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THE REACTIONS OF NITROSYL–PHOSPHINE COMPLEXES OF Co, Rh AND Ir WITH QUINONES AND SOME ACTIVATED OLEFINS

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SUMMARY

Compounds of formula $M(NO)(PPh_3)_2L$ where M = Co, Rh, Ir and L is an activated olefin or an *ortho*- or *para*-quinone, have been synthesised by the direct interaction of $M(NO)(PPh_3)_3$ with the ligands. The type of bonding between the metal atoms and the unsaturated ligands is discussed on the basis of IR and NMR spectra. The results obtained in the present work agree with the conclusions reached for the related bis(triphenylphosphine)platinum(0) complexes, previously described.

The reactivity of some of the new nitrosyl compounds towards small molecules has also been studied and compared to that of the related Pt^0 complexes.

INTRODUCTION

As a part of our investigations into the chemistry of triphenylphosphine derivatives of platinum(0), we have previously studied the interaction of $Pt(PPh_3)_3$ with activated olefins[1] and *ortho*- or *para*-quinones[2]. Our studies have shown that in the co-ordination of these complexes the most important factor affecting the nature of the metal–ligand bond is the π-back-bonding from the metal to the ligands (olefins or quinones). Recently some papers appeared mainly concerning oxidative addition reactions to nitrosyl complexes of general formula $M(NO)(PPh_3)_3$ (M = Rh, Ir)[3a,3b] or $M(NO)_2(PPh_3)_2$ (M = Ru, Os)[4a,4b], in which the metals are formally in a d^{10} configuration with −1 or −2 oxidation state respectively[5a], and some similarity with the behaviour of d^{10} complexes such as $Pt(PPh_3)_3$ was pointed out.

We have now investigated the interaction of nitrosyl–phosphine complexes $M(NO)(PPh_3)_3$ (M = Co, Rh, Ir) with ligands (L) such as activated olefins and *ortho*- and *para*-quinones. Our aim was to compare complexes of metals in a real d^{10} configuration [compounds such as $Pt(PPh_3)_2L$[1,2]] and in a formal d^{10} configuration [compounds such as $M(NO)(PPh_3)_2L$] in respect of the nature, stability, and reactivity of the metal–ligand (L) bond.

In this comparative study, the presence of the nitrosyl group in the compounds investigated is a point of particular interest. This interest arises from the controversial nature of the electronic structure of this molecule[6] and the possible deformations from linearity of the M–N–O angles[7], which could give a greater flexibility to the real electronic density and consequently to the π–σ donor–acceptor properties of the metals in these complexes than, for example, in the related (triphenylphosphine)platinum(0) derivatives[1,2].

Preparation, properties and reactivity

Complexes of formula $M(NO)(PPh_3)_2L$ (M=Co, L=maleic anhydride, fumaronitrile; M=Rh, L=maleic anhydride, tetracyanoethylene; M=Ir, L=maleic anhydride) are formed by interaction of $M(NO)(PPh_3)_3$ with the olefin. With tetra-

TABLE 1

ANALYTICAL DATA FOR COMPOUNDS OF FORMULA $M(NO)(PPh_3)_2L$

	M	L	Colour	M.p. (°C)	Analyses, found (calcd.) (%)			
					C	H	N	Mol.wt.[a]
(I)	Rh	1,4-Benzoquinone	Brown	205	65.00	4.31	1.66	
					(65.80)	(4.44)	(1.83)	(765)
(II)	Co	1,4-Naphthoquinone	Brown	200	68.71	4.32	1.73	
					(71.50)	(4.66)	(1.81)	(771)
(III)	Rh	1,4-Naphthoquinone	Red-brown	90 (dec.)	67.38	4.48	1.74	
					(67.60)	(4.41)	(1.72)	(815)
(IV)	Rh	2,3,5,6-Tetrachloro-	Brown	196	55.00	3.24	1.64	
		-1,4-benzoquinone			(55.70)	(3.32)	(1.55)	(903)
(V)	Rh	3,4,5,6-Tetrachloro-	Red-brown	165	54.93	3.40	1.46	1580[b]
		-1,2-benzoquinone			(55.70)	(3.32)	(1.55)	(903)
(VI)	Ir	3,4,5,6-Tetrachloro-	Pale-brown	183	54.28	3.36	1.44	
		-1,2-benzoquinone·(C_6H_6)			(54.00)	(3.36)	(1.31)	(1070)
(VII)	Rh	1,2-Naphthoquinone	Brown	115 (dec.)	66.88	4.56	1.71	
					(67.60)	(4.41)	(1.72)	(815)
(VIII)	Co	Maleic anhydride	Brown	122	66.57	4.38	1.78	
					(67.40)	(4.50)	(1.97)	(711)
(IX)	Rh	Maleic anhydride	Red-brown	143	63.30	4.34	1.91	636
					(63.40)	(4.24)	(1.85)	(755)
(X)	Ir	Maleic anhydride	Pale-orange	187	56.91	3.71	1.68	740
					(56.80)	(3.78)	(1.65)	(844)
(XI)	Co	Fumaronitrile	Deep-green	158	66.87	4.43	5.85	
					(69.40)	(4.62)	(6.06)	(691)
(XII)	Pt[c]	Fumaronitrile	Creamy-white	201	59.95	4.17	3.39	780
					(60.00)	(4.00)	(3.50)	(797)
(XIII)	Rh	Tetracyanoethylene	Pale-brown	193	63.73	3.65	9.04	790
					(64.10)	(3.82)	(8.90)	(785)
(XIV)	Rh	Carbon monoxide	Red	107	63.81	4.31	1.92	
					(64.6)	(4.37)	(2.04)	(685)

[a] $CHCl_3$ solution. [b] See text. [c] This compound corresponds to $Pt(PPh_3)_2$(fumaronitrile).

cyanoethylene a more complex reaction (M = Co, Ir) takes place in some cases, giving products which are under investigation. In the case of the reaction of fumaronitrile with $Rh(NO)(PPh_3)_3$ the product was different from that obtained by similar treatment of $Co(NO)(PPh_3)_3$. Its elemental analysis (see experimental) suggests a stoichiometry of the type: $Rh(PPh_3)_2(C_8N_4O_2H_x)$. Its nature is under investigation.

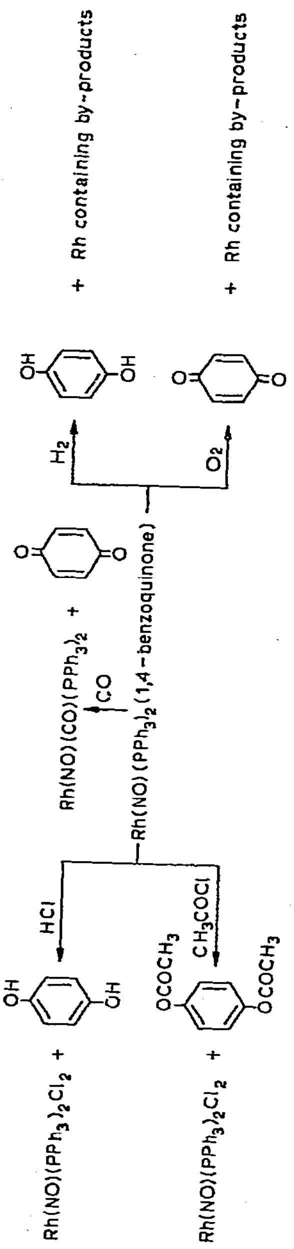
Complexes with *ortho*- and *para*-quinones, which can be regarded as derivatives of 1,4- or 1,3-cyclohexadiene respectively, were also prepared. Compounds of formula $M(NO)(PPh_3)_2L$ (M = Co, L = 1,4-naphthoquinone; M = Rh, L = 1,4-benzoquinone, 2,3,5,6-tetrachloro-1,4-benzoquinone, 1,4-naphthoquinone, 1,2-naphthoquinone, 3,4,5,6-tetrachloro-1,2-benzoquinone; M = Ir, L = 3,4,5,6-tetrachloro-1,2-benzoquinone) were obtained. With other olefins, such as acrylonitrile or methyl fumarate, or quinones such as 2,3,5,6-tetramethyl-1,4-benzoquinone, no reaction was observed using the same experimental conditions as for the other ligands reported above. On the other hand, when the reaction was carried out in solution, interaction obviously occurred but no characterisable materials could be isolated. The cobalt derivative with 1,4-naphthoquinone was the only cobalt–quinone compound we were able to prepare. In reaction with other quinones, complex mixtures of products were obtained, but they were not fully characterised. The iridium complexes, were more difficult to obtain owing to the low reactivity of $Ir(NO)(PPh_3)_3$, while the cobalt complexes were the most unstable towards air.

The compounds obtained are reported in Table 1 with the relevant analyses. $Pt(PPh_3)_2$(fumaronitrile) is described for the first time in the present work. For some of the cobalt derivatives, repeated analyses were done; the results reported in Table 1 are the best we found. As with all the other compounds, recrystallisation was unsuccessful. However, IR data (see later) were in agreement with the reported formulations. Except for the (tetrachloro-1,2-benzoquinone)rhodium compound, the quinone derivatives showed low values for their molecular weights when determined by osmometry. This could be due to a dissociation in solution, but an interaction with the solvent or with air is more likely, since these derivatives are particularly reactive (see later). The slight association in chloroform found for the (tetrachloro-1,2-benzoquinone)rhodium derivative, as in the case of the analogous platinum(0) derivative[2], cannot be easily explained. The olefin derivatives showed values of the molecular weights not too far from the theoretical values, possibly because of the lower reactivity of these compounds (see later).

We have investigated the reactivity of these complexes; in particular the reactivity of $Rh(NO)(PPh_3)_2$(1,4-benzoquinone) and $Rh(NO)(PPh_3)_2$(maleic anhydride) towards small molecules was studied. The results are summarized in Schemes 1 and 2.

$Rh(NO)(PPh_3)_2$(1,4-benzoquinone) (Scheme 1) readily reacts with molecules such as CO, H_2, and O_2, while the analogous platinum derivative is completely inert[2]. With carbon monoxide, the quinone ligand is readily displaced with formation of $Rh(NO)(CO)(PPh_3)_2$, previously unknown. Particularly interesting is the activation of hydrogen with reduction of benzoquinone to hydroquinone, which can be related to the recent report on the homogeneous catalytic hydrogenation of cyclohexene by $Rh(NO)(PPh_3)_3$[3a]. Real d^{10} systems, such as ML_4 (M = Ni, Pd, Pt), have never been found to be capable of activating molecular hydrogen at atmospheric pressure. This point emphasizes the importance of the nitrosyl group and makes more tenuous the comparison of these nitrosyl compounds with the platinum(0) derivatives. The

SCHEME 1



SCHEME 2

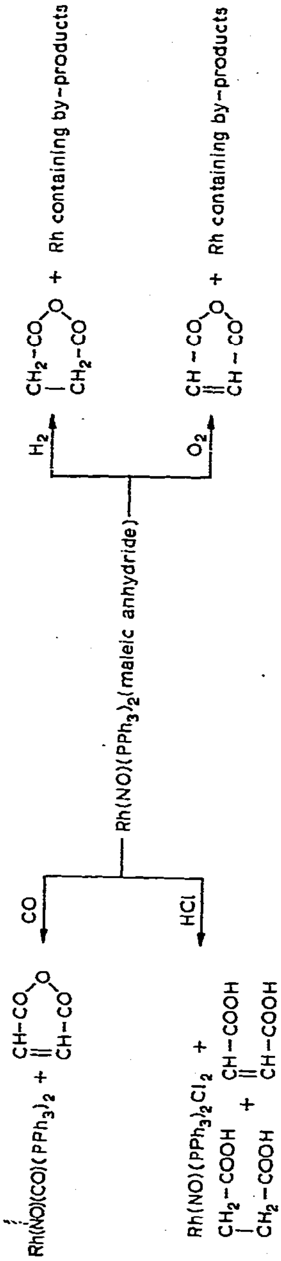


TABLE 2

IR STRETCHING FREQUENCIES FOR COMPOUNDS OF FORMULA $M(NO)(PPh_3)_2L$
L = quinone or olefin; nujol; cm^{-1}[a].

Compound	ν(NO)	ν(CO)	ν(CN)
(I)	1645	1615, 1582	
(II)	1705	1633, 1595(m)	
(III)	1667	1635, 1597(m)	
(IV)	1690	1665, 1630(m)	
(V)	1648	1423	
(VI)	1592	1425	
(VII)	1623	1433	
(VIII)	1700	1805, 1735	
(IX)	1630	1800, 1730	
(X)	1672	1813, 1750	
(XI)	1715		2212
(XII)[b]			2213
(XIII)	1650		2218
(XIV)	1670[c]	1972[c]	

[a] All bands are strong, unless otherwise stated. [b] This compound corresponds to $Pt(PPh_3)_2$(fumaronitrile). [c] CCl_4 solution.

reactions with gaseous HCl and with CH_3COCl probably follow a similar pattern, involving the hydride hydrogens or the acetyl groups bound to the metal[2]. An initial oxidative addition on the metal is required, followed by a subsequent reduction of the quinone moiety to hydroquinone or hydroquinone acetate. The reaction with oxygen and hydrogen gives rhodium-by-products which we were unable to identify, and in which NO was no longer present.

It is interesting to note that during the reaction with H_2, even when well-deoxygenated solvent was used some triphenylphosphine oxide was found in the reaction mixture, probably being formed through oxidation by nitric oxide[5b].

The reactions of $Rh(NO)(PPh_3)_2$(maleic anhydride) (Scheme 2) generally follow the pattern described above for the 1,4-benzoquinone derivative. With gaseous HCl, succinic acid was formed instead of the corresponding anhydride, probably because of the presence of traces of water. When all the reactions were carried out using exactly the same experimental conditions, the 1,4-benzoquinone compound reacted more rapidly than the maleic anhydride derivative.

Infrared spectra

As observed in the corresponding platinum(0) derivatives[2] the coordination of the ligand (L) is completely different in the *ortho*- and the *para*-quinone compounds. In fact, all the quinone complexes show a shift of the ν(CO) to lower wavenumbers, but with the derivatives of *para*-quinones this shift is small (ca. 50–20 cm^{-1}) (see Table 2), while with the *ortho*-quinone derivatives the shift is higher (ca. 250–300 cm^{-1}).

We assume that, as in the case of the platinum(0) compounds, in complexes of *para*-quinones there is no direct interaction of the carbonyl groups of the quinone moiety with the metal, but only a perturbation. On the contrary, in complexes derived from *ortho*-quinones the interaction with the metal occurs via the two *ortho* carbonyl groups, without interaction with the pseudo-butadiene-π-olefinic system[2]. This interpretation is confirmed by the NMR data (see later) and by some preliminary results on the X-ray structure of $Pt(PPh_3)_2$ (3,4,5,6-tetrachloro-1,2-benzoquinone)[8]. In this platinum complex the quinone moiety is bonded as an *ortho*-phenolate to the platinum atom in a square planar arrangement, the metal being oxidised from platinum(0) to platinum(II). In a recent study of the interaction of *ortho*-quinones with iridium(I) complexes, the same kind of bonding was found[9].

It is interesting to point out that, whereas the interaction of tetrachloro-1,4-benzoquinone with $Pt(PPh_3)_3$ gives an oxidative addition with abstraction of one chlorine atom from the quinone[2], in the case of the rhodium derivative the simple substitution product is obtained. This is confirmed by the IR spectrum (Table 2), in which the ν(CO) is shifted much more to lower wavenumbers than in the case of the platinum derivative, the shift being of similar magnitude to that in the other *para*-quinone compounds. Moreover the ν(CO) band is split after coordination into a doublet [$\Delta\nu$(CO) 35 cm^{-1}], which was not well resolved in the case of the platinum complex. In the former case this can be interpreted as arising from a strong π-back donation from the metal, with a relevant distortion of the ligand from planarity[10], while in the latter case there was only a perturbation of the quinone D_{4h} symmetry.

Finally, in the far IR spectrum no ν(Rh–Cl) bands were detected. The trend of the ν(NO) stretching frequencies in the quinone derivatives is not easily interpretable. The absorptions are higher in the substituted compounds $M(NO)(PPh_3)_2$(quinone) than in the starting materials $M(NO)(PPh_3)_3$, as one would expect since the ligands used are strong π-acceptor systems. The anomalous value for the (tetrachloro-1,2-benzoquinone)iridium derivative is not unusual for nitrosyl–iridium compounds; in fact the compounds $IrX_2(NO)(PPh_3)_2$ always show a ν(NO) lower than in $Ir(NO)(PPh_3)_3$ as a consequence of the distortion from linearity of the M–N–O bond angle[3b,7]. A change in the mode of nitrosyl bonding may also be involved in the *ortho*-quinone derivatives, while the *para*-quinone compounds probably have linear M–N–O arrangement. In view of the normal oxidation state of the metal and on the basis of the π-back donation, the ν(NO) band should be higher in the *ortho*-quinone compounds (where the metal is formally in the +1 oxidation state) than in the *para*-derivatives (where the metal is still in a −1 oxidation state), whereas the opposite is actually found. Also the different stereochemistry in the two series of compounds may be relevant, as the *ortho*-quinone derivatives presumably have a trigonal bipyramidal arrangement, while the *para*-quinone derivatives probably have a tetrahedral or a square pyramidal structure. Some X-ray structural investigations are in progress to clarify this problem. Nevertheless in the series of *para*-quinone compounds, the ν(NO) increases in the order: 1,4-benzoquinone < 1,4-naphthoquinone < 2,3,5,6-tetrachloro-1,4-benzoquinone, as would be expected on the basis of π-back donation arguments. Analogously, the ν(NO) is higher in the (tetrachloro-1,2-benzoquinone)-rhodium compound than in the 1,2-naphthoquinone derivative.

In the olefin complexes (Table 2) the C=O and C≡N groups are probably not direct involved in the π-coordination. In fact the absorptions due to these groups show a shift to lower wavenumbers of ca. 10–50 cm^{-1}. When these groups participate directly in the bonding with metal as a π-bonded pseudo-butadiene ligand, the shifts are higher, as previously discussed[1].

The absorption due to the double bond of the olefinic system involved in the coordination is not easily detectable in the IR spectrum, probably because it is shifted into the complex region below 1500 cm^{-1}, as a result of the decrease in the carbon–carbon bond order. These absorptions should also be weak, as the ligands used here are symmetrical and probably only slightly distorted by coordination[1].

The tetracyanoethylene and fumaronitrile derivatives show always shifts of the ν(CN) to lower wavenumbers after coordination, which may be taken as evidence for the coordination *via* the double bond of the cyano-olefins[11]. Furthermore, in the olefinic series of compounds the ν(NO) is higher in the substituted derivatives than in the starting materials, as expected.

Comparing the observed IR data with those for the corresponding platinum(0) derivatives[1,2], it appears that the ligands (L) have a similar electronic interaction (σ and π bonds) with the metal even though metals with presumably different "softness" are involved. In the compounds investigated here this probably comes about because of the presence of the nitrosyl group, which can assist the metal by adapting its electron donor–acceptor interaction to the actual electronic situation on the metal[3a]. For example, if one considers the series of compounds $M(NO)(PPh_3)_2$-(maleic anhydride) (M = Co, Rh) and $Pt(PPh_3)_2$ (maleic anhydride)[1], one finds that the carbonyl frequencies of the ligand (L) are nearly always in the same position (1725–1735 and 1800–1805 cm^{-1}), which indicates a rather similar metal–ligand electronic interaction (NMR data confirm this assumption; see later). In the case of M = Ir, the ν(CO) bands of the ligand are less perturbed after coordination. Moreover, this compound also shows marked differences in the IR spectrum for other ligand absorptions, whereas by contrast, the absorptions are rather similar for M = Co, Rh and Pt. This seems to suggest a different geometry for the coordinated maleic anhydride in the iridium compound. The nitrosyl stretching frequencies, however, lie in a wider range (from 1700 cm^{-1} in the cobalt derivative to 1635 cm^{-1} in the rhodium compound) than in the unsubstituted derivatives $M(NO)(PPh_3)_3$ for which the range is narrower (from 1633 cm^{-1} for cobalt to 1600 cm^{-1} for iridium)[3a,3b,12], suggesting that the nitrosyl group has a similar limiting maximum value of π-back donation, irrespective of the metal in the unsubstituted compounds.

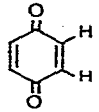
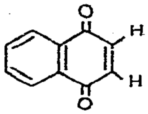
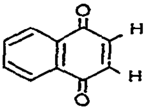
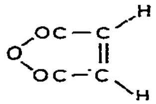
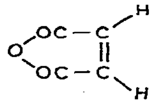
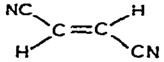
The same conclusions can be reached considering the series of compounds $M(NO)(CO)(PPh_3)_2$, in which the ν(CO) lie between 1940 and 1972 cm^{-1}, while the ν(NO) are between 1645 and 1714 cm^{-1} [5a]. Finally, in the series of compounds $Rh(NO)(PPh_3)_2L$, the ν(NO) increase in the order: PPh_3 < maleic anhydride < 1,4-benzoquinone < 1,4-naphthoquine ≃ carbon monoxide < tetracyanoethylene < 2,3,5,6-tetrachloro-1,4-benzoquinone, which could correspond to the increased π-acceptor capacity of the ligands.

NMR spectra

The ^1H NMR spectra of the complexes are reported in Table 3. The most important feature is the large shift to high field of the signals of the protons bound to the double bond of the olefins or of the *para*-quinone, which is typical of olefin-complexes of low valent transition metals[1]. These shifts are generally lower than those found in the related platinum(0) derivatives, but are still significant. Previously we have related the magnitude of this shift to the amount of π-back donation from the metal to the ligand[1,2]. On this basis, a significant π-back donation from the metal

TABLE 3

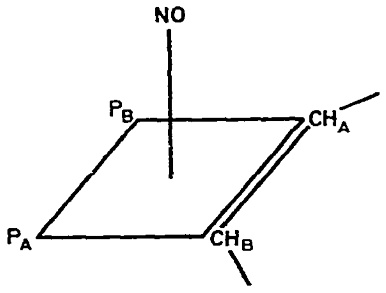
^{1}H NMR DATA[a] FOR COMPOUNDS OF FORMULA $M(NO)(PPh_3)_2L$ AND FOR THE CORRESPONDING FREE LIGANDS

M	Ligand	τ_H	Solvent
Rh		3.30 4.85	CCl_4 $CDCl_3$
Co		3.10 5.45 [doublet; $J(^{31}P–^1H) \simeq 6$ Hz]	CCl_4 C_6D_6
Rh		3.10 5.83	CCl_4 $CDCl_3$
Rh		2.90 5.98	CCl_4 $CDCl_3$
Ir		2.90 6.62 [doublet; $J(^{31}P–^1H) \simeq 7$ Hz]	CCl_4 C_6D_6
Pt[b]		3.65 7.50 [doublet; $J(^{31}P–^1H) \simeq 6$; $J(^{195}Pt–^1H) \simeq 60$ Hz]	$CDCl_3$ $CDCl_3$

[a] The upper value corresponds to the free ligands; fine structures not always well resolved were found, probably due to coupling with ^{31}P. [b] This compound corresponds to $Pt(PPh_3)_2$(fumaronitrile); its NMR spectrum is completely in accord with those of other platinum(0)–olefin complexes[11] already described.

must also be present in this series of compounds. Different geometries could also account for the differences in chemical shifts. The two protons involved in the coordination are equivalent, their signals appearing as doublets [$J(^{31}P–^1H) \simeq 6–7$ Hz; compounds (II) and (X)] or as broad singlets, complicated by fine structure. This fine structure can be attributed, in the case of rhodium complexes, to a coupling with ^{103}Rh which usually shows a small coupling[13]. The structure which probably explains this behaviour is shown in the figure; in a nearly square pyramidal arrangement with the metal on the basal plane, the proton H_A is coupled only with the phosphorus P_A in the *trans*-position while the proton H_B is coupled only with P_B. As in the case of the platinum(0)–maleic anhydride derivative[1], the coupling with the phosphorus in a *cis* position is not detectable.

In the other cases, the coordination around the metal is probably closer to a tetrahedral arrangement, which makes the coupling with the phosphorus in a pseudo-*trans*-position slightly weaker and the coupling with the phosphorus in a pseudo-*cis*-position slightly stronger[2]. In this way the signal can appear as a broad non-resolved singlet. However the broadness of the signal could be also due to a rotation or libration of the olefinic system around the metal–ligand axis. This second explanation is



less probable, such a solution never having been observed for low valent olefin complexes. Moreover the ^1H NMR spectrum of compound (IX) does not change on going from room temperature down to $-50°$.

In the case of the 1,4-benzoquinone derivative, repeated quantitative measurements of the relative areas of the peaks due to the phosphines and to the high field olefinic protons showed that only one double bond is involved in the coordination. The signal due to the two hydrogens of the double bond further away from the metal probably lies under the resonances due to the phosphines, in a region where the free ligand itself absorbs. This fact is related to a feature we pointed out above, namely that the absence of direct π-back donation from the metal does not greatly affect the resonance of the protons not involved in the coordination. Moreover, if both double bonds were bound to the metal, we should have a rather improbable penta-coordination of the metal, which is still in a d^{10} configuration. In the case of $Pt(PPh_3)_2$ (benzoquinone), *both* the double bonds were involved in the tetrahedral coordination around the metal atom.

In the complex derived from 1,2-naphthoquinone the hydrogens of the unsaturated system did not show any appreciable shift to high field, confirming once more that the interaction with the metal occurs *via* the two *ortho*-carbonyl groups[2].

CONCLUSIONS

From the spectroscopic properties of the complexes here investigated it is clearly demonstrated that the metals can be considered as "flexible" d^{10} systems, with the $-M(NO)(PPh_3)_2$ moiety acting as a "flexible" donor base towards differently demanding strong π-acids such as activated olefins and quinones. With *ortho*-quinones the charge transfer from the metal is probably higher, as in the related platinum(0) compounds[2], and the complexes must be considered as derivatives of metals in a $+1$ oxidation state. The more marked reactivity of these compounds compared with that of platinum(0) derivatives cannot be explained simply by a weaker metal–ligand (L) bond, as it is clear that a similar σ–π interaction is present in these nitrosyl complexes and in related $Pt(PPh_3)_2L$ compounds. As previously suggested in the discussion of the reactivity of these nitrosyl derivatives, this difference could perhaps be better accounted for in terms of different kinetic behaviour associated with the presence of the nitrosyl group, which seems to be able readily to change the electronic density on the metal. This view agrees with the very different kinetic behaviour of $Ni(CO)_4$ and $Co(NO)(CO)_3$ in their substitution reactions, the former following a S_N1 mechanism[14] and the latter a S_N2 mechanism[15].

EXPERIMENTAL

All the reactions were carried out under nitrogen at room temperature, with stirring, but the work-up of reaction mixtures was carried out in the air. Dry solvents were used. Some of the ligands were purified before use (see below). Melting points were determined on a Leitz Heiztischmikroskop and were not corrected. Molecular weights were measured on a Mechrolab Osmometer. IR spectra were recorded with Perkin–Elmer 457 and 621 grating spectrometers. Proton NMR spectra were recorded with a Varian-100 instrument and with a Perkin–Elmer R-10 spectrometer operating at 60 Mc, using tetramethylsilane as internal standard. All the NMR spectra were recorded with the samples under a nitrogen atmosphere. Some of the compounds, as previously pointed out, reacted, even under nitrogen, with chlorinated solvents, which are the only solvents in which they are sufficiently soluble and no NMR data are thus available. The compounds and their relevant analytical data are reported in Table 1; other properties are given in the same Table.

Preparation of starting materials

$Rh(NO)(PPh_3)_3$ and $Ir(NO)(PPh_3)_3$ were prepared as previously reported briefly[16a,16b]. While this paper was in preparation, the full report of the syntheses of these compounds appeared[3b,17].

$Co(NO)(PPh_3)_3$. Hydrated cobalt dichloride (1.0 g) in ethanol (50.0 ml), *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (3.6 g) and solid sodium borohydride (0.6 g) were added in rapid succession to a well-stirred solution of triphenylphosphine (6.0 g) in boiling methanol (150.0 ml). The mixture was heated under reflux for 1 h and filtered while hot; the violet microcrystalline precipitate was successively washed with boiling ethanol, hot water, methanol, and n-hexane, and then dried *in vacuo*. (Found: C, 72.9; H, 5.05; N, 1.47. $C_{54}H_{45}NOP_3Co$ calcd.: C, 74.0; H, 5.14; N, 1.6%.) This compound had an IR spectrum and a m.p. identical to those already reported[12].

Nitrosylbis(triphenylphosphine)(1,4-benzoquinone)rhodium (I)

To a suspension of $Rh(NO)(PPh_3)_3$ (370.0 mg) in diethyl ether (40 ml) solid *para*-benzoquinone (87.0 mg) was added. After 3 h the violet-brown compound was filtered off, washed with diethyl ether and dried *in vacuo*.

Nitrosylbis(triphenylphosphine)(1,4-naphthoquinone)cobalt (II)

To a suspension of $Co(NO)(PPh_3)_3$ (584.0 mg) in diethyl ether (40.0 ml), solid 1,4-naphthoquinone (previously crystallised from ligroin) (211.0 mg) was added. The mixture was stirred for 5 h. A brown compound was then filtered off, washed with diethyl ether and dried *in vacuo*.

Nitrosylbis(triphenylphosphine)(1,4-naphthoquinone)rhodium (III)

This reaction was carried out as for (II), except that a longer reaction time was used (24 h).

Nitrosylbis(triphenylphosphine)(2,3,5,6-tetrachloro-1,4-benzoquionone)rhodium (IV)

Solid tetrachloro-1,4-benzoquinone (104.0 mg) was added to a suspension of $Rh(NO)(PPh_3)_3$ (200.0 mg) in diethyl ether (50 ml). After 4 h the brown product was filtered off, washed with a little diethyl ether and dried *in vacuo*.

Nitrosylbis(triphenylphosphine)(3,4,5,6-tetrachloro-1,2-benzoquinone)rhodium (V)

This compound was prepared under the conditions used for (IV).

Nitrosylbis(triphenylphosphine)(3,4,5,6-tetrachloro-1,2-benzoquinone)iridium (VI)

To a suspension of $Ir(NO)(PPh_3)_3$ (800.0 mg) in diethyl ether (30 ml) and benzene (5 ml), solid tetrachloro-1,2-benzoquinone (105.0 mg) was added. After 24 h the brown-green compound was filtered off, washed with diethyl ether and dried *in vacuo.*

Nitrosylbis(triphenylphosphine)(1,2-naphthoquinone)rhodium (VII) „

This compound was prepared as (V) using $Rh(NO)(PPh_3)_3$ (250.0 mg) and 1,2-naphthoquinone (46.0 mg).

Nitrosylbis(triphenylphosphine)(maleic anhydride)cobalt (VIII)

To a suspension of $Co(NO)(PPh_3)_3$ (300.0 mg) in diethyl ether (40.0 ml) recrystallised maleic anhydride (50.0 mg) was added. After 1 h the brown compound was filtered off, washed with diethyl ether and dried *in vacuo.*

Nitrosylbis(triphenylphosphine)(maleic anhydride)rhodium (IX)

The red compound was prepared using the conditions used for (VIII).

Nitrosylbis(triphenylphosphine)(maleic anhydride)iridium (X)

To a suspension of $Ir(NO)(PPh_3)_3$ (182.0 mg) in diethyl ether (40.0 ml) and benzene (5.0 ml), solid maleic anhydride (53.0 mg) was added. After 24 h the pale-orange product was filtered off, washed with diethyl ether and dried *in vacuo.*

Nitrosylbis(triphenylphosphine)(fumaronitrile)cobalt (XI).

To a suspension of $Co(NO)(PPh_3)_3$ (670.0 mg) in diethyl ether (50.0 ml) and benzene (5.0 ml), solid fumaronitrile (79.0 mg) was added. After 24 h the deep green product was filtered off, washed with diethyl ether and dried *in vacuo.*

Bis(triphenylphosphine)(fumaronitrile)platinum(0) (XII)

To a suspension of $Pt(PPh_3)_3$[18] (450.0 mg) in n-hexane (50.0 ml) solid fumaronitrile (46.0 mg) was added. After 3 h the creamy-white compound was filtered off, washed with diethyl ether and n-hexane and dried *in vacuo.*

Nitrosylbis(triphenylphosphine)(tetracyanoethylene)rhodium (XIII)

To a solution of $Rh(NO)(PPh_3)_3$ (228.0 mg) in toluene (50.0 ml) solid, freshly sublimed, tetracyanoethylene (64.0 mg) was added. After 2 h the palebrown precipitate was filtered off, washed with a little toluene and diethyl ether and dried *in vacuo.*

Nitrosylcarbonylbis(triphenylphosphine)rhodium (XIV)

Carbon monoxide was bubbled through a suspension of $Rh(NO)(PPh_3)_3$ (220.0 mg) in n-hexane. After 4 h a brick-red product was filtered off, washed several times with n-hexane and dried *in vacuo.* This compound is rather unstable in solution; osmometric molecular weight determinations were always lower than the theoretical values.

Bis(triphenylphosphine)(tetracyanoethylene)platinum(0)

This compound, already described in the literature[11], was prepared by this improved synthesis. To a suspension of $[Pt(PPh_3)_2(CH_2{=}CH_2)]$[19] (270.0 mg) in diethyl ether (30.0 ml), solid tetracyanoethylene (70.0 mg) was added. After 2 h the creamy-white product was filtered off, washed with diethyl ether and dried *in vacuo*. Its IR spectrum and m.p. were identical to those reported.[11]

Reaction of $Rh(NO)(PPh_3)_3$ with fumaronitrile

To a suspension of $Rh(NO)(PPh_3)_3$ (484.0 mg) in n-hexane (50.0 ml), solid fumaronitrile (103.0 mg) was added. After 24 h a yellow-green product was filtered off, washed with a little ethanol and n-hexane and then dried *in vacuo*. m.p. 107°. (Found: C, 63.98; H, 4.13; N, 6.65; O, 3.56%.)

Reactivity of $Rh(NO)(PPh_3)_2$(1,4-benzoquinone) towards CO, H_2, HCl and CH_3COCl

The organic materials recovered from the reaction mixtures were always identified using IR and NMR spectroscopy.

(*a*). *With CO.* Carbon monoxide was bubbled through a N_2 degassed suspension of [$Rh(NO)(PPh_3)_2$(1,4-benzoquinone); compound (I)] (120.0 mg) in n-hexane (50.0 ml). After 2 h a brick-red product was filtered off, washed with diethyl ether and dried *in vacuo*. This material was shown to be $Rh(NO)(CO)(PPh_3)_2$ from its IR spectrum. In the mother liquor 1,4-benzoquinone was present.

(*b*). *With O_2.* Oxygen was bubbled through a suspension of (I) (210.0 mg) in diethyl ether (40.0 ml). After 24 h the suspended material was filtered off. Its IR spectrum did not show the presence of a nitrosyl group. The free quinone was obtained from the filtrate.

(*c*). *With H_2.* Hydrogen was slowly bubbled through a suspension of (I) (155.0 mg) in well-deoxygenated n-hexane (70.0 ml). After 3 days the brown suspension was evaporated to dryness and the residue washed several times with water. The IR spectrum of the brown solid material did not show the presence of NO groups. Hydroquinone was identified in the water.

(*d*). *With HCl.* Gaseous HCl was bubbled through a suspension of (I) (200.0 mg) in diethyl ether (40.0 ml). After 1 h the pale-brown product was filtered off, washed with diethyl ether and dried *in vacuo*. It was shown to be $Rh(NO)(PPh_3)_2Cl_2$ by means of its IR spectrum. The ethereal filtrate was shown to contain hydroquinone.

(*e*). *With CH_3COCl.* Acetyl chloride (1 ml) was added to a suspension of (I) (230 mg) in diethyl ether (50.0 ml). After 1 h $Rh(NO)(PPh_3)_2Cl_2$ was filtered off and hydroquinone diacetate was shown to be present in the mother liquor.

Reactivity of $Rh(NO)(PPh_3)_2$(maleic anhydride) towards O_2, H_2, CO, HCl

The organic materials recovered from the reaction mixtures were always identified using IR and NMR spectroscopy.

(*a*). *With O_2.* This reaction was carried out using the conditions described for the 1,4-benzoquinone derivative. The presence of maleic anhydride was noted in the mother liquor.

(*b*). *With CO.* The reaction was carried out for 24 h in benzene solution. Maleic anhydride was identified in the residue.

(*c*). *With H_2*. This reaction was also carried out in benzene solution. The residue was shown to contain succinic anhydride.

(*d*). *With HCl.* Ethanol (40.0 ml) was saturated with gaseous HCl and Rh(NO)-$(PPh_3)_2$(maleic anhydride) (230.0 mg) was added. After 2 h (Rh(NO)$(PPh_3)_2Cl_2$ was filtered off. The filtrate was shown to contain maleic and succinic acids.

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