PREPARATION AND REACTIONS OF NITROSYL–TETRAZENE DERIVATIVES OF Rh AND Ir

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SUMMARY

Compounds of formula $[M(NO)(PPh_3)(N_4R_2)]$ (I) (M=Rh, Ir; R=SO$_2$-C$_6$H$_4$CH$_3$) have been obtained by the interaction of $M(NO)(PPh_3)_3$ with *p*-toluene-sulphonyl azide in benzene. These new compounds are formulated as tetrazene derivatives on the basis of chemical and spectroscopic data. They react with ligands, L, (*e.g.* CO, PPh$_3$) to give pentacoordinated species of formula $[M(NO)(PPh_3)-(L)(N_4R_2)]$.

The tetrazene derivatives yield the new nitrosyl compounds, $M(NO)(PPh_3)Cl_2$ (II) on treatment with HCl, the nitrogen-containing residue being converted into RN$_3$ and RNH$_2$ species. The compounds (II) are coordinatively unsaturated, and react with ligands L in the same manner as compounds (I), giving new derivatives of formula M(NO)(PPh$_3$)(L)Cl$_2$.

IR and NMR spectra of the new compounds are reported and discussed. The presence in solution of a structure in which the chelate tetrazene ring has opened {*e.g.* [M(NO)(PPh$_3$)(NR)(N$_3$R)]} is suggested by NMR studies.

INTRODUCTION

The reaction of Pt(PPh$_3$)$_3$ with organic azides was studied in our laboratories[1]. From reactions in non-polar solvents, compounds of formula Pt(PPh$_3$)$_2$(N$_4$R$_2$) (R=SO$_2$C$_6$H$_4$CH$_3$, SO$_2$C$_6$H$_5$) were isolated, and it was suggested that these compounds could be either tetrazene derivatives or bis-azo compounds. More recently, a series of azo–platinum compounds of formula $[Pt(PPh_3)_3-N=N-C_6H_4-R]^+$ (BF$_4^-$) was isolated[2]. Their chemical behaviour was completely different from that of the Pt(PPh$_3$)$_2$(N$_4$R$_2$) complexes (see later), indicating that the latter are not bis-azo compounds.

In continuation of our investigations on the reactions of unsaturated organic systems towards d^{10} derivatives such as Pt(PPh$_3$)$_3$, we have now studied the reactions of formally d^{10} derivatives such as M(NO)(PPh$_3$)$_3$ (M=Rh, Ir) with organic sul-

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phonyl azides. The close similarity between the reactions of the triphenylphosphine derivatives of platinum (0) and those of the formally rhodium (−I) and iridium (−I) nitrosyl compounds has already been pointed out[3], and has been confirmed in the present investigation.

RESULTS AND DISCUSSION

Preparation and properties of $[M(NO)(PPh_3)(N_4R_2)]$ *(I)*

From the reaction of $M(NO)(PPh_3)_3$ complexes (M = Rh, Ir) with *p*-toluene-sulphonyl azide in dry benzene, compounds of formula $[M(NO)(PPh_3)(N_4R_2)]$ (Table 1) have been obtained [eqn. (1)]. Although $Co(NO)(PPh_3)_3$ reacts under these experimental conditions, no characterizable compounds were obtained.

$$M(NO)(PPh_3)_3 + 4 RN_3 \rightarrow M(NO)(PPh_3)(N_4R_2) + 2 Ph_3P=NR + 3 N_2 \quad (1)$$
$$(I)$$
$$(M = Rh, Ir; R = SO_2C_6H_4CH_3)$$
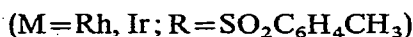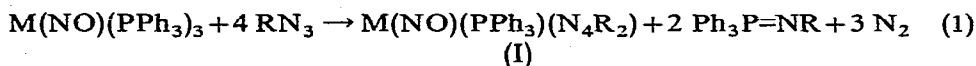
The compounds of type (I) showed a fairly high reactivity. In particular, with gaseous HCl in dry diethyl ether, the organic moiety was completely displaced, with
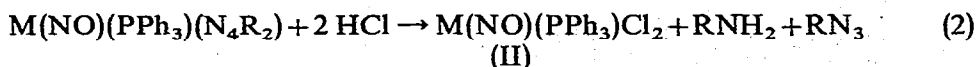
TABLE 1

ANALYTICAL DATA

| Compound[a]		Colour	M.p. (°C)	Analyses, found (calcd.)(%)		
				C	H	N
(Ia)	$[(PPh_3)Rh(NO)(N_4R_2)]$	Violet	148	50.3 (50.4)	3.7 (3.8)	8.9 (9.2)
(Ib)	$[(PPh_3)Ir(NO)(N_4R_2)] \cdot C_6H_6$	Light brown	161	49.4 (49.0)	3.74 (3.76)	7.4 (7.5)
(IIa)	$(PPh_3)Rh(NO)Cl_2$	Orange	>260	46.6 (46.2)	3.12 (3.22)	2.71 (3.0)
(IIb)	$(PPh_3)Ir(NO)Cl_2$	Brown	>240	38.5 (39.0)	2.43 (2.7)	2.45 (2.52)
(IIIa)	$[(PPh_3)_2Rh(NO)(N_4R_2)]$	Deep brown	132	58.9 (58.6)	4.4 (4.3)	6.5 (6.8)
(IIIb)	$[(PPh_3)_2Ir(NO)(N_4R_2)]$	Red-orange	142	53.8 (54.0)	3.92 (3.96)	6.01 (6.27)
(IVa)	$[(PPh_3)(CO)Rh(NO)(N_4R_2)]$	Light brown	155	49.95 (50.02)	3.46 (3.68)	8.53 (8.88)
(IVb)	$[(PPh_3)(CO)Ir(NO)(N_4R_2)]$	Light green	162	44.86 (45.0)	3.0 (3.3)	7.76 (7.97)
(V)	$(PPh_3)(CO)Rh(NO)Cl_2$	Yellow-green	>230	45.4 (46.0)	2.93 (3.03)	2.84 (2.81)
(VI)	$(PPh_3)(Py)Rh(NO)Cl_2$	Brown-orange	184–186	49.90 (50.06)	3.51 (3.67)	4.95 (5.14)
(VII)	$(PPh_3)(SbPh_3)Rh(NO)Cl_2$	Brick red	192	52.3 (52.8)	3.67 (3.65)	1.7 (1.7)
(VIII)	$(PPh_3)(Py)_2Ir(NO_2)Cl_2$	Cream	198	44.8 (46.0)	3.1 (3.43)	5.3 (5.75)

[a] $R = SO_2C_6H_4CH_3$ for all compounds.

formation of the corresponding azide and amide [eqn. (2)]. The compounds of type (II)

$$M(NO)(PPh_3)(N_4R_2) + 2 HCl \rightarrow M(NO)(PPh_3)Cl_2 + RNH_2 + RN_3 \qquad (2)$$
$$\text{(II)}$$

are easily obtained from this reaction (Table 1).

It has already been found[4] that by reaction of a tetrazene derivative such as π-$C_5H_5Co(N_4R_2)$ (R = C_6H_5) with HCl, the nitrogenated ring is transformed into the corresponding amide, while the azide was not detected, probably because it was converted into RNH_2 under the reaction conditions. This seems to be a rather general reaction of the tetrazenic ligand when bound to a metal, and we have observed the same reaction in the case of the platinum derivative [eqn. (3)]. This unexpected ring

$$Pt(PPh_3)_2(N_4R_2) + 2 HCl \rightarrow Pt(PPh_3)_2Cl_2 + RNH_2 + RN_3 \qquad (3)$$
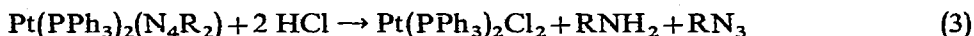
opening suggests that the organic moiety may be present in the Rh, Ir and Pt derivatives as a tetrazene ring (α), stabilized by coordination on the metal, but in equilibrium with open forms such as (β), in which the chelate ring has been broken:

$$(\beta) \qquad\qquad (\alpha) \qquad\qquad (\beta) \qquad\qquad (4)$$
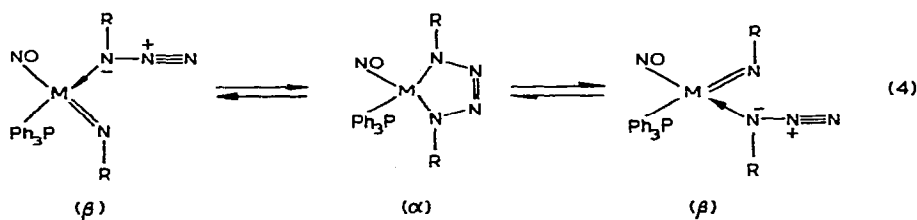
A structure corresponding to a bis-azo derivative is not consistent with the reaction with HCl reported above.

X-ray crystallography of related compounds has shown[5] that the form (α) is probably the only one present in the solid state. Consistently the IR spectra (Table 2) of the compounds (I) show a nitrosyl absorption $v(NO)$ at around 1850–1900 cm^{-1}

TABLE 2

IR (NUJOL, cm^{-1}) AND ^{1}H NMR (CDCl$_3$, ppm) DATA

Compound[a]	M	$v(NO)$	$v(CO)$	$v_{as}(SO_2)$	$v_s(SO_2)$	$v(N-S)$	$\tau(CH_3)$
(Ia)	Rh	1890		1340	1165	920, 875	7.67
(Ib)	Ir	1890		1355	1170	940, 875	7.65
(IIa)	Rh	1690					
(IIb)	Ir	1950					
(IIIa)	Rh	1765		1315	1150	940, 910	7.77
(IIIb)	Ir	1750	—	1325	1160	940, 910	7.75
(IVa)	Rh	1700	2090	1335	1165	915, 900	7.65, 7.70
(IVb)	Ir	1645	2080	1345	1170	925, 900	7.64, 7.70
(V)	Rh	1690	2090				
(VI)	Rh	1640					
(VII)	Rh	1615					

[a] Compound (VIII) which analyses as $(PPh_3)(Py)_2Ir(NO_2)Cl_2$, has an IR spectrum with bands at 1390, 1325 and 835 cm^{-1} assignable to a nitrogen-bonded NO_2 group (see text).

TABLE 3

METHYL RESONANCES FOR DIFFERENT ARRANGEMENTS OF THE $SO_2C_6H_4CH_3$ RESIDUE

Compound[a]	$[Ir(NO)(PPh_3)(N_4R_2)]$ (room temperature)	$[Ir(NO)(PPh_3)(N_4R_2)]$ $< -50°$	$Ph_3P=NR$	N_3R
$\tau(CH_3)$[b]	7.65 (A)	7.54 (B), 7.71 (C)	7.73 (D)	7.56 (E)
$\Delta\tau$	A−E=0.09	C−B=0.17	D−E=0.17	E−B=0.02

[a] $R=SO_2C_6H_4CH_3$. [b] $CDCl_3$ as solvent.

in the solid state, but no bands assignable to a metal bonded RN_3 species. The bands characteristic of N–S and SO_2 stretching modes are in the expected positions (Table 2). However, the chemical behaviour supports an equilibrium with open species such as (β), in agreement with our observation that the single NMR peak of the methyl group observed at room temperature collapses at low temperature, and, in the case of the iridium compound, gives place to two distinct signals (Table 3) at temperatures lower than −50°. On raising the temperature, the single peak reappears, as expected for a fast exchange equilibrium between an open and closed ring. The chemical shifts of the two peaks obtained at low temperatures are consistent with (β) forms: the two methyl signals are well separated ($\Delta\tau$ 0.17), while the methyl resonances of the tolyl residue are rather insensitive to the nature of the moiety to which they are bound. In the phosphinimino adduct (Table 3) a substantial $\Delta\tau$ with respect to free azide was observed. In agreement with this, the two methyl signals in the iridium compound at low temperature are closer to the resonances of free azide and the phosphinimino adduct (Table 3) [$\Delta\tau$(D−E) 0.17], and an average value is observed at room temperature*.

    In compounds (I), the absorptions ν(NO) are at rather high values and this allows us to say confidently that the nitrosyl ligand is present as linear NO^+ [6]. Nevertheless, it is difficult to describe the oxidation state of the metal in tetrazene derivatives[5], because the organic moiety can be considered either as a bis-σ-ligand or as a ligand forming two-electron dative bonds from the 1,4 positions of the tetra-azadiene group. This problem appears to be rather similar to that involving the bonding formed by a ligand such as butadiene, discussed by Mason in terms of contributions to the bond of the excited state of the diene[7]. Thus we cannot assign any reasonable oxidation state to the metal, and consequently it is difficult to define a structure for compounds (I).

Reactions of $[M(NO)(PPh_3)(N_4R_2)]$ *with donor ligands*

    Compounds (I) react easily with ligands L such as PPh_3 and CO, even under heterogeneous conditions, forming pentacoordinated species of formula $[M(NO)-(PPh_3)(L)(N_4R_2)]$ (Table 1). The compounds (IIIa) and (IIIb) (L = PPh_3) are probably the products formed initially in reaction (1). By treating $Ir(NO)(PPh_3)_3$ with a stoichiometric amount of azide we succeeded in isolating such a compound, whilst in the presence of excess azide the extra phosphine ligand is easily displaced as a phos-
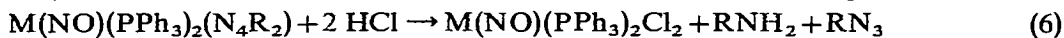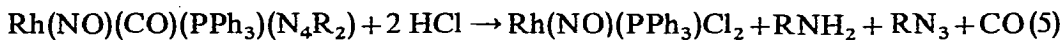
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* A more accurate investigation on the temperature variation of the NMR spectra of the tetrazene derivatives is in progress, in collaboration with Dr. L. Cavalli, Montecatini–Edison S.p.A.

phinimino derivative and the reaction product is (Ib). The carbonylation reaction of (I) must be conducted in the presence of a small amount of benzene. In this case compounds (I) clathrate a benzene molecule, forming more reactive crystalline intermediate species, whose ν(NO) absorptions lie some 10 cm^{-1} lower than those of (I) (Nujol mull). These clathrated forms can be obtained by washing compounds (I) with a little benzene and can be reconverted into the non-solvated forms by prolonged stirring in n-hexane. As expected, the solution IR spectra (e.g. in CHCl$_3$) of both forms show identical NO stretching frequencies.

Compound (Ia) easily reacts also with bases such as pyridine. However in this case we were unable to obtain the pure pentacoordinated adduct. Repeated elemental analyses and ^{1}H NMR spectra showed that the product was probably a mixture of [Rh(NO)(PPh$_3$)(Py)(N$_4$R$_2$)] and [Rh(NO)(Py)$_2$(N$_4$R$_2$)].

The CO molecule is weakly bound in compound (IVa). This complex slowly reverts to compound (Ia) even in solid state. This gas evolution is greatly accelerated in vacuo (1 mmHg). However when M = Ir, loss of CO was not observed. Carbon monoxide is easily displaced by PPh$_3$ (M = Rh) with formation of (IIIa). In the case of M = Ir, a mixture of compounds is obtained, among which [Ir(NO)(CO)(PPh$_3$)$_2$-(N$_4$R$_2$)] is probably present, together with [Ir(NO)(PPh$_3$)$_2$(N$_4$R$_2$)].

Compounds (IIIa) and (IV) react with HCl in a similar way to compounds (I) [eqns. (5) and (6)].

$$Rh(NO)(CO)(PPh_3)(N_4R_2) + 2\ HCl \rightarrow Rh(NO)(PPh_3)Cl_2 + RNH_2 + RN_3 + CO \quad (5)$$

$$M(NO)(PPh_3)_2(N_4R_2) + 2\ HCl \rightarrow M(NO)(PPh_3)_2Cl_2 + RNH_2 + RN_3 \quad (6)$$

In the reaction (5), the carbon monoxide is also displaced during the reaction with HCl, but in reaction (6) the known M(NO)(PPh$_3$)$_2$Cl$_2$ compounds were obtained rather than M(NO)(PPh$_3$)Cl$_2$.

The pentacoordinated species show a ν(NO) absorption notably lower than in the starting materials (Table 2) because of the increased electronic density on the metal due to the presence of the fifth ligand. At the same time the ν(CO) frequencies are very high [ca. 2100 cm^{-1}, compounds (IVa), (IVb)], and lie in a region which has been taken as an indication for an oxidation state + 3 for the metal[8]. However, as we have already pointed out, the concomitant presence of the tetraazadiene and NO ligands renders meaningless any discussion of the actual oxidation state of the metal in these compounds. In the compounds (III), only one methyl resonance could be detected in the NMR spectra. The high-field shift of the methyl peak with respect to the free azide is, in general, very low (ca. τ 0.2) (Table 2), as for compounds (I).

When the fifth ligand L is a group other than PPh$_3$ [compounds (IVa), (IVb)], two methyl signals of equal intensity and very similar τ value were always detected in the NMR spectra (Table 2). It seems reasonable to assume that this trend is a consequence of the asymmetry of the metal coordination, in which the two ligands, PPh$_3$ and L, introduce a slightly different chemical environment about the two methyl groups of the tetrazadiene ring. An interpretation in terms of a slow equilibrium (4) makes it difficult to explain why such an equilibrium is not detectable when L = PPh$_3$. Moreover, when L = PPh$_3$ we were unable to obtain two methyl signals even by lowering the temperature to $-60°$. This seems to imply that for these compounds the closed form of the tetrazene ring is the major form present in solution at room temperature.

Properties and reactions of $M(NO)(PPh_3)Cl_2$

Compound (IIa) showed in the far IR spectrum (Nujol mull) two bands at 348 and 340 cm^{-1}, assignable to terminal Rh–Cl stretchings. Two other absorptions were detected at 290 and 250 cm^{-1}. However, Rh(NO)(PPh$_3$)$_2$Cl$_2$, which presumably has a monomeric structure analogous to the corresponding iridium derivative[6], also showed these two absorptions, together with only one terminal v(Rh–Cl) at 340 cm^{-1}.

Repeated molecular weight measurements in CHCl$_3$ gave values about twice those expected for compound (IIa) (Found: 950, 1025, 1030). However the yellow material recovered from the CHCl$_3$ solution did not show any v(NO) in the IR spectrum, whilst some new bands, probably attributable to an NO$_3$ group, were detected. We believe that compound (IIa) is an unsaturated monomeric species, easily oxidised in solution to form a dimeric NO$_3$ derivative. The latter has not been further investigated.

A monomeric structure for compounds (II) seems to be also supported by the ready reaction of these compounds with ligands L (see Experimental). Compounds (II), showed a similar reactivity to that of compounds (I) with respect to ligands L such as CO, PPh$_3$, SbPh$_3$. With these ligands, pentacoordinated species of formula M(NO)(PPh$_3$)(L)Cl$_2$ (Table 1) were obtained. The danger of considering the variations of v(NO) (Table 2) in terms of the basicity of the added ligands is illustrated dramatically by the values of v(NO) in compounds (II), M(NO)(PPh$_3$)Cl$_2$, where v(NO) changes from 1950 cm^{-1} (M = Ir) to 1690 cm^{-1} (M = Rh). Thus by changing only the metal atom in two complexes of the same stoichiometry, we can have two extreme values of v(NO), probably corresponding to a different mode of bonding of the NO molecule.

However, it is relevant to point out that in the carbonyl derivative (V), the v(NO) value is practically unchanged with respect to the starting material (IIa), whilst v(CO) is very high (Table 2), as in the case of compounds (IV). The same behaviour was observed for the two derivatives Rh(NO)(PPh$_3$)$_2$Cl$_2$ and Rh(NO)(CO)-(PPh$_3$)$_2$Cl$_2$[8]. This seems to imply a rather weak interaction between the metal and carbon monoxide in the rhodium derivative (V).

The product of the carbonylation of the iridium derivative (IIb) was studied only by means of IR spectroscopy, and it showed a pattern similar to (V) [v(NO) 1950, v(CO) 2080 cm^{-1}]. It has already been suggested that the high value of v(CO) in Rh(NO)(CO)(PPh$_3$)$_2$Cl$_2$ [v(CO) 2080 cm^{-1}][8] is probably a consequence of the strong σ-bonding *trans* influence of the presumed *trans* NO$^-$ group [v(NO) 1630 cm^{-1}]. However in our case, while when M = Rh [v(NO) 1690 cm^{-1}] we may have the same type of situation, when M = Ir [v(NO) 1950 cm^{-1}] the nitrosyl ligand is definitely present as NO$^+$, which corresponds to a metal in a formal +I oxidation state; this electronic situation does not agree with the latter interpretation, invoking the trans influence. When L = Py, the expected pentacoordinated adduct (VI) was obtained in the case of rhodium whilst the iridium derivative did not react easily. In this latter case the course of the reaction showed a marked sensitivity also to the small amount of oxygen probably present under our experimental conditions, and by conducting the reaction in an oxygen atmosphere, a compound analysing as Ir(NO$_2$)-(PPh$_3$)(Py)$_2$Cl$_2$ (VIII) was obtained (Table 1). This compound did not show any band assignable to v(NO) in the IR spectrum. The absorptions, which we attribute to the

NO_2 group, were found at 1390, 1325 and 835 cm^{-1} (Table 2), and lie in a region which is usually taken to be evidence for the presence of an NO_2 group bound to the metal through nitrogen[9]. The same absorptions were observed in the mixture recovered when the reaction was carried out over a long period under nitrogen without rigorous exclusion of oxygen; the absorptions of the unreacted material were also present.

Reactions of M(NO)(PPh₃)₃ in other solvents and with different organic azides

In our studies on zerovalent platinum triphenylphosphine complexes, we have observed a completely different reaction towards sulphonyl azides in a polar protic solvent such as ethanol. Similarly, in the case of the nitrosyl complexes investigated here (M = Co, Rh), we have observed that in ethanol a completely different reaction pattern takes place with *p*-toluene sulphonyl azide. (We did not observe any reaction at room temperature for M = Ir). However we were unable to characterise the reaction products of the Co and Rh nitrosyl, which appear to be mixtures of different compounds. These decomposed when purification by column chromatography was attempted. The crude reaction mixtures, which are not properly crystalline, show broad IR absorption bands at around 2100–2150 cm^{-1}, indicating that a N_3 group is present, and that an oxidative addition to the substrate has been the main reaction.

Less reactive azides such as benzoyl azide do not react under nitrogen with $Rh(NO)(PPh_3)_3$ in benzene as solvent. However, in presence of oxygen, reaction takes place rather quickly, with formation of a green material in which N_3, NO and CO groups are present (IR evidence). In the IR spectrum no bands assignable to the NO_2 group were found. The presence of N_3 was confirmed by carbonylation, which gave a light green compound, the IR spectrum of which showed a band at about 2200 cm^{-1} assignable to an NCO group. At the moment, in spite of elemental analyses, we cannot assign a definite formulation to these compounds, and this reaction needs more investigation.

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. Except for compounds (I), all the derivatives were obtained in good yields. With compounds (I) a large amount of the product is lost in each case during the purification from the phosphinimino adduct (see below), owing to its partial solubility in organic solvents such as benzene or acetone.

$Rh(NO)(PPh_3)_3$ and $Ir(NO)(PPh_3)_3$ were prepared as described in the literature[10]. IR spectra were recorded with Perkin–Elmer model 457 and 621 instruments. ^1H NMR spectra were recorded under nitrogen in $CDCl_3$, with a Perkin–Elmer R-10 instrument operating at 60 MHz and on a Varian-100 instrument, and with tetramethylsilane as internal standard. Melting points were determined on a Leitz Heiztischmikroskop, and are not corrected.

Elemental analyses were carried out by the Analytical Laboratories of Milan University (Table 1).

{(PPh₃)Rh(NO)[N₄(SO₂C₆H₄Me)₂]} (Iₐ)

To a solution of *p*-toluene sulphonyl azide (1.35 g) in benzene (40 ml) Rh(NO)-

(PPh$_3$)$_3$ (1.5 g) was added with stirring. Gas evolution was noted. After 12 h the violet precipitate was filtered off and washed with a little benzene. The Ph$_3$P=NSO$_2$C$_6$-H$_4$Me was removed by repeated washing with a little acetone/benzene (1/2).

{(PPh$_3$)Ir(NO)[N$_4$(SO$_2$C$_6$H$_4$Me)$_2$]} · C$_6$H$_6$ (Ib)
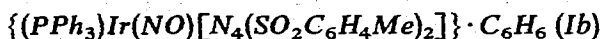
To a suspension of Ir(NO)(PPh$_3$)$_3$ (2.0 g) in benzene (50 ml) *p*-toluene sulphonyl azide (2.3 g) was added with stirring. Slow gas evolution was noted. After 24 h the light brown precipitate was filtered off and washed with benzene. In order to remove the phosphinimino Ph$_3$P=NSO$_2$C$_6$H$_4$Me completely, the precipitate was washed with benzene/acetone. (see Ia).

### [(PPh$_3$)Rh(NO)Cl$_2$] (IIa)
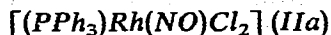
Dry HCl was slowly bubbled for 5 min through ethyl ether (40 ml), and (Ia) (0.2 g) was then added with stirring. The orange compound formed rapidly, and was quickly filtered off, washed with ether, and dried *in vacuo*. The mother liquor was evaporated to dryness, and the oily residue was extracted with hot water. On cooling, white H$_2$NSO$_2$C$_6$H$_4$Me precipitated, and was identified by its IR spectrum. The insoluble material was shown to be N$_3$SO$_2$C$_6$H$_4$Me by its IR spectrum.
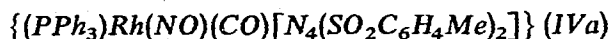
[(PPh$_3$)Ir(NO)Cl$_2$] (IIb)
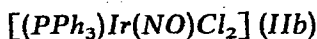
The brown compound was prepared as described for (IIa), a longer reaction time (15 min) being necessary. Again the mother liquor contained sulphonyl azide and sulphonyl amide.

{(PPh$_3$)$_2$Rh(NO)[N$_4$(SO$_2$C$_6$H$_4$Me)$_2$]} (IIIa)
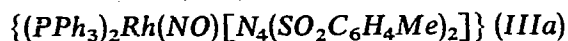
(Ia) (0.2 g) was added to a solution of PPh$_3$ (0.28 g) in ethyl ether. A brown compound rapidly formed, and was filtered off, washed several times with ether, and dried *in vacuo*.

{(PPh$_3$)$_2$Ir(NO)[N$_4$(SO$_2$C$_6$H$_4$Me)$_2$]} (IIIb)
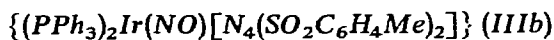
The red-orange compound was prepared as described for (IIIa).

### {(PPh$_3$)Rh(NO)(CO)[N$_4$(SO$_2$C$_6$H$_4$Me)$_2$]} (IVa)

Carbon monoxide was bubbled through a suspension of (Ia) in n-hexane containing a little benzene (ratio 10/1), until the suspended solid became brown-coloured (7–8 h). The brown compound was then filtered off and dried for a few minutes. (This compound loses CO easily, as indicated in the Discussion.)

{(PPh$_3$)Ir(NO)(CO)[N$_4$(SO$_2$C$_6$H$_4$Me)$_2$]} (IVb)
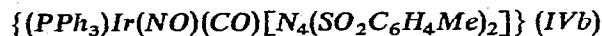
The light-green compound was prepared as described for (IVa), a longer reaction time being necessary (15 h)

[(PPh$_3$)Rh(NO)(CO)Cl$_2$] (V)
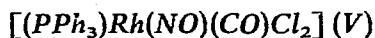
CO was bubbled for 1 h through a suspension of (IIa) (0.15 g) in n-hexane/ether (60 ml; 4/1). The yellow-green compound was filtered off and dried *in vacuo*.

(PPh$_3$)Rh(NO)(Py)Cl$_2$ (VI)
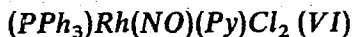
An ethereal solution of pyridine (0.3 ml) was added to a suspension of (IIa)

(0.1 g) in ethyl ether (40 ml) with stirring. After 30 min the brown compound was filtered off, washed several times with ether and dried *in vacuo.*

$(PPh_3)Rh(NO)(SbPh_3)Cl_2$ *(VII)*

SbPh$_3$ (0.3 g) was added with stirring to a suspension of (IIa) (0.13 g) in ethyl ether (40 ml). After 4 h, the brick red compound was filtered off, washed with ether, and dried *in vacuo.*

$(PPh_3)Ir(Py)_2(NO_2)Cl_2$ *(VIII)*

By conducting the reaction as for (VI), a mixture of compounds was obtained after many hours (see text). When the reaction was carried out in the air, compound (IIb) quickly changed into a cream material, which was filtered off, washed with ether, and dried *in vacuo.*

Other reactions

(*a*). *(IIIa)* + *HCl.* Dry HCl was bubbled through an ethereal suspension of (IIIa). After 2 h the suspended solid was filtered off and washed with ether. It was identified as $(PPh_3)_2Rh(NO)Cl_2$ by its IR spectrum and melting point. The presence of $N_3SO_2C_6H_4Me$ and $H_2NSO_2C_6H_4Me$ was detected in the filtrate [see (IIa)].

(*b*). *(IIIb)* + *HCl.* Dry HCl was bubbled through chloroform for 15 min and then (IIIb) was introduced. The resulting yellow-green solution was stirred for 1 h, then evaporated to dryness and the residue was treated with ether. $(PPh_3)_2Ir(NO)Cl_2$ was recovered as an insoluble product, and identified by its IR spectrum, while *p*-toluenesulphonyl azide and *p*-toluenesulphonyl amide were detected in the mother liquor [see (IIa)].

(*c*). *(IIa) or (IIb)* + *PPh$_3$.* (IIa) or (IIb) was added with stirring to an ethereal solution of PPh$_3$. After ca. 1 h, the compound was filtered off and washed with ether. It was identified as $(PPh_3)_2Rh(NO)Cl_2$ or $(PPh_3)_2Ir(NO)Cl_2$ by its IR spectra.

(*d*). *(IVa)* + *PPh$_3$.* (IVa) was added with stirring to a benzene solution of PPh$_3$. Fast gas evolution was noted. After 30 min the brown solution was evaporated to dryness, and the residue treated with ether. The ether-insoluble compound was identified as (IIIa) by its IR spectrum.

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