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SOME (PHENYLAZO)PHENYL-2*C*, *N'*-RHODIUM COMPLEXES CONTAINING TRIFLUOROPHOSPHINE

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SUMMARY

Azobenzene (HAzb) reacts with $[RhCl(C_2H_4)_2]_2$ to give $[RhCl(Azb)_2]_2$ (I). The latter reacts with $[RhCl(PF_3)_2]_2$ yielding $[RhCl(Azb)(PF_3)]_2$ (II) which contains both Rh^{III} and Rh^{I}. Both PF_3 groups are attached to the same rhodium atom. (II), which is also readily formed from PF_3 and $[RhCl(Azb)(CO)]_2$, (III), reacts with CO to reform (III). There is ready intermolecular phosphine exchange in (II) and the mixed carbonyl–trifluorophosphine complex $[Rh_2Cl_2(Azb)_2(PF_3)(CO)]$ (IV) is obtained by mixing solutions of (II) and (III). Bridge cleavage occurs when (II) or (IV) are treated with Ph_3P. Me_2NPF_2 reacts with (III) to yield $RhCl(Me_2NPF_2)_3$. (I) is the other product of these latter reactions. $[RhCl(PF_3)_2]_2$ acts as a catalyst for the reduction of azobenzene to hydrazobenzene.

INTRODUCTION

One of the products obtained from the reaction between azobenzene (HAzb) and $[RhCl(CO)_2]_2$ was originally reported by Craik *et al.*[1] as $Rh_2Cl_2(Azb)_2(CO)_3$ but reformulated later by Bruce *et al.*[2,3] as $[RhCl(Azb)(CO)]_2$ (III). In view of the known similarity between the coordinating properties of carbon monoxide and fluorophosphines[1-6] and the NMR spectroscopic advantages of the latter, we undertook the synthesis of the trifluorophosphine analogue of (III) to help establish its formulation. After completion of this work Hoare and Mills[7] reported a full X-ray analysis of (III). Here we present some synthetic and catalytic results on these and related systems.

RESULTS AND DISCUSSION

When trifluorophosphine is bubbled through a benzene solution of (III) at reflux temperature, CO is completely displaced and dark red crystals of di-μ-chloro-[bis(trifluorophosphine)rhodium(I)] [bis(phenylazophenyl-2*C*,*N'*)rhodium(III)], (II), are obtained in 85% yield (see Scheme).

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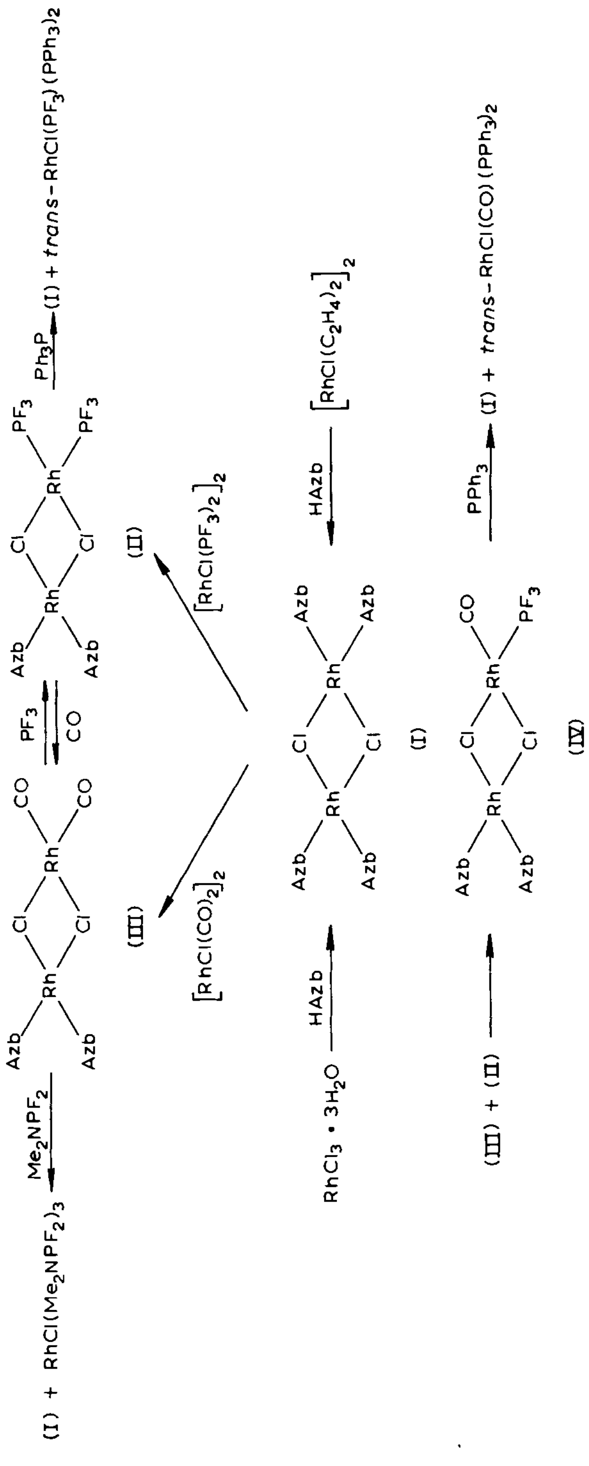
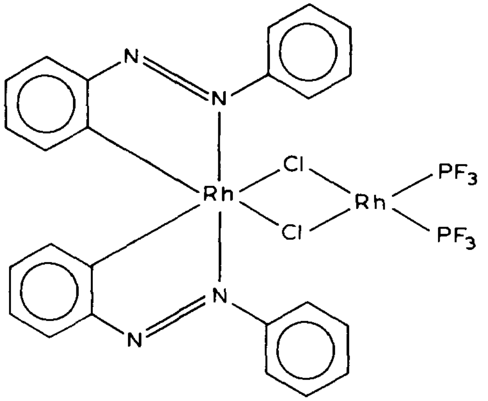
SCHEME


(I) + RhCl(Me2NPF2)3
Me2NPF2
Azb
Rh
Cl
CO
PF3
(III)
(II)
[RhCl(CO)2]2
[RhCl(PF3)2]2
Ph3P
(I) + trans-RhCl(PF3)(PPh3)2
RhCl3 • 3H2O
HAzb
(I)
[RhCl(C2H4)2]2
(III) + (II)
(IV)
PPh3
(I) + trans-RhCl(CO)(PPh3)2



(II)

Treatment of (II) with an excess of CO in refluxing hexane completely regenerates the starting carbonyl complex (III). Complex (II) can also be obtained in good yield from the reaction between $[RhCl(PF_3)_2]_2$[8-10] and $[RhCl(Azb)_2]_2$. The latter compound was previously made together with $RhCl_3(PhNH_2)_2$ from $RhCl_3 \cdot 3H_2O$ and azobenzene[2,3], but we find that a more convenient route is from $[RhCl(C_2H_4)_2]_2$.

The presence of two PF_3 ligands attached to one rhodium atom in (II) was unambiguously established by analysis of the ^{19}F NMR spectrum (Fig. 1) which is very similar to $[RhCl(PF_3)_2]_2$[9] and showed the characteristic pattern of lines expected for the X part of an $[X_3A]_2$ spin system, (X = fluorine; A = phosphorus), each line being further split into a 1/1 doublet by interaction with the ^{103}Rh nucleus ($I = \frac{1}{2}$, 100% abundant).

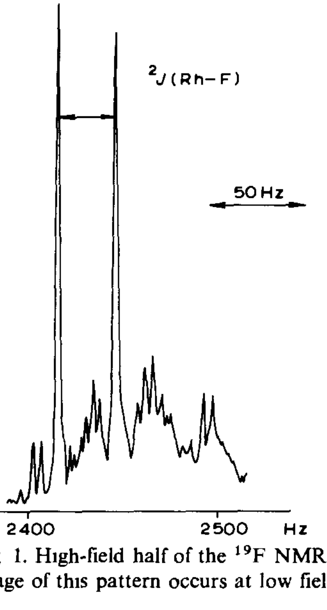
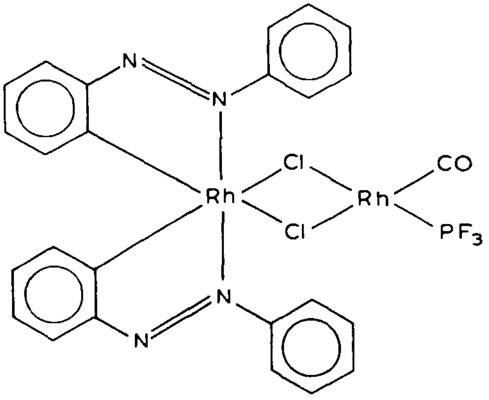


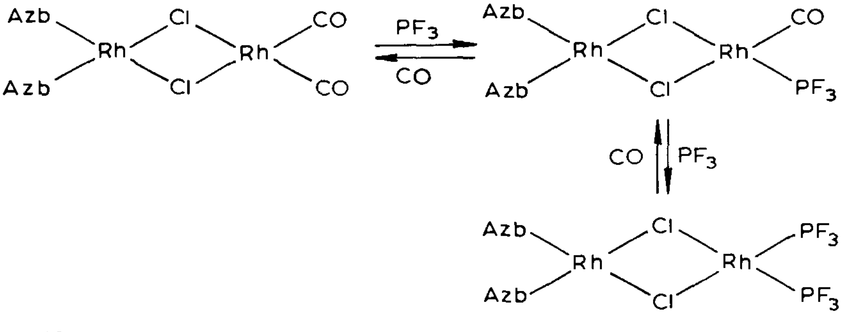
Fig 1. High-field half of the ^{19}F NMR spectrum (at 94.1 MHz) of $[RhCl(Azb)(PF_3)]_2$ An exact mirror image of this pattern occurs at low field

In previous papers we have shown that there is a ready intermolecular exchange of phosphine ligands in many square planar rhodium(I) phosphine complexes[8,9]. This is also found to be the case in the present compounds, thus mixing benzene solutions of (II) and (III) at room temperature immediately yields the mixed carbonyl–trifluorophosphine complex di-μ-chloro[(carbonyl)(trifluorophosphine)rhodium(I)][bis(phenylazophenyl-2*C*,*N*′)rhodium(III)], (IV), (see Scheme).



(IV)

The changes in (*a*) the C–O stretching region of the infrared spectrum of (III) on addition of (II) and (*b*) the ^{19}F NMR spectrum of (II) on stepwise addition of (III) which are shown in Figs. 2 and 3 confirm the existence of the equilibria



The ^{19}F NMR spectrum of (IV) which is similar to that observed previously for $[RhCl(CO)(PF_3)]_2$[8] and $[RhCl(C_2H_4)(PF_3)]_2$[9] consists of a widely spaced doublet of doublets arising from spin coupling with the rhodium and phosphorus nuclei.

The observation of three, rather than one, carbonyl stretching modes in (IV) and in the 1/1 mixture of (II) and (III) is analogous to the behaviour of $[RhCl(CO)(PF_3)]_2$[8]. Complex (IV) reacts with triphenylphosphine with preferential loss of trifluorophosphine and formation of (I) and *trans*-$RhCl(CO)(PPh_3)_2$.

Complex (II) also undergoes bridge cleavage on treatment with triphenylphosphine to yield (I) and the known *trans*-$RhCl(PF_3)(PPh_3)_2$. An analogous reaction has been reported for (III)[2]. Bridge cleavage occurs when (III) is treated with an excess of

TABLE 1

^{19}F NMR DATA FOR SOME DINUCLEAR RHODIUM–TRIFLUOROPHOSPHINE COMPLEXES

Complex	$\varphi_F{}^a$	$^1J(P–F)^{b,c}$	$^3J(P–F')^{b,c}$	$^2J(Rh–F)^b$	$^2J(P–P')^b$	*Ref.*
$[RhCl(Azb)(PF_3)]_2$	19 3	1333±2	20±2	32 0	58±2	This work
$[Rh_2Cl_2(Azb)_2(CO)(PF_3)]$	20 3	1346		35 3		This work
$[RhCl(PF_3)_2]_2$	17.0	1328	19	31 5	63 5±1	9
$[RhCl(CO)(PF_3)]_2$	18 6	1343		34 0		8

[a] In ppm rel to CCl_3F [b] In Hz [c] $^1J(P–F)$ and $^3J(P–F')$ have opposite signs

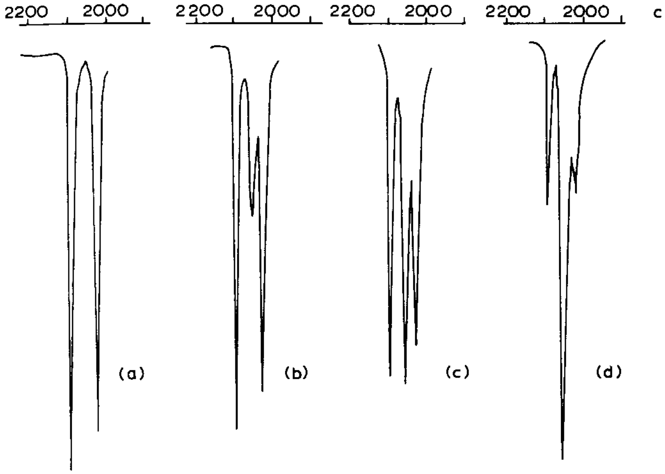


Fig 2 Carbonyl stretching region of the infrared spectrum of a solution of $[RhCl(Azb)(CO)]_2$ (III) with different added amounts of $[RhCl(Azb)(PF_3)]_2$ (II) Ratio (III)/(II) (a) 1/0 (b) 4/1 (c) 2/1 (d) 1/1

(dimethylamino)difluorophosphine at room temperature, producing (I) and $RhCl(Me_2NPF_2)_3$[11].

The similarity between the carbonyl and the trifluorophosphine complexes (III) and (II) was further evidenced by the ready $LiAlH_4$ reduction of azobenzene to hydrazobenzene (≈90% conversion) in the presence of catalytic amounts of $[RhCl(PF_3)_2]_2$. Azobenzene is not normally affected by $LiAlH_4$, but $[RhCl(CO)_2]_2$[9] and certain other metal halides[12] catalyse the reduction to hydrazobenzene.

EXPERIMENTAL

$[RhCl(CO)_2]_2$, $[RhCl(C_2H_4)_2]_2$, $[RhCl(Azb)_2CO]_2$, and $[RhCl(PF_3)_2]_2$ were made by literature methods[3,8,9].

Synthesis of $[RhCl(Azb)_2]_2$ *from* $[RhCl(C_2H_4)_2]_2$

To a suspension of dimeric rhodium ethylene chloride (0.194 g, 0.5 mmol) in ethanol was added a solution of azobenzene (0.400 g, 2 mmol) in ethanol and the

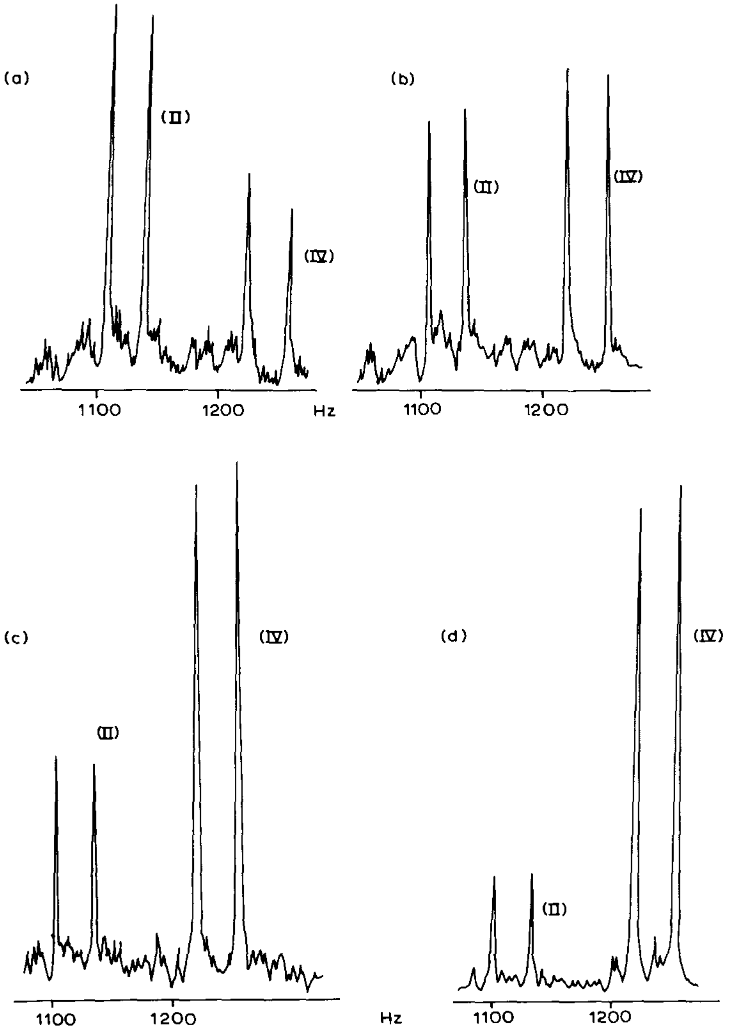


Fig. 3. Low-field half of the ^{19}F NMR spectrum of (II) with successive addition of (III). Ratio of (II)/(III) (a) 4/1 (b) 2/1 (c) 1.5/1 (d) 1/1.

mixture was boiled under reflux for 5 h. The solution turned dark red and removal of ethanol gave complex (I) as dark red crystals (0.330 g, 75%) after recrystallisation from benzene/light petroleum. The complex was identified by comparison of its infrared spectrum and melting point with an authentic sample.

Reaction of $[RhCl(Azb)_2]_2$ *with* $[RhCl(PF_3)_2]_2$

A mixture of (I) (0.100 g, 0.1 mmol) and $[RhCl(PF_3)_2]_2$ (0.063 g, 0.1 mmol) in benzene solution was refluxed for 4 h. The product was extracted with hexane and after removal of solvent and pumping off traces of $[RhCl(PF_3)_2]_2$ gave dark red crystals of (II) (0.130 g, 80%). (Found: C, 36.5; H, 2.8; N, 6.0. $C_{12}H_9N_2ClF_3PRh$

calcd.: C, 35.3; H, 2.2; N, 6.9%.) IR spectrum 3060 w, 3000 (sh), 2930 vs, 2860 s, cm^{-1} (chloroform solution) 1570 s, 1552 (sh), 1316 (sh), 1304 ms, 1258 ms, 1236 ms, 1200 w, 1170 (sh), 1156 ms, 1114 ms, 1080 m, 1042 s, 1024 m, 1003 m, 963 w, 927 vs, 916 ms, 985 vs, 855 vs, 838 m, 832 (sh), 770 vs, 726 s, 714 s, 692 vs, 667 m, 656 m, cm^{-1} (Nujol mull).

Reaction of $[RhCl(CO)(Azb)]_2$ *with* PF_3

PF_3 was passed through a refluxing benzene solution of $[RhCl(CO)(Azb)]_2$ (0.100 g, 0.15 mmol) for 1 h to yield, after removal of the solvent, dark red crystals of (II) (0.105 g, 85%) whose IR spectrum and NMR spectrum were identical with the sample obtained by the alternative route.

Reaction of $[RhCl(PF_3)(Azb)]_2$ *with CO*

Carbon monoxide was bubbled through a hexane solution of (II) (0.120 g, 0.15 mmol) at room temperature for 15 min. Bands at 2080 and 2010 cm^{-1} appeared in the spectrum of the solution, while bands in the P–F stretching region ($\approx$900 cm^{-1}) disappeared. Removal of the solvent gave orange crystals of (I) (0.090 g, 0.13 mmol) (86% yield) identified by comparison with an authentic sample.

Reaction between $[RhCl(Azb)(PF_3)]_2$ *and* PPh_3

Complex (II) (0.100 g, 0.12 mmol) was refluxed with triphenylphosphine (0.063 g, 0.24 mmol) in benzene for 5 h to yield yellow crystals of *trans*-$RhCl(PF_3)(PPh_3)_2$ (0.078 g, 0.09 mmol) after recrystallisation from ethanol/petroleum. The complex was identified by its IR, m.p.[9], and by analysis. (Found: C, 56.9; H, 4.1. $C_{36}H_{30}ClF_3P_3Rh$ calcd.: C, 57.6; H, 4.05%.) The second product was identified as $[RhCl(Azb)_2]_2$ (IV) (0.040 g) by comparison with an authentic sample.

Reaction between $[Rh_2Cl_2(Azb)_2CO(PF_3)]$ *(IV) and* PPh_3

A benzene solution of (IV) (0.113 g, 0.15 mmol) and triphenylphosphine (0.157 g, 0.6 mmol) stirred for 1 h at room temperature gave, after recrystallisation from benzene/ethanol, yellow crystals of *trans*-chlorobis(triphenylphosphine)carbonylrhodium(I), (0.037 g, 36%) identified by its IR spectrum and by analysis. Evaporation of the red filtrate gave red crystals of (I) (0.032 g, 42%) after recrystallisation from benzene/petroleum ether. The complex was characterised by its m.p. IR, and NMR spectra.

Reduction of azobenzene by $LiAlH_4$ *in the presence of* $[RhCl(PF_3)_2]_2$

No reaction was observed when a solution of azobenzene (1.82 g, 10 mmol) in ether was added to a suspension of $LiAlH_4$ (0.37 g, 1 mmol) in ether, however addition of a small crystal of $[RhCl(PF_3)_2]_2$ to the solution induced boiling of the solvent and the colour of the solution changed from orange to yellow.

After 1 h the ether was reduced and the reaction mixture poured on to a saturated solution of potassium sodium tartrate to remove excess $LiAlH_4$. The product was extracted with ether from the aqueous layer dried over $MgSO_4$ and removal of solvent yielded yellow crystals (1.6 g, 90%), identified by IR and NMR as almost pure hydrazobenzene. The product (m.p. 125°· lit. 126°) was further purified by recrystallisation from an ethanol/ether mixture.

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