Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ortho-METALLATION REACTIONS

V*. REACTIONS OF RHODIUM COMPLEXES WITH AZOBENZENE

M. I. BRUCE, M. Z. IQBAL and F. G. A. STONE
Department of Inorganic Chemistry, The University, Bristol BS8 1TS (Great Britain)

(Received February 21st, 1971)

SUMMARY

Hydrated rhodium(III) chloride reacts with azobenzene (HAzb) affording $RhCl_3(PhNH_2)_2$ and the dimeric $[(Azb)_2RhCl]_2$. The latter reacts with donor ligands to give $(Azb)_2RhCl(L)$, ($L = PPh_3$, tetrahydrofuran). With $[Rh(CO)_2Cl]_2$, azobenzene affords an unusual Rh^I–Rh^{III} complex, $[(Azb)_2RhCl_2Rh(CO)_2]$, which can also be obtained from $[Rh(CO)_2Cl]_2$ and $[(Azb)_2RhCl]_2$. These complexes contain the *ortho*-metallated (phenylazo)phenyl-2*C*,*N′* ligand, and their spectroscopic properties are summarised.

INTRODUCTION

The *ortho*-metallation reaction, involving metallation of a phenyl ring *ortho* to a substituent containing a donor atom, with formation of complexes containing chelate groups, has been reported for several types of ligand. Previous papers[1,2] have described some investigations on the azobenzene (HAzb) system, where *ortho*-metallation results in the formation of complexes containing the (phenylazo)phenyl-2*C*,*N′* ligand (Azb).

Early reports of the interaction of azobenzene with rhodium-containing complexes appear to be limited[3] to the formation of monomeric $(Azb)_2RhCl$ and its tetrahydrofuran adduct from reactions with $RhCl_3 \cdot 3\,H_2O$, and the synthesis of $[(\pi\text{-}C_8H_{12})(Azb)RhCl]_2$ from $[(\pi\text{-}1,5\text{-}C_8H_{12})RhCl]_2$. The structure of $(Azb)_2Rh(OAc)$, prepared from dimeric $[(Azb)_2RhCl]_2$, has been reported[4], together with the complex $(Azb)_2Rh_2Cl_2(CO)_3$.

This paper is concerned with a study of the reactions of azobenzene with several rhodium complexes, which have clarified some early discrepancies. A preliminary account of some of this work has appeared[5].

RESULTS AND DISCUSSION

The reaction between $RhCl_3 \cdot 3\,H_2O$ and azobenzene, carried out in ethanol

---

* For Part IV, see ref. 1.

TABLE 1

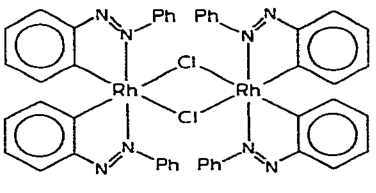
ANALYTICAL DATA

	Complex	*M.p.* (°*C*)	*Analysis found* (*calcd.*) (%)			
			C	*H*	*N*	*M*
(I)	$[RhCl_3(PhNH_2)_2]_n$	275 dec.	36.4 (36.4)	3.4 (3.55)	6.7 (7.1)	
(II)	$[(Azb)_2RhCl]_2$[a]	184–186 dec.	57.1 (57.55)	3.7 (3.6)	10.65 (11.2)	977[b] (1000)
(III)	$(Azb)_2RhCl(PPh_3)$	153–155	64.95 (65.0)	4.8 (4.8)	5.0 (5.5)	
(IV)	$(Azb)_2RhCl(THF)$	174 dec.[c]	58.8 (58.7)	4.75 (4.55)	9.75 (9.8)	
(V)	$(Azb)_2RhCl_2Rh(CO)_2$[d]	190–191	44.95 (44.9)	2.7 (2.6)	8.1 (8.05)	717[b,e] (695)
(VI)	$RhCl(CO)_2(PhNH_2)$[f]	140 dec.	33.5 (33.4)	2.45 (2.45)	4.85 (4.85)	314 (287)
(VII)	$[(Azb)Rh(CO)_2Cl]_n$	178–180	44.8 (44.25)	3.45 (3.95)	7.85 (7.95)	1271[g] (363)
(VIII)	$(Azb)Rh(CO)_2$	153–155 dec.	48.95 (49.4)	3.35 (2.65)	8.4 (8.25)	

[a] Cl, 6.95 (7.1)%. [b] Osmometric (C_6H_6). [c] Lit. m.p. 170° (ref. 3). [d] Cl, 9.85 (10.2); O, 4.7 (4.6); Rh, 28.85 (29.6)%. [e] High resolution on parent ions: $C_{26}H_{18}Cl_2N_4O_2Rh_2$: 693.893 (693.892), 695.889 (695.888), 697.881 (697.886). [f] Cl, 12.4 (12.35); O, 11.25 (11.15); Rh, 35.55 (35.8)% [g] Osmometric (acetone).

at reflux temperature for several hours, results in the precipitation of an orange solid (I), in about 25% yield. This complex (Table 1) was found to be identical with the product from the reaction of aniline with $RhCl_3 \cdot 3\ H_2O$. Complex (I) is completely insoluble in the usual organic solvents, and neither osmometric data nor proton NMR spectra could be obtained. The presence of ν(NH) bands in the infrared spectrum (Table 2) suggests that (I) is indeed an aniline derivative. Our findings contrast with the earlier report[6] of the isolation of the trisubstituted complex $RhCl_3(PhNH_2)_3$ from a similar reaction with aniline as the reactant. The structure of (I) is unknown, but it may be a chlorine-bridged dimer or polymer.

The filtrate from the synthesis of complex (I) affords a chilli-red crystalline solid (II) in 40% yield, which appears to be the same complex as that described by Japanese workers[3]. In agreement with this, analytical data accord with the formula $(Azb)_2RhCl$, but both solution molecular weights and mass spectra (including high resolution studies) indicate that complex (II) is a dimer, presumably containing chlorine-bridges. The proton NMR spectrum (Table 3) is entirely consistent with the presence of chelating (phenylazo)phenyl-2*C*,*N*′ groups.



(II)

Complex (II) shows a surprising reluctance to react with Lewis bases, L, to give complexes of the type $(Azb)_2RhCl(L)$. Triphenylphosphine, for example, requires prolonged refluxing with (II) to give yellow $(Azb)_2RhCl(PPh_3)$ (III); we were unable to isolate any new product with *p*-toluidine. These sluggish reactions with Group V

TABLE 2

INFRARED SPECTRAL BANDS (cm^{-1})

	Complex	$\nu(CO)$	*Other bands*
(I)	$(PhNH_2)_2RhCl_3$		3278 (sh), 3262 m, 3167 ms, 3100 m, 1597 ms, 1580 m, 1562 ms, 1492 s, 1218 w, 1182 (sh), 1170 s, 1162 (sh), 1139 s, 1072 m, 1032 m, 920 w, 848 w, 814 m, 775 ms, 770 (sh), 742 (sh), 730 m, 703 s[d].
(II)	$[(Azb)_2RhCl]_2$		3052 m, 1574 s, 1553 (sh), 1485 ms, 1448 s, 1321 (sh), 1304 ms, 1262 ms, 1240 ms, 1200 w(br), 1170 (sh), 1158 m, 1112 m, 1078 w, 1043 ms, 1025 m, 1003 vw, 961 w, 942 vw, 920 w, 862 vw, 841 w, 773 vs, 732 s, 721 ms, 694 s, 669 (sh), 660 w[d].
(III)	$(Azb)_2RhCl(PPh_3)$		3055 ms, 1575 ms, 1550 w, 1437 s, 1305 m, 1258 m, 1239 m, 1193 m, 1159 m, 1115 (sh), 1093 ms, 1078 (sh), 1029 m, 1004 m, 915 w, 840 w, 776 ms, 753 ms, 734 ms[d].
(IV)	$(Azb)_2RhCl(THF)$		3052 m, 1574 s, 1155 (sh), 1485 ms, 1450 s, 1322 (sh), 1306 ms, 1262 ms, 1242 ms, 1200 w(br), 1172 (sh), 1158 m, 1114 m, 1078 w, 1045 ms, 1027 m, 1005 w, 963 w, 946 vw, 921 w, 866 vw, 841 w, 774 vs, 734 s, 723 ms, 697 s, 683 vw, 663 vw[d].
(V)	$[(Azb)Rh(CO)Cl]_2$	2080 vs, 2010 vs, 2062 (sh), 1980 (sh)[a,b]	1579 ms, 1557 m, 1385 m(br), 1238 w, 1157 w, 1112 w, 769 s, 760 (sh), 729 s, 719 (sh), 698 ms[a]. 3065 m, 1386 ms, 1319 m, 1306 m, 1260 m, 1239 m, 1169 (sh), 1157 m, 1112 m, 1045 m, 960 w, 942 w, 916 w, 770 s, 760 (sh), 729 ms, 719 m, 694 ms[b].
(VI)	$(PhNH_2)Rh(CO)_2Cl$	2018 vs, 2025 ms, 2016 (sh), 2005 vs[b] 2092 vs, 2017 vs[c]	3247 ms, 3196 m, 3104 w, 3043 w, 1604 ms, 1568 ms, 1495 ms, 1221 m, 1182 w, 1131 (sh), 1105 s, 1073 w, 1033 w, 1007 w, 825 vw, 812 vw, 763 s, 731 w, 703 s, 682 m[d].
(VII)	$[(Azb)Rh(CO)_2Cl]_n$	2080 vs, 2010 vs[a] 2088 s, 2018 s[c]	1572 ms, 1555 m, 1357 m(br), 1301 w, 1157 w, 767 s, 725 ms, 715 m, 692 ms[d].
(VIII)	$(Azb)Rh(CO)_2$	2081 vs, 2012 vs[a]	3042 w, 1573 s, 1553 (sh), 1319 (sh), 1305 ms, 1259 ms, 1238 ms, 1203 vw, 1170 (sh), 1158 m, 1113 m, 1077 w, 1043 ms, 1030 w, 1005 w, 978 vw, 963 w, 949 w, 922 w, 868 w, 842 w, 782 (sh), 772 s, 765 (sh), 734 s, 723 ms, 718 (sh), 704 (sh), 696 s, 683 w, 664 w[d].

[a] Cyclohexane. [b] CS_2. [c] $CHCl_3$. [d] Nujol.

TABLE 3

PROTON NMR SPECTRA[a]

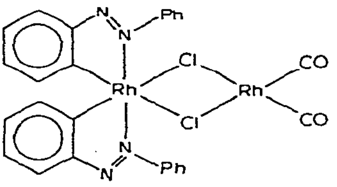
	Compound	τ
(II)	$[(Azb)_2RhCl]_2$	1.80 q, 1.93 d, 2.00 t, 2.56 m, 2.94 dq, 3.10 m
(III)	$(Azb)_2RhCl(PPh_3)$	1.86 m, 2.13 m, 2.7–3.4 m(br)
(V)	$(Azb)_2RhCl_2Rh(CO)_2$	1.82 q, 2.00 q, 2.40 m, 2.82 qd, 3.04 m
(VI)	$(PhNH_2)Rh(CO)_2Cl$	2.72 d, 2.90 m, 3.80 (br)(NH)
(VIII)	$(Azb)Rh(CO)_2$	1.85 w, 2.05 q, 2.42 m, 2.68 q, 2.90 td, 3.07 m

[a] All measured in $(CD_3)_2CO$ except (III) $(CDCl_3)$.

donors contrast with the ready formation of a mononuclear adduct $(Azb)_2RhCl$(THF) (IV) with tetrahydrofuran. This complex may be obtained by simple recrystallisation of (II) from tetrahydrofuran, and its formation recalls the facile halogen-bridge cleavage in $[Ru(CO)_3Cl_2]_2$ by this reagent[7].

Azobenzene reacts with $[Rh(CO)_2Cl]_2$ to give two complexes, characterised as orange-yellow (Azb)Rh(CO)Cl (V), and purple $RhCl(CO)_2(PhNH_2)$ (VI), respectively, and a deep green solid (VII). The compounds could be separated by column chromatography. The relative yields of the three derivatives vary with reaction conditions, and typical reactions are described in the Experimental section. Short reaction times resulted in none of the deep green compound (VII) being produced.

Osmometric measurements, together with the observation of a parent ion in the mass spectrum, showed that (V) was dimeric, *i.e.* $[(Azb)Rh(CO)Cl]_2$. The ν(CO) region of the infrared spectrum showed two strong and equally intense bands,



(V)

suggesting two *cis* carbonyl groups. The proton NMR spectrum showed signals characteristic of an *ortho*-metallated (phenylazo)phenyl group, and was similar to that of complex (II). The presence of the azobenzene moiety was confirmed by the isolation of azobenzene on treatment of (V) with $LiAlH_4$.

Addition of triphenylphosphine or triphenylarsine, expected to cleave the halogen bridge, afforded yellow products showing only one ν(CO) band. More detailed examination of these materials showed that no azobenzene ligand was present, and that the complexes were in fact the well-known $RhCl(CO)(Ph_3E)_2$ (E = P or As) derivatives. Furthermore, the yields of these complexes approached very closely, but never exceeded, 50% of the total rhodium content of (V). The orange filtrates from these experiments, initially assumed to contain the free azobenzene ligand from (V), were found to contain instead, a second rhodium-containing compound identified as complex (II).

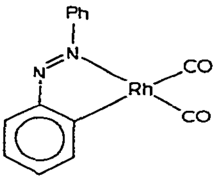
These results suggested that complex (V) was an aggregate of complex (II) with $Rh(CO)_2Cl$, and this was confirmed by the isolation of (V) from a reaction between (II) and $[Rh(CO)_2Cl]_2$. This unusual complex can thus be considered to contain both Rh^I and Rh^{III}, and probably has the structure illustrated. The indicated stereochemistry, with the metal–carbon σ bonds *trans* to the chlorine atoms, is based on the structure determined for the complex $[(Azb)_2Rh(OAc)]$[4]. The purple complex (VI) could be sublimed readily, and while initial analyses agreed with the composition $[(C_{12}H_{10}N_2)Rh_2(CO)_4Cl_2]_n$, molecular weight measurements indicated that $n=\frac{1}{2}$. The mass spectrum contained only ions from $[Rh(CO)_2Cl]_2$ above *m/e* 100; at lower *m/e* values, organic fragment ions derived from an apparent parent at *m/e* 93 were found. The infrared spectrum contained two strong ν(CO) bands, and also two strong ν(NH) bands; the proton NMR spectrum was unlike that of any known azobenzene complex. The mass spectral data led us to consider its formulation as the known[8] aniline complex, $Rh(CO)_2(PhNH_2)Cl$, and this was readily confirmed by an independent synthesis.

The dark green compound (VII) is polymeric (osmometry), and analyses correspond to the formulation $[(Azb)Rh(CO)_2Cl]_n$ (n=4–5). No ν(NH) bands are present in the infrared spectrum; two strong ν(CO) bands occur in the region normally associated with $LRh(CO)_2Cl$ complexes containing nitrogen-donor ligands, L. We suggest that this complex is a true azobenzene–rhodium complex, *i.e.* that *ortho*-metallation has not occurred. Polymerisation can occur by metal–metal bond formation [as suggested for other solid (amine)$Rh(CO)_2Cl$ complexes[8]], or by utilisation of both lone pairs in the azo function in coordination to different metal atoms.

Transfer of phenylazophenyl groups from palladium to rhodium occurred in reactions between $[(Azb)PdCl]_2$ and $[Rh(CO)_2Cl]_2$, and orange crystals showing two ν(CO) bands were thereby obtained. This complex was characterised as $[(Azb)Rh(CO)_2]$ (VIII), the proton NMR spectrum again confirming that the *ortho*-metallated ligand is present.

Attempts to prepare an azobenzene derivative from $(Ph_3P)_3RhCl$ were unsuccessful, the only products being $[(Ph_3P)_2RhCl]_2$ and some triphenylphosphine oxide.

The proton NMR spectra of the complexes containing the (phenylazo)phenyl-2*C*,*N*′ ligand (Table 3) showed the characteristic peaks associated with this group[1,2]. Low-field multiplets at τ 1.80 and 1.96, and between τ 2.75–3.10, show first-order coupling, and are partly overlapped by the broad resonances due to the C_6H_5 groups, at τ 2.55 and 3.12, in complex (III). The chemical shifts of these signals in complexes (II) and (V) differ by only 0.05–0.1 ppm, confirming the close similarity of environment suggested by our proposed structures. The spectrum of complex (VIII) was not well resolved, but signals in the same regions as those described above in which the multi-

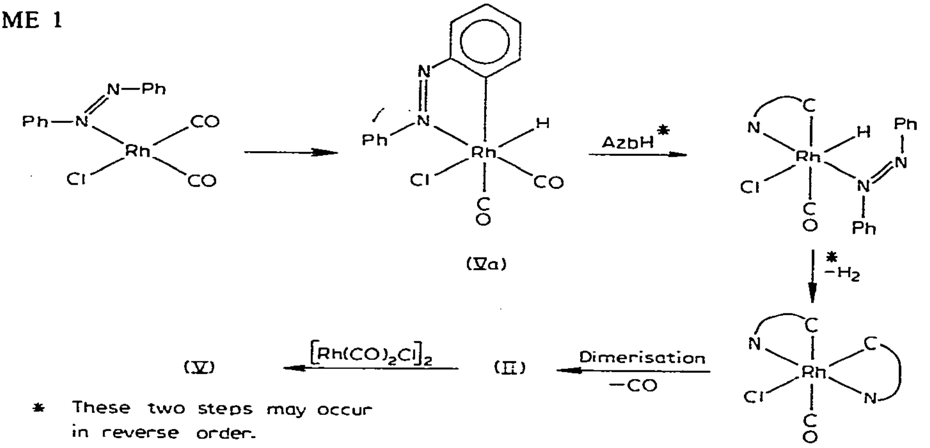


(VIII)

plet structure is only partly resolved, suggest that an *ortho*-metallated ligand is present.

The formation of complex (II) probably occurs via an electrophilic attack by a coordinated rhodium atom on an *ortho* carbon atom, with elimination of HCl, following an initial reaction in which the nitrogen is attached to the metal. The reaction is analogous to the well-known *ortho*-metallation of azobenzene and related ligands by palladium chloride[9]. In the case of complex (V), it is likely that the first step is coordination of azobenzene to the rhodium atom, followed by an oxidative-addition reaction, which results in the formation of the intermediate (Va). Subsequent reaction with a second molecule of azobenzene, via an *ortho*-metallation reaction with elimination of hydrogen, and coordination, giving (II), can then be followed by combination with excess $Rh(CO)_2Cl$ to afford complex (V) (Scheme 1).

SCHEME 1



* These two steps may occur in reverse order.

EXPERIMENTAL

General experimental details have been given earlier[2]. Dimeric rhodium carbonyl chloride was prepared by the carbonylation of $RhCl_3 \cdot 3\ H_2O$, either directly[10], or in methanol solution[11].

Reactions of azobenzene

(*a*). *With* $RhCl_3 \cdot 3\ H_2O$. A mixture of azobenzene (1.82 g, 10 mmol) and commercial hydrated rhodium(III) chloride (1.05 g, $\approx$4 mmol) in ethanol (70 ml) was refluxed for 6 h. The buff-coloured solid which separated was filtered, and washed well with methanol, acetone and ether, to give complex (I) (401 mg, 25%). Evaporation of the filtrate, and recrystallisation from a benzene/light petroleum (b.p. 40–60°) mixture gave complex (II) as a red crystalline solid (1.0 g, 40%). Recrystallisation from tetrahydrofuran gave the adduct (IV) as deep red crystals.

(*b*). *With* $[Rh(CO)_2Cl]_2$. A mixture of $[Rh(CO)_2Cl]_2$ (3.08 g, 7.92 mmol) and azobenzene (3.8 g, 17 mmol) in light petroleum (b.p. 100–120°) (120 ml) was refluxed for 6 h. Removal of solvent and chromatography of a dichloromethane extract gave an orange band [9/1 light petroleum/ether (b.p. 40–60°)] which afforded complex (V) as orange crystals, purified by recrystallisation from an ether/light petroleum (b.p.

40–60°) mixture as fine orange needles (1.93 g, 35%). Ether/light petroleum (b.p. 40–60°) (1/1) eluted complex (VI) as a deep purple-green dichroic solid, which could be sublimed at 90–100° (0.1 mmHg) (986 mg, 22%). Ether eluted a deep green band which afforded a deep green crystalline complex (VII) (935 mg, 5%).

In another experiment, reaction using methanol as a solvent gave only a small amount of complex (VII) (56 mg, 2.5%), together with an unstable deep brown complex (m.p. 181°), which was not further investigated. (Found: C, 18.9; H, 1.65; O, 6.15; Rh, 40.0%.)

Complexes (V) and (VI) were obtained in 32 and 1.5, and 24 and 14% yields, respectively, when benzene and hexafluorobenzene were used as solvents.

Reaction of complex (II) with triphenylphosphine

Refluxing a mixture of complex (II) (100 mg, 0.1 mmol) and PPh_3 (100 mg, 0.4 mmol) in benzene (25 ml) for 9.5 h, followed by recrystallisation from ether/light petroleum (b.p. 40–60°) gave complex (III) as yellow crystals (49 mg, 32%).

Reactions of complex (V)

(*a*). *With triphenylphosphine.* Treatment of complex (V) (112 mg, 0.16 mmol) with triphenylphosphine (84 mg, 0.32 mmol) in dichloromethane (10 ml) at room temperature for 30 min gave an insoluble yellow crystalline solid, which was filtered and washed with ether and light petroleum (b.p. 40–60°) to give $(Ph_3P)_2Rh(CO)Cl$ [55 mg, 48% (based on Rh in complex (I))], m.p. and mixed m.p. 190–194°, identified from its infrared spectrum [ν(CO), 1977 cm^{-1} ($CHCl_3$)] and by analysis. (Found: C, 63.8; H, 4.30. $C_{37}H_{30}ClOP_2Rh$ calcd.: C, 64.3; H, 4.35%.) Evaporation of the filtrate gave complex (II), identified by infrared and NMR spectrometry and by analysis. (Found: C, 58.4; H, 3.90; Cl, 6.95; N, 10.45%.)

(*b*). *With triphenylarsine.* A similar reaction using complex (V) (140 mg, 0.2 mmol) and $AsPh_3$ (123 mg, 0.4 mmol) in dichloromethane (8 ml) for 20 h at room temperature gave $(Ph_3As)_2Rh(CO)Cl$ [76 mg, 49% (based on Rh in complex (I))], m.p. and mixed m.p. 195–196°, identified from its infrared spectrum [ν(CO), 1978 cm^{-1} ($CHCl_3$)] and by analysis. (Found: C, 57.35; H, 4.00. $C_{37}H_{30}As_2ClORh$ calcd.: C, 57.05; H, 3.85%.) Evaporation of the filtrate gave complex (II), m.p. and mixed m.p. 184–186°, also identified from its infrared spectrum.

Reaction of $[Rh(CO)_2Cl]_2$ with aniline

Addition of excess aniline to a solution of $[Rh(CO)_2Cl]_2$ (388 mg, 1 mmol) in benzene (10 ml) gave an immediate deep green-purple solid, whose precipitation was completed by addition of a small amount of light petroleum (b.p. 40–60°). Filtration, washing with light petroleum, and final purification by sublimation 80–100° (0.1 mmHg) gave deep purple-green dichroic complex (II) (400 mg, 70%), shown to be identical with the product isolated as above by m.p. [140–141° (dec.)], infrared and NMR spectrometry, and analysis. (Found: C, 33.8; H, 2.45; N, 4.85%.)

Reaction of complex (II) with $[Rh(CO)_2Cl]_2$

A mixture of complex (II) (250 mg, 0.25 mmol) and $[Rh(CO)_2Cl]_2$ (195 mg, 0.5 mmol) in benzene (40 ml) was refluxed for 9 h, after which time the complex had dissolved. Chromatography of the concentrated solution gave complex (V) (122 mg, 35%), identified by m.p. and mixed m.p., infrared and NMR spectrometry, and analysis. (Found: C, 44.4; H, 3.1; N, 7.5%.) Methanol eluted a small amount of an unidentified, rather unstable deep brown crystalline complex (5 mg), m.p. 219° (dec.). (Found: C, 40.5; H, 2.7; N, 6.9%.)

Reaction between $[(Azb)PdCl]_2$ and $[Rh(CO)_2Cl]_2$

A mixture of $[(Azb)PdCl]_2$ (222 mg, 0.33 mmol) and $[Rh(CO)_2Cl]_2$ (132 mg, 0.34 mmol) in benzene (30 ml) was refluxed for 3.5 h. Removal of solvent and chromatography gave complex (VIII), recrystallised from ether/n-hexane as orange crystals (90 mg, 40%).

Degradation experiments

(*a*) *Complex* (*V*). Addition of a filtered ethereal solution of $LiAlH_4$ (excess) to one of complex (V) (170 mg, 0.24 mmol) at 0°, followed by cautious addition of ethanol to destroy excess $LiAlH_4$, and chromatography, gave a mixture of aniline and azobenzene, eluted with ether/light petroleum (b.p. 40–60°) (1/9), and identified from their mass and infrared spectra. Separation by extraction of a light petroleum solution with dilute acetic acid gave azobenzene (35 mg, 36%); basification of the acetic acid layer and reextraction with light petroleum gave some aniline, identified by comparison with an authentic sample.

(*b*) *Complex* (*II*). A similar reduction of complex (II) in tetrahydrofuran solution gave aniline, identified spectroscopically.

(*c*) *Complex* (*V*). Dissolution of complex (V) in concentrated H_2SO_4, followed by dilution with water and work-up in the usual way gave an orange solid, identified as azobenzene (m.p. and mixed m.p. 67°). About 10% of the original complex could also be recovered from the reaction mixture.

Reaction of azobenzene with $(Ph_3P)_3RhCl$

Addition of azobenzene (200 mg, 1.1 mmol) to $(Ph_3P)_3RhCl$ (924 mg, 1 mmol) in benzene (75 ml) caused immediate precipitation. After 5 h at 20°, the solid was filtered under nitrogen and washed with benzene and n-hexane to give $[(Ph_3P)_2RhCl]_2$ (X) (152 mg, 23%), m.p. 130–131°. (Found: C, 65.9; H, 4.8. $C_{36}H_{30}ClP_2Ph$ calcd.: C, 65.2, H, 4.55%.) Concentration of the filtrate and chromatography gave Ph_3PO (methanol) (176 mg, 63%), m.p. and mixed m.p. 156°. A dichloromethane fraction gave a small amount (15 mg) of a red crystalline material, m.p. 198° (dec.) which could not be identified. (Found: C, 52.75; H, 4.35; N, 9.65%.)

ACKNOWLEDGEMENT

M.Z.I. thanks the Panjab University, Lahore, West Pakistan, for study leave (1967–1970).

REFERENCES

1 R. L. Bennett, M. I. Bruce, B. L. Goodall, M. Z. Iqbal and F. G. A. Stone, *J. Chem. Soc. Dalton*, in press.

2 M. I. Bruce, M. Z. Iqbal and F. G. A. Stone, *J. Chem. Soc. A*, (1970) 3204; (1971) 2820.

3 T. Joh, N. Hagihara and S. Murahashi, *Nippon Kagaku Zasshi*, 88 (1967) 786.

4 A. R. M. Craik, G. R. Knox, P. L. Pauson, R. J. Hoare and O. S. Mills, *Chem. Commun.*, (1971) 168.
5 M. I. Bruce, B. L. Goodall, M. Z. Iqbal and F. G. A. Stone, *Chem. Commun.*, (1971) 661.
6 J. Meyer and H. Kienitz, *Z. Anorg. Allg. Chem.*, 242 (1939) 292.
7 M. I. Bruce and F. G. A. Stone, *J. Chem. Soc. A*, (1967) 1238.
8 D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, (1965) 1900.
9 A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, 87 (1965) 3272;
A. C. Cope and E. C. Friedrich, *J. Amer. Chem. Soc.*, 90 (1968) 909.
10 J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, 8 (1966) 211.
11 S. H. H. Chaston and F. G. A. Stone, *J. Chem. Soc. A*, (1969) 500.