

Dicarbonylnitrosylbis(triphenylphosphine)ruthenium(0) *tetraphenylborate* was prepared similarly. However in order to obtain this species in an analytically pure state all manipulations were carried out under carbon monoxide atmospheres and all solutions were saturated with this gas. This is necessary due to the general instability of the cation *in solution* and its ready loss of carbon monoxide in the presence of sodium chloride, a result of the readily occurring reverse reaction which gives the neutral precursor. All the ruthenium complexes are unstable in alcohols and recrystallization must be effected from dichloromethane–ether.

Dicarbonylnitrosylbis(triphenylphosphine)ruthenium(0) *hexafluorophosphate* was also obtained similarly, using $NaPF_6$, although in an impure state. The analytically pure material was obtained in lower yield as the dichloromethane solvate by recrystallization (×2) from dichloromethane–ether.

Analogous complexes containing tricyclohexylphosphine where prepared similarly.

Reaction of Nitrosonium Hexafluorophosphate with $Ru_3(CO)_9(PPh_3)_3$.—Deep red $Ru_3(CO)_9(PPh_3)_3$ (0·20 g) was

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[15] E. L. Muetterties, personal communication.

[16] See C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 1972, **11**, 1094; D. M. P. Mingos and J. A. Ibers, *ibid.*, 1971, **10**, 1479.

[17] D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 2345.

[18] F. G. Moers, *Chem. Comm.*, 1971, 79.

added to a solution of nitrosonium hexafluorophosphate (0·15 g) in methanol (6 ml). The suspension was stirred overnight causing a colour change to give the light buff hue of $[Ru(CO)_2(NO)(PPh_3)_2]PF_6$. The product (0·11 g) was filtered off and recrystallized from dichloromethane–ether as described above.

Protonation of Tricarbonylbis(triphenylphosphine)ruthenium(0).—A few drops of hexafluorophosphoric acid (60%) were added to a vigorously stirred suspension of $Ru(CO)_3(PPh_3)_2$ (0·5 g) in dry ether (6 ml). The suspension slowly decolourized and after 10 min it was filtered off to give a white product (0·51 g); this was washed with ether. Difficulty was encountered in purifying this material owing to its ready deprotonation, however a pure sample was obtained by recrystallization from slightly acidified (HPF_6) acetonitrile solution (Found: C, 54·5; H, 3·6; P, 11·0. $C_{39}H_{31}F_6O_3P_3Ru$ requires C, 54·8; H, 3·7; P, 10·9%). I.r. spectrum (Nujol): ν(CO) and ν(RuH) 2126m, 2076vs, 2056vs, and 2024m cm^{-1}. The ^1H n.m.r. spectrum (liquid SO_2) shows a high-field triplet at τ 16·2 (J_{PH}, 15·5 Hz integrating as 1 : 30 with the phenyl protons).

Carbonylnitrosyltris(triphenylphosphine)osmium(0) *Tetraphenylborate*.—A solution of $[Os(CO)_2(NO)(PPh_3)_2]BPh_4$ (0·040 g) and triphenylphosphine (0·055 g) in acetone (1·5 ml) was heated under reflux for 6 h. The solvent was evaporated from the cool solution and the resulting material was crystallized from dichloromethane–ether to give the product (0·034 g). Recrystallization may be effected from dichloromethane and ethanol or ether.

Carbonylnitrosyltris(triphenylphosphine)ruthenium(0) *tetraphenylborate* was prepared similarly using a 50% excess of triphenylphosphine. The cation was added to an acetone solution of the ligand, it being unstable in acetone alone. Gentle warming for 15 min completed reaction. Purification was difficult owing to the instability of the product in solution, however satisfactory analytical data was obtained after two recrystallizations from dichloromethane–ether.

Carbonylnitrosyltris(methyldiphenylphosphine)osmium(0) *Tetraphenylborate*.—A solution of methyldiphenylphosphine (0·135 g) and $[Os(CO)_2(NO)(PPh_3)_2]BPh_4$ (0·150 g) in acetone (6 ml) was heated under reflux for 30 min. The cool solution was evaporated and the resulting material was crystallized from dichloromethane–ethanol or ether to give the product (0·121 g).

Carbonylnitrosyltriphenylphosphine(1,2-*bisdiphenylphosphinoethane*)*osmium*(0) *tetraphenylborate* was prepared similarly.

Carbonylnitrosyl(trimethyl phosphite)bis(triphenylphosphine)osmium(0) *Tetraphenylborate*.—A solution of trimethyl phosphite (0·011 g) and $[Os(CO)_2(NO)(PPh_3)_2]BPh_4$ (0·050 g) in acetone (4 ml) was stirred at room temperature for 30 min. Addition of ether to the resulting solution gave the crystalline product (0·046 g) which was recrystallized from tetrahydrofuran–ether. ^1H N.m.r. spectrum (CD_2Cl_2): resonances at τ 2·55 and 3·15 (50H, broad multiplets, C_6H_5P and C_6H_5B) and 8·05 (9H, d, CH_3OP, J_{PH} 11·5 Hz).

Dicarbonylnitrosylbis(triphenylphosphine)osmium(0) *Hexafluorophosphate* (*Alternative Preparation*).—A suspension of $OsH(CO)Cl(PPh_3)_3$ (0·300 g) and MNTS (0·105 g) in ethanol (15 ml) was stirred under reflux for 3 h. The resultant brown suspension was filtered off and taken up in dichloromethane (25 ml) to give a red solution. Silver hexafluorophosphate (0·069 g) in acetone (1 ml) was added to the mixture causing an immediate colour change; after shaking for a few seconds [*] the resultant yellow solution was filtered into a flask cooled to −196 °C. This frozen solution was then allowed to warm up to room temperature under an atmosphere of carbon monoxide and was quickly saturated with this gas. The light orange solution obtained was reduced in volume and the product (0·210 g) was crystallized as described above.

Carbonylnitrosyltris(triphenylphosphine)osmium(0) *Hexafluorophosphate*.—The yellow solution, as obtained in the previous experiment, was filtered onto a solution of triphenylphosphine (0·120 g) in dichloromethane (6 ml). Evaporation followed by recrystallization from dichloromethane–ethanol gave the product (0·280 g) as crystals.

Carbonylnitrosyltriphenylphosphine(1,2-*bisdiphenylphosphinoethane*)*osmium*(0) *hexafluorophosphate* was obtained similarly.

The ruthenium hexafluorophosphate salts were obtained similarly but using very little or no acetone in the preparation of solutions containing the yellow intermediate species.

Nitrosylbis(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(0) *Tetraphenylborate*.—To a solution of dppe (0·050 g) in acetone (15 ml) was added $[Ru(CO)_2(NO)(PPh_3)_2]BPh_4$ (0·030 g). The resulting solution was heated under reflux for 2 h during which time a colourless to pink colour change was observed. The solution was reduced in volume after which ethanol was added to it; as the mixture was slowly cooled red crystals formed. The product (0·031 g) was filtered off and washed with ethanol and ether.

Nitrosylbis(1,2-*bisdiphenylphosphinoethane*)*osmium*(0) *Tetraphenylborate*.—A solution of $[Os(CO)_2(NO)(PPh_3)_2]BPh_4$ (0·060 g) and dppe (0·350 g) in isobutyl methyl ketone (16 ml) was heated under reflux for 6 h. The resulting pink solution was evaporated and the residual material was extracted with ether, leaving a pink solid (0·052 g). Crystallization of this material from acetone–ethanol gave the product as red crystals which were washed with ethanol and dried *in vacuo*.

Reaction of $[Os(CO)_2(NO)(PPh_3)_2]BPh_4$ *with Chlorine*.—A few drops of a solution of Cl_2 in CCl_4 (4% w/v) were added to a stirred solution of $[Os(CO)_2(NO)(PPh_3)_2]BPh_4$ (0·020 g) in dichloromethane (2 ml). The solvent was evaporated and methanol was added to the residue to give a white solid (0·014 g). Comparison of i.r. data with those of an authentic sample indicated formation of $Os(CO)_2(PPh_3)_2Cl_2$.[19] Recrystallization could be effected from chloroform–ethanol.

A similar reaction was observed for $[Os(CO)_2(NO)(PCy_3)_2]BPh_4$ giving $Os(CO)_2(PCy_3)_2Cl_2$; ν(CO) (Nujol) 2019vs and 1943vs cm^{-1}. Corresponding reactions with the analogous ruthenium cations gave a mixture of $RuNOL_2Cl_3$ and $Ru(CO)_2L_2Cl_2$ ($L = PPh_3$ or PCy_3), the nitrosyl complex being the substantially predominant portion of the mixture; ν(NO) (Nujol) $L = PPh_3$, 1877 vs cm^{-1} (lit.,[20] 1877 cm^{-1}); $L = PCy_3$, 1836vs cm^{-1}.

Reaction of $[Os(CO)_2(NO)(PPh_3)_2]BPh_4$ *with Tetra-n-butylammonium Iodide*.—Tetra-n-butylammonium iodide (0·018 g) was added to a stirred solution of $[Os(CO)_2(NO)(PPh_3)_2]BPh_4$ (0·050 g) in dichloromethane (6 ml). The solvent was evaporated and the residue was extracted with

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[*] Rapid removal of AgCl is essential at this stage otherwise decomposition of the complex occurs and metallic silver is produced.

[19] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, 1966, **88**, 3504.

[20] M. B. Fairy and R. J. Irving, *J. Chem. Soc.* (*A*), 1966, 475.

benzene (10 ml). Evaporation of the filtered benzene solution followed by recrystallization of the residual solid from dichloromethane–ethanol gave the product *iodocarbonylnitrosylbistriphenylphosphineosmium*(0) (0·035 g) which was washed with ethanol and dried *in vacuo*.

The corresponding osmium chloride and the ruthenium chloride and iodide complexes were prepared similarly and were all identified by comparison of their i.r. data with those of an authentic sample.[8,21] Similar behaviour was also found for the tricyclohexylphosphine cations with these halides.

Methoxycarbonylcarbonylnitrosylbis(triphenylphosphine)osmium(0).—A stirred suspension of $[Os(CO)_2(NO)(PPh_3)_2]BPh_4$ (0·090 g) in anhydrous methanol (4 ml) was treated with sodium methoxide in methanol solution (0·4M; 1 ml) previously prepared by the dissolution of clean sodium. During 30 min the stirred suspension gradually became light brown; it was then filtered off, washed on the sinter with methanol (2 × 2 ml), and dried; yield 0·059 g. ^1H N.m.r. spectrum (C_5D_5N) shows a singlet at τ 7·27 (CH_3OCO).

Hydridocarbonylnitrosylbis(triphenylphosphine)osmium(0).—Sodium borohydride (0·020 g) was taken up in dry tetrahydrofuran (5 ml) and $[Os(CO)(NO)(PPh_3)_3]PF_6$ (0·090 g) was added to it. The resulting suspension was stirred for 30 min giving a clear orange solution. Addition of an excess of ethanol to the mixture caused precipitation of a brown solid which was filtered off, washed with water and ethanol, and dried; yield 0·058 g. ^1H N.m.r. spectrum (CD_2Cl_2) shows a triplet at τ 15·04 (J_{PH}, 24 Hz).

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[21] K. R. Laing and W. R. Roper, *Chem. Comm.*, 1968, 1568.