Derivatives of Pentacarbonylnitratorhenium(I) with some Nitrogen, Phosphorus, and Arsenic Donor Ligands

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Reactions of pentacarbonylnitratorhenium(I) with pyridine (py), 2,2′-bipyridyl (bipy), 2,2′2″-terpyridyl (terpy), triphenylphosphine, and triphenylarsine yield the *fac*-disubstituted derivatives, $Re(CO)_3L_2NO_3$, in which the covalent metal–nitrate bond is retained. Tricarbonylnitratobis(triphenylphosphine)rhenium(I) has been shown to exhibit *fac–mer* isomerisation.

SUBSTITUTION reactions of the mononuclear carbonyl halides of manganese and rhenium fall into two classes: (*a*) those in which the metal–halogen bond is retained yielding complexes of the type $MX(CO)_{5-n}L_n$ (n usually 1 or 2), and (*b*) those in which the covalent metal–halogen bond is broken, yielding complexes of the type $[M(CO)_{6-n}L_n]X$ (n usually 2, L = unidentate ligand).[1] Pentacarbonylnitratomanganese(I) has been found to behave similarly.[2,3] The isolation of several type (*a*) derivatives of pentacarbonylnitratorhenium(I) with n = 2 and X = NO_3, described here, suggests that the rhenium–nitrate bond is at least as strong as that of its manganese analogue. Type (*b*) complexes or those of type (*a*) with n = 1 could not be isolated under any of the conditions employed.

TABLE 1

Analytical data and properties

Compound	M.p. (°C)	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N
fac-$Re(CO)_3(py)_2NO_3$ [a]	172	31·9	2·05	8·35	32·15	2·05	8·65
fac-$Re(CO)_3(bipy)NO_3$ [b]	274—276	32·9	1·65	8·75	32·9	1·65	8·7
fac-$Re(CO)_3(terpy)NO_3$ [b]	238	38·55	1·75	9·7	38·25	1·95	9·9
fac-$Re(CO)_3(PPh_3)_2NO_3$ [a]	171—172	54·95	3·65	1·7	54·6	3·5	1·65
mer-$Re(CO)_3(PPh_3)_2NO_3$ [c]	192—193	54·15	3·5	1·55	54·6	3·5	1·65
fac-$Re(CO)_3(AsPh_3)_2NO_3$ [a]	168	49·35	3·25	1·6	48·95	3·15	1·45

[a] Colourless. [b] Yellow. [c] Dark brown.

TABLE 2

I.r. carbonyl stretching and nitrate [a] vibrations (cm^{-1})

Complex	$\nu(CO)$ [b]	$\nu_{as}(NO_2)$ [c]	$\nu_s(NO_2)$ [c]	$\nu_s(N{-}O)$ [c]	$\pi(ONO_2)$ [c]
fac-$Re(CO)_3(py)_2NO_3$	2034s, 1930s, 1894s	1484s	1277s	996m	799w
fac-$Re(CO)_3(bipy)NO_3$	2035s, 1932s, 1884s	1476s	1279s	999m	800w
fac-$Re(CO)_3(terpy)NO_3$	2027s, 1937s, 1910s	1472s	1278s	996m	791w
fac-$Re(CO)_3(AsPh_3)_2NO_3$	2042s, 1963s, 1920s	1494s	1268s	998m	796w
fac-$Re(CO)_3(PPh_3)_2NO_3$	2039s, 1963s, 1916s	1474s	1270s	996m	798w
mer-$Re(CO)_3(PPh_3)_2NO_3$	2040w, 1944s, 1865s	1550s, 1540m, 1522s, 1512m	1239s	996s	*d*

[a] Assignments refer to C_s unidentate bonding. [b] $CHCl_3$ solution. [c] Nujol mull. [d] Not observed.

EXPERIMENTAL

The preparation of pentacarbonylnitratorhenium(I) and the methods of analysis for C, H, and N have been described previously.[4] I.r. spectra were recorded, with a Perkin-Elmer 521 spectrometer, for mulls in Nujol or halogenocarbon oil between silver chloride (4000—600 cm^{-1}) and polythene-protected caesium iodide (600—250 cm^{-1}) windows. Conductivity measurements were made by means of a Mullard conductivity bridge and a dip-type cell with bright platinum electrodes.

fac-$Re(CO)_3L_2NO_3$.—All compounds of this type (L = py, PPh_3, or $AsPh_3$, or L_2 = bipy or terpy) were prepared by heating mixtures of $Re(CO)_5NO_3$ with a slight excess of the ligand in ethanol under reflux for 2 h. The product crystallised either during refluxing or on cooling. The crystals were filtered off, washed with ether, and dried under vacuum at room temperature. Analytical data and properties are given in Table 1.

mer-$Re(CO)_3(PPh_3)_2NO_3$.—On heating *fac*-$Re(CO)_3(PPh_3)_2NO_3$ (m.p. 171—172°) to 180—190° at 10^{-2} mmHg for several hours, it was transformed into the microcrystalline *mer*-isomer (m.p. 192—193°). Similar treatment of *fac*-$Re(CO)_3(AsPh_3)_2NO_3$ (170°; 0·1 mmHg) brought about no change in either physical appearance or i.r. spectrum.

RESULTS AND DISCUSSION

The i.r. spectra of the complexes $Re(CO)_3L_2NO_3$ (L = py or L_2 = bipy) in the carbonyl stretching region (Table 2) are consistent with a *fac*-arrangement of carbonyl groups in an essentially octahedral co-ordination sphere.[2,3] Bands assigned to vibrations of the nitrate groups are similar in both position and intensity to those of $Re(CO)_5NO_3$,[4] for which *X*-ray structural studies[5] reveal a $Re{-}ONO_2$ unit of C_s local symmetry, *i.e.* unidentate nitrate bonding is involved. These complexes are therefore structurally similar to $M(CO)_3L_2X$ [M = Mn or Re, L_2 = $(py)_2$ or bipy, X = halogen] and

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[1] F. Calderazzo, 'Halogen Chemistry,' Academic Press, London, 1967, vol. 3, p. 383.

[2] C. C. Addison and M. Kilner, *J. Chem. Soc.* (*A*), 1966, 1249.

[3] C. C. Addison and M. Kilner, *J. Chem. Soc.* (*A*), 1968, 1539.

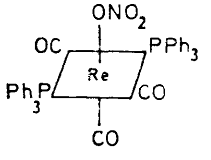
[4] C. C. Addison, R. Davis, and N. Logan, *J. Chem. Soc.* (*A*), 1970, 3333.

[5] J. Hilton and S. C. Wallwork, unpublished results.

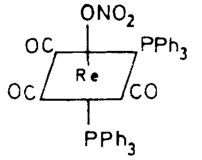
$Mn(CO)_3L_2NO_3$ [$L_2 = (py)_2$ or bipy].[1,2] The metal–nitrate bond in the latter two manganese compounds is relatively weak. The greater strength of the rhenium–nitrate bond is indicated by the observations that both the compounds $Re(CO)_3L_2NO_3$ [$L_2 = (py)_2$ or bipy] are stable in chloroform and nitromethane, and that no reaction occurs between PPh_3 and $Re(CO)_3(bipy)NO_3$ even on heating to 100° for 10 h in nitromethane. Reaction of $Re(CO)_5NO_3$ with 2,2′,2″-terpyridyl provides a further indication of rhenium–nitrate bond strength. The product could be formulated as either $[Re(CO)_3(terpy)]^+NO_3^-$ or $Re(CO)_3(terpy)NO_3$, with a bidentate terpyridyl group in the latter. However, the compound is a non-electrolyte in nitromethane solution and its i.r. spectrum (Table 2) is characteristic of a co-ordinated unidentate nitrate group. The spectrum in the carbonyl stretching region also suggests an overall co-ordination geometry which is the same as those of the pyridine and bipyridyl complexes. A complex of similar structure, $Mn(CO)_3(terpy)Cl$, has been reported.[6]

There are also differences between the extent of substitution of MPh_3 (M = P or As) into $Re(CO)_5NO_3$ and $Mn(CO)_5NO_3$. The rhenium compound reacts with 2 mol. equiv. of MPh_3 to produce *fac*-$Re(CO)_3(MPh_3)_2NO_3$ exclusively; *mer*-$Re(CO)_3(PPh_3)_2NO_3$ can be obtained by heating the *fac*-isomer. Attempts to prepare the monosubstituted complex $Re(CO)_4(AsPh_3)NO_3$ from equimolar quantities of $Re(CO)_5NO_3$ and $AsPh_3$ were unsuccessful; in chloroform solution no reaction occurred below 35°, and then only the *fac*-disubstituted complex was isolated. It has recently been demonstrated, however, that the complex $Re(CO)_4(PPh_3)NO_3$ can be prepared from $[Re(CO)_4PPh_3]_2$ and N_2O_4.[7]

Because the *fac*-form of $Re(CO)_3(PPh_3)_2NO_3$ contains no CO groups in *trans*-positions, this form retains the maximum metal–carbon bond strengths, and it is reasonable that this should be the form which is normally isolated. The presence of one weak and two strong bands in the carbonyl stretching region for the isomer produced on heating indicates that this is one of the *mer*-forms (I) and (II), and the greater separation of the two strong bands favours form (I). In this case the Re–C bonding opposite to the more weakly π-bonding NO_3 group is stronger (and hence the corresponding CO frequency, 1865 cm^{-1}, is lower) than when the CO group is *trans* to the PPh_3 ligand. The conditions of its formation (at 180°) also suggest that the isomer has the configuration (I) rather than (II). Relief of steric crowding of adjacent PPh_3 groups in the *fac*-form is then overcome, since PPh_3 groups are in *trans*-positions. With the $AsPh_3$ ligand, no *mer*-isomer is formed even on heating, possibly because of the greater metal–ligand π-bonding in this case.



(I)



(II)

The nitrate frequencies in the i.r. spectra of the three complexes $Re(CO)_3(MPh_3)_2NO_3$ (M = P or As), listed in Table 2, are again characteristic of unidentate bonding. In the case of *mer*-$Re(CO)_3(PPh_3)_2NO_3$ the wider separation of $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ indicates stronger bonding of the nitrate ligand; splitting of $\nu_{as}(NO_2)$ also occurs in this case.

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[6] M. C. Ganorkar and M. H. B. Stiddard, *J. Chem. Soc.*, 1965, 5346.

[7] R. Davis, *J. Organometallic Chem.*, 1972, **40**, 183.