ortho-Metallation Reactions. Part IV.[1] Reactions of Benzylideneaniline and Benzylidenemethylamine

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Reactions between benzylideneaniline (bzaH) or benzylidenemethylamine (bzmH) and $MeM(CO)_5$ (M = Mn or Re), $PdCl_2$, $Ru_3(CO)_{12}$, or $[Ru(CO)_3Cl_2]_2$, have afforded complexes containing *ortho*-metallated bza or bzm ligands. With $[Rh(CO)_2Cl]_2$ a variety of derivatives, including the rhodium(I)–rhodium(III) complex $(bza)_2Rh$-μ-$Cl_2Rh(CO)_2$, and $[(amine)Rh(CO)_2Cl]$ (amine = $PhNH_2$ or bzmH), are formed.

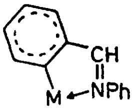
THE reactions of azobenzene with a number of transition-metal compounds have been described in previous papers.[1,2] Earlier, it was reported[3] that the related ligand benzylideneaniline (benzalaniline, PhCH=NPh, bzaH) reacts with palladium chloride[3] to give complexes in which the ligand chelates to the metal *via* the nitrogen lone-pair and a metal–carbon σ-bond to the *ortho*-carbon of the phenyl ring (I), *i.e.* the ligand is *C,N'*-bonded. Recently, Russian workers[4] have reported a similarly bonded cyclopentadienylnickel complex obtained from 2-bromobenzylideneaniline.

In contrast with the reactions of azobenzene with iron carbonyls, which result in rearrangement reactions to give complexes containing *o*-semidine ligands, benzylideneaniline gives complexes containing metallocycles, *e.g.* (II), of stoicheiometry $(C_{13}H_{11}N)Fe_2(CO)_6$.[5]

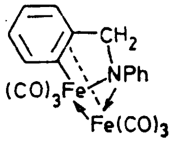
Related ligands have been briefly studied, *e.g.* enimines react with iron carbonyls to give complexes of the type (III),[5] and Kang and Maitlis[6] found that cinnamaldehydeanil reacted with $[Rh(CO)_2Cl]_2$ to give (IV), where the ligand is monodentate, being bonded by nitrogen alone; at higher temperatures, a bis(ligand) complex (V) was formed.

The wide range of *C,N'*-bonded complexes which we have prepared from azobenzene prompted an examination of representative reactions of benzylideneaniline to compare and contrast its behaviour with azobenzene, and with other related ligands. At the same time, similar reactions of benzylidenemethylamine, PhCH:NMe (bzmH), were studied, in part because replacement of the *N*-phenyl group by methyl would lead to simpler proton n.m.r. spectra being obtained.

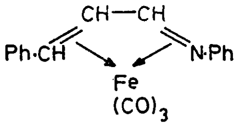
We have found metal–methyl compounds to be very useful reagents in reactions with these ligands. With benzylideneaniline, methyl-manganese- and -rhenium-pentacarbonyls reacted to give fair yields of yellow crystalline complexes (VI) and (VII), the analyses of which (Table 1) were consistent with the formula $C_{13}H_{10}NM(CO)_4$ (M = Mn or Re). A similar manganese complex (VIII) was formed from benzylidenemethylamine. Their i.r. spectra (Table 2) showed four ν(CO) bands very similar in position and relative intensities to those of the analogous (2*C,N'*-phenylazo)phenylmetal complexes.[2]



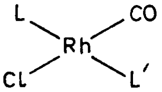
(I) M = PdCl/2
(VI) M = Mn(CO)$_4$
(VII) M = Re(CO)$_4$



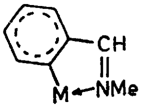
(II)



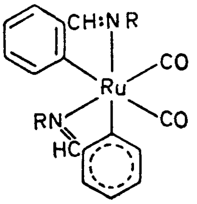
(III)



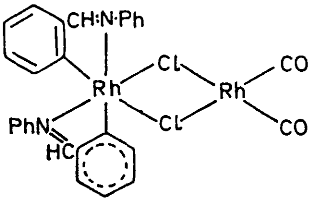
(IV) L = CO, L′ = PhCH:CH·CH:NPh
(V) L = L′ = PhCH:CH·CH:NPh
(XIII) L = CO, L′ = bzaH
(XV) L = CO, L′ = bzmH



(VIII) M = Mn(CO)$_4$
(XVII) M = Pd(π-C_5H_5)



(X) R = Ph
(XI) R = Me



(XIV)

The proton n.m.r. spectra (see below) confirmed that these compounds contained a chelating *o*-$C_6H_4CH:NR$ (R = Ph or Me) group, and they are therefore formulated as shown. The crystal structure of (VI) has been determined,[7] and confirms the proposed geometry. The

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[1] Part III, M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Organometallic Chem.*, 1971, **31**, 275.

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

[3] S. P. Molnar and M. Orchin, *J. Organometallic Chem.*, 1969, **16**, 196.

[4] Y. A. Ustynyuk, V. A. Chertkov, and I. V. Barinov, *J. Organometallic Chem.*, 1971, **29**, C53.

[5] M. M. Bagga, W. T. Flannigan, G. R. Knox, P. L. Pauson, F. J. Preston, and R. I. Reed, *J. Chem. Soc.* (*C*), 1968, 36.

[6] J. W. Kang and P. M. Maitlis, *Canad. J. Chem.*, 1968, **46**, 897.

[7] M. I. Bruce, B. L. Goodall, M. Z. Iqbal, F. G. A. Stone, R. J. Doedens, and R. G. Little, *Chem. Comm.*, 1971, 1595.

major feature of interest is the rotation of the non-metallated ring out of the plane of the fused five-six-membered ring system containing the metal, in contrast to the coplanarity found in the azobenzene derivative, Rh(azb)$_2$(OAc).[8] Other studies [9,10] on the parent ligand and its cation have indicated that the twist of the aniline ring is *ca.* 55°.

The complex Fe(π-C_5H_5)(CO)$_2$Me did not react with benzylideneaniline on refluxing for 18 h, u.v. irradiation for **72** h, or reflux under u.v. irradiation for 24 h. With [Fe(π-C_5H_5)(CO)$_2$]$_2$, a 48 h reflux period at 100° gave a 20% yield of the tetramer [Fe(π-C_5H_5)(CO)]$_4$. This is the highest yield synthesis yet reported for this cluster complex, and it is of interest that it seems to be formed on refluxing [Fe(π-C_5H_5)(CO)$_2$]$_2$ with other nitrogen-containing ligands if these do not form stable complexes (*cf.* the original discovery of [Fe(π-C_5H_5)(CO)]$_4$ by prolonged refluxing of a mixture of the dimer with tetramethyltetrazene [11]).

TABLE 1

Analytical data

	Complex	M.p. (°C)	Found (required) values (%)			
			C	H	N	M [a]
(VI)	Mn(bza)(CO)$_4$	90·5—91·5	58·95 (58·8)	3·05 (2·9)	4·05 (4·05)	347 (347)
(VII)	Re(bza)(CO)$_4$	115·5—116	43·05 (42·7)	2·3 (2·1)	3·0 (3·0)	479 (479)
(VIII)	Mn(bzm)(CO)$_4$	76—77	50·95 (50·7)	2·95 (2·8)	4·95 (4·9)	285 (285)
(IX)	[Ru(bzm)(CO)$_2$Cl]$_2$	240—243				748 (748)
(X)	Ru(bza)$_2$(CO)$_2$	230—232	65·2 (65·0)	4·0 (3·9)	5·4 (5·4)	518 (518)
(XI)	Ru(bzm)$_2$(CO)$_2$	228—229	55·05 (55·0)	4·05 (4·1)	7·0 (7·15)	392 (392)
(XIII)	Rh(bzaH)(CO)$_2$Cl	97—99	48·2 (47·9)	2·8 (2·9)	3·7 (3·75)	
(XIV)	[Rh(bza)(CO)Cl]$_2$ [b]	220—220·5	48·3 (48·5)	2·8 (3·0)	3·7 (4·0)	801 [c] (693)
(XV)	Rh(bzmH)(CO)$_2$Cl [d]	89—91 dec.	38·7 (38·4)	2·9 (2·85)	4·5 (4·45)	327 [c] (314)
(XVI)	[Pd(bzm)Cl]$_2$ [e]	>250	37·0 (36·9)	3·85 (3·7)	5·3 (5·4)	
(XVII)	Pd(bzm)(C_5H_5)	105—106	52·7 (52·9)	4·62 (4·5)		289 (289)

[a] Mass spectrometry. Cl: 9·4 (10·2)%. [c] Osmometric (C_6H_6). [d] Cl: 11·0 (11·3)%. [e] Cl: 14·3 (13·65)%.

TABLE 2

ν(CO) Bands (cm^{-1})

	Complex	ν(CO)	Solvent
(VI)	Mn(bza)(CO$_4$)	2070s, 1982s, 1945m	C_6H_{12}
(VIII)	Mn(bzm)(CO)$_4$	2073s, 1987s, 1979m, 1941m	C_6H_{12}
(VII)	Re(bza)(CO)$_4$	2090s, 1987s, 1981s, 1941m	C_6H_{12}
(IX)	[Ru(bzm)(CO)$_2$Cl]$_2$	2039s, 1972s	$CHCl_3$
(X)	Ru(bza)$_2$(CO)$_2$	2030s, 1949s	$CHCl_3$
(XI)	Ru(bzm)$_2$(CO)$_2$	2013s, 1932s	C_6H_{12}
(XIII)	Rh(bzaH)(CO)$_2$Cl	2090s, 2038m, 2014s	C_6H_{12}
(XV)	Rh(bzmH)(CO)$_2$Cl	2081s, 2011sh, 2007s	C_6H_{12}
(XIV)	[Rh(bza)(CO)Cl]$_2$	2077s, 2006s	C_6H_{12}

No reaction was observed between either of the ligands and nickelocene; with [Ru(CO)$_3$Cl$_2$]$_2$, only a small yield of the binuclear complex [Ru(bzm)-(CO)$_2$Cl]$_2$ (IX), characterised by i.r. and mass spectrometry, was obtained. This complex is probably analogous to the azobenzene derivative, [Ru(azb)(CO)$_2$Cl]$_2$.[2]

The reactions of both ligands with $Ru_3(CO)_{12}$ proceeded readily, affording yellow crystals of Ru(CO)$_2$(C_6H_4CH:NR)$_2$ [(X), R = Ph; (XI), R = Me]. The i.r. spectra of these complexes showed two strong ν(CO) bands, and the mass spectra confirmed the presence of two carbonyl groups. The proton n.m.r. spectra showed that chelated *o*-C_6H_4CH:NR (R = Ph or Me) groups were present. In addition two methine resonances were found, showing that these protons on the two ligands are in different environments. In (XI), two N*Me* resonances are also observed. This feature enables the overall structure of these complexes to be determined as shown, although the absolute configuration has not been determined.

Other ruthenium complexes, probably polynuclear, were present in the filtrate after the isolation of the above complexes, but decomposed during conventional work-up procedures (sublimation of excess of benzylideneaniline, chromatography, or recrystallisation).

A number of interesting reactions were found with rhodium compounds.[12] Dimeric rhodium carbonyl chloride reacted with benzylideneaniline more readily than with azobenzene giving a mixture that was separable from an excess of benzylideneaniline only with difficulty. The products of this reaction were the dichroic purple-green complex Rh(PhNH$_2$)(CO)$_2$Cl (XII), identified by comparison with an authentic sample; benzaldehyde, identified spectroscopically, and confirmed as its 2,4-dinitrophenylhydrazone; and two other complexes. One of these was formed in larger amounts using short reaction times, and was most conveniently separated by chromatography and sublimation, when it formed purple crystals of composition Rh(bzaH)(CO)$_2$Cl (XIII). Recrystallisation of this material afforded pale yellow crystals, which on standing turned purple; re-sublimation of either form gave a purple solid. This cycle of crystallisation and sublimation to give respectively pale yellow and purple solids could be repeated indefinitely. The properties of (XIII) [two ν(CO) bands, and a proton n.m.r. resembling that of the free ligand, and unlike that of the *ortho*-metallated complexes]

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[8] A. R. M. Craik, G. R. Knox, P. L. Pauson, R. J. Hoare, and O. S. Mills, *Chem. Comm.*, 1971, 168.

[9] A. van Putten and J. W. Pavlik, *Tetrahedron*, 1971, **27**, 3007, 3301.

[10] H. B. Bürgi and J. D. Dunitz, *Helv. Chim. Acta*, 1971, **54**, 1255.

[11] R. B. King, *Inorg. Chem.*, 1966, **5**, 2227.

[12] M. I. Bruce, B. L. Goodall, M. Z. Iqbal, and F. G. A. Stone, *Chem. Comm.*, 1971, 661.

suggested that it was an amine complex of the type $Rh(amine)(CO)_2Cl$, with amine = benzylideneaniline. The striking colour changes can be attributed to some weak metal–metal interaction in the solid (purple), which is removed when discrete molecules are present in solution (pale yellow) or one crystalline form. The bulky nature of the ligand probably prevents a suitable alignment of molecules in the crystal lattice. Since the change from yellow to purple is accelerated by heating, a thermal rearrangement within the lattice probably occurs to give the metal–metal interaction.

A second complex was obtained, especially after longer reaction times, with the composition Rh(bza)(CO)Cl (XIV). Molecular weight measurements showed that this complex was dimeric, and solution i.r. spectra contained two ν(CO) bands. The proton n.m.r. confirmed the presence of an *ortho*-metallated benzylideneaniline ligand. Addition of triphenylphosphine gave an immediate yellow precipitate of $RhCl(CO)(PPh_3)_2$. These properties of (XIV) are similar to those of the complex $[Rh(azb)(CO)Cl]_2$,[13] and we suggest that (XIV) is another example of a Rh^I–Rh^{III} complex. As with the ruthenium complexes (X) and (XI), two methine resonances were found in the proton n.m.r. spectrum of (XIV). The two ligands attached to the rhodium(III) atom are thus in different environments, and in contrast to the azobenzene complex, it is likely that one metal–carbon σ bond is *trans* to chlorine, and the second is *trans* to nitrogen, as shown.

The isolation of the aniline–rhodium carbonyl complex (XII) and benzaldehyde from this reaction, indicates that in the presence of the metal complex, there is an unusual reversal of the base-catalysed dehydration reaction used to synthesise the anil. Reaction of benzylideneaniline with hydrated rhodium(III) chloride also gives aniline, isolated as the insoluble complex $[Rh(PhNH_2)_2Cl_3]_n$ (XIVa), and benzaldehyde; in this reaction nearly 70% recovery of aniline as the complex was achieved. The source of the water required for this reverse reaction may be the hydrated metal chloride.

Reaction between benzylidenemethylamine and $[Rh(CO)_2Cl]_2$ affords $[Rh(bzmH)(CO)_2Cl]_n$ (XV), similar in stoicheiometry to (XIII). This compound is probably another example of an $Rh(amine)(CO)_2Cl$ complex, in which the ligand is co-ordinated *via* the nitrogen atom only. Complexes (XIII) and (XV) are similar to (IV), mentioned above;[6] however, we were unable to find any evidence for a disubstituted compound $Rh(amine)_2(CO)Cl$.

With palladium(II) chloride, benzylidenemethylamine afforded a brown solid, presumably the dimeric $[Pd(bzm)Cl]_2$ (XVI). Thallium cyclopentadienide converted this to $Pd(bzm)(\pi\text{-}C_5H_5)$ (XVII), which was sufficiently soluble for characterisation by proton n.m.r. spectroscopy, as well as volatile enough to afford a mass spectrum. We have previously found these cyclopentadienyl derivatives to be very useful in the characterisation of the palladium complexes. However, attempts to obtain a similar compound from $[Pd(bza)Cl]_2$ gave only an unstable red solid, and no discrete palladium complex could be isolated.

The formation of the above complexes may occur by two routes. The first, exemplified by the reaction involving palladium(II) chloride, may be considered as an electrophilic metallation of the aromatic ring, analogous to the well known mercuration reaction, and followed by chelation of the palladium by the nitrogen atom. This mechanism is unlikely to be one by which complexes containing metals in low oxidation states react, and a second route, involving initial co-ordination of the nitrogen atom, is favoured. The resulting electron-rich complex then undergoes an intramolecular oxidative addition or elimination reaction, resulting in the formation of a metal–carbon σ-bond. Use of methyl–metal compounds results in the loss of methane;[2] alternatively hydrogen or hydrogen chloride may be eliminated from the appropriate hydride or chloride precursors.

In most cases, only the end product, containing the *ortho*-metallated ligand, has been observed. With $[Rh(CO)_2Cl]_2$, however, the formation of complex (XIII) may represent the intermediate stage mentioned above. However, we have been unable to convert (XIII) into any *ortho*-metallated complex such as $Rh(bzm)(CO)_2$ [analogous to $Rh(azb)(CO)_2$ described earlier[13]].

Proton N.m.r. Spectra.—The proton n.m.r. spectra (Table 3) of the complexes containing 2*C*,*N*′-benzylideneaniline ligands show several features common to those of phenylazophenyl complexes.[1,2] However, the separation of the resonances of the *ortho*-metallated ring is not as great, probably because of the relative lack of shielding by the CH group compared with the lone-pair of the unco-ordinated nitrogen of the ligand. As with the other complexes, the resonance of the phenyl group partially overlaps the other aromatic resonances.

In contrast, simpler proton n.m.r. spectra were obtained from the benzylidenemethylamine complexes. The spectrum of complex (VIII) was analysed in detail. The methine proton, C*H*=NMe, resonated at τ 1·92 as a quartet, which arose from a 1·5 Hz coupling to the N*Me* group. This appeared as a doublet at τ 6·47. The protons of the aromatic ring gave three signals centred on τ 2·22 dd, 2·64 dd, and 3·02. The highest field resonance was an AB quartet also showing coupling to the other two protons. Overlapping signals caused the formation of a quintet, the four outer lines of which were doublets, while the central resonance was a triplet. The coupling constants are listed in Table 3.

There is some ambiguity in the exact assignment of these resonances, namely, whether the proton *ortho* to the metal atom gives rise to the signal at τ 2·22, or the one at τ 2·64. On the basis of experiments with substituted compounds of this and related types, which will be described later, we favour the latter assignment.

Mass Spectra.—The mass spectra of carbonyl-containing complexes exhibited ions arising from the usual stepwise loss of carbonyl groups after ionisation. The

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[13] M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Organometallic Chem.*, 1972, in the press.

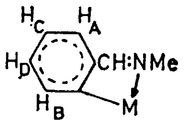
cyclopentadienyl derivative (XVII) showed loss of the C_5H_5 group to give the ion $[C_6H_4CHNMePd]^+$. Subsequent fragmentation of ions of this type is complex. Low *m/e* ions were found corresponding to $[C_3H_3]^+$, $[C_5H_5]^+$, and $[C_6H_5]^+$ in all complexes; a medium intensity ion at *m/e* 91 ($[C_6H_5N]^+$) was also found. Characteristically intense ions were found at *m/e* 104 ($[CH{=}NPh]^+$) and 180 ($[C_6H_4CHNPh]^+$) for the benzylideneaniline derivatives, and at *m/e* 42 ($[CH{=}NMe]^+$) and 118 ($[C_6H_4CHNMe]^+$) for the benzylidenemethylamine complexes. However, the presence of ions at *m/e* 180 or 118 is not diagnostic of the presence of *ortho*-metallated ligands.

TABLE 3

Proton n.m.r. spectra

	Complex	Chemical shifts (τ)		Coupling constants (Hz)	Solvent
(*a*) *Benzylideneaniline derivatives*					
		C*H*:NPh	Others		
(VI)	Mn(bza)(CO)$_4$	1·44s	2·07dq, 2·22dq, 2·7m		(CD$_3$)$_2$CO
(VII)	Re(bza)(CO)$_4$	1·51s	2·10m, 2·7m		(CD$_3$)$_2$CO
		1·70s	2·15dd, 2·47dd, 2·8m		CS$_2$
(X)	Ru(bza)$_2$(CO)$_2$	2·13s, 2·16s	2·64dd, 2·8—3·8br		CS$_2$
(XIV)	[Rh(bza)(CO)Cl]$_2$	1·29s, 1·32s	2·39, 2·61, 2·84, 3·05m		(CD$_3$)$_2$CO
(XIII)	Rh(bzaH)(CO)$_2$Cl	1·65s	2·53s, 2·59s, 2·75s		CS$_2$

(*b*) *Benzylidenemethylamine derivatives*



		C*H*:N*Me*		H$_A$	H$_B$	H$_{C,D}$		
(VIII)	Mn(bzm)(CO)$_4$	1·92q	6·47d	2·22dd	2·64dd	3·02m	J_{AC}, 7·0; J_{AD}, 1·5; J_{BC}, 1·8; J_{BD}, 7·2; J_{CD}, 7·3; J_{MeH}, 1·5	CS$_2$
(XI)	Ru(bzm)$_2$(CO)$_2$	1·47q, 1·85q	6·09d, 6·90d	2·19dd	2·60dt	2·91td	J_{MeH}, 1·5 (both)	(CD$_3$)$_2$CO
(XVII)	Pd(bzm)(C$_5$H$_5$)	2·17q	6·25d	2·48qd	3·06td	3·22dd	J_{MeH}, 1·5	(CD$_3$)$_2$CO
(XV)	Rh(bzmH)(CO)$_2$Cl	1·66q	6·34d	1·75d, 2·60m			J_{MeH}, 1·8	(CD$_3$)$_2$CO

EXPERIMENTAL

Spectroscopic and experimental methods were similar to those described previously.[1,2] Solvents were dried and distilled before use. Analytical data are given in Table 1.

Reactions of Benzylideneaniline.—(a) *With* Mn(CO)$_5$Me. A mixture of benzylideneaniline (181 mg, 1 mmol) and Mn(CO)$_5$Me (210 mg, 1 mmol) was refluxed in light petroleum (25 ml) for 2 h. Chromatography gave a yellow fraction, eluted with light petroleum. Some Mn$_2$(CO)$_{10}$ (2 mg) was removed by sublimation (90°/0·1 mm), and two recrystallisations of the residue from light petroleum gave fine yellow needles of *tetracarbonyl*-2C,N′-(N-*phenylformimidoyl*)*manganese* (VI) (130 mg, 37%).

(b) *With* Re(CO)$_5$Me. A similar reaction using benzylideneaniline (400 mg, 2·2 mmol) and Re(CO)$_5$Me (511 mg, 1·5 mmol) in refluxing light petroleum (30 ml) for 4 h gave a yellow fraction (9 : 1 light petroleum–ether) on chromatography. Excess of benzylideneaniline was removed by sublimation at 100° (0·1 mm); chromatography of the residue as before, and crystallisation from light petroleum gave bright yellow needles of *tetracarbonyl*-2C,N′-(N-*phenylformimidoyl*)*rhenium* (VII) (214 mg, 30%).

(c) *With* Ru$_3$(CO)$_{12}$. Refluxing a mixture of Ru$_3$(CO)$_{12}$ (600 mg, 0·97 mmol) and benzylideneaniline (165 mg, 0·97 mmol) in light petroleum (50 ml) for 6 h gave a deep red solution. The cool mixture when set aside overnight, deposited crystals, which were recrystallised from benzene to give yellow *dicarbonylbis*-[2C,N′-(N-*phenylformimidoyl*)]-*ruthenium* (X) (160 mg, 40%).

(d) *With* [Rh(CO)$_2$Cl]$_2$. A mixture of [Rh(CO)$_2$Cl]$_2$ (780 mg, 2 mmol) and benzylideneaniline (780 mg, 4·3 mmol) was refluxed in light petroleum (40 ml) for 30 min. The filtered pale yellow solution was kept at −10° overnight, and the deep purple solid that separated was purified by sublimation (80°/0·1 mm) to give pure (XII) (68 mg, 6%), identified by m.p. and mixed m.p. (140—141° decomp.), and from its i.r. and mass spectra. Evaporation of the filtrate and chromatography gave a pale yellow fraction (3 : 1 light petroleum–ether); purification by sublimation of the pale yellow residue obtained on evaporation of solvent afforded purple crystals of *benzylideneaniline*(*dicarbonylchloro*)-*rhodium* (XIII) (75 mg, 5%), which could be recrystallised from an ether–light petroleum mixture as pale greenish yellow crystals, which slowly turned purple.

Longer reaction times afforded more RhCl(CO)$_2$(PhNH$_2$) (up to 285 mg, 25%), accompanied by benzaldehyde (up to 212 mg, 50%; 2,4-dinitrophenylhydrazone, m.p. 236°), and a third complex, identified as (XIV) (100 mg, 7%), eluted with 1 : 1 ether–light petroleum mixtures.

(e) *With hydrated* RhCl$_3$. A mixture of hydrated RhCl$_3$ (1·0 g, 5 mmol) and benzylideneaniline (1·8 g, 10 mmol) was refluxed in ethanol (100 ml) for 6 h. The yellow solid which separated was filtered off, and washed with ether and light petroleum to give the solid *complex* (XIVa) (1·3 g, 66%). The filtrate was concentrated and chromatography gave benzaldehyde, identified as above, and by analysis of the hydrazone (Found: C, 54·9; H, 3·6; N, 19·5. $C_{13}H_{10}N_4O_2$ requires C, 54·5; H, 3·5; N, 19·6%).

(f) *With* [Fe(CO)$_2$(π-C$_5$H$_5$)]$_2$. U.v. irradiation of a mixture of benzylideneaniline (362 mg, 2 mmol) and [Fe(CO)$_2$(π-

$C_5H_5)]_2$ (354 mg, 1 mmol) in light petroleum (30 ml) for 48 h gave a pale greenish brown solution. Removal of solvent and chromatography of the residue gave $[Fe(\pi\text{-}C_5H_5)CO]_4$ (60 mg, 20%) as the only isolable product, identified by analysis (Found: C, 48·05; H, 3·5; N, 0%; *M*, 596. $C_{24}H_{20}Fe_4O_4$ requires C, 48·3; H, 3·4; N, 0%; *M*, 596) and spectroscopically [ν(CO): 1638 ($CHCl_3$) and 1650 cm^{-1} (cyclohexane); lit.,[11] 1620 cm^{-1} (KBr disc)].

Reactions of Benzylidenemethylamine.—(a) *With* $Mn(CO)_5Me$. A mixture of $Mn(CO)_5Me$ (300 mg, 1·42 mmol) and the ligand (170 mg, 1·42 mmol) was refluxed in light petroleum (50 ml) for 5½ h. Removal of solvent and chromatography (light petroleum) afforded yellow crystals of *complex* (VIII) (283 mg, 70%).

(b) *With* $[Rh(CO)_2Cl]_2$. A solution of $[Rh(CO)_2Cl]_2$ (300 mg, 0·77 mmol) and benzylidenemethylamine (184 mg, 1·54 mmol) was refluxed in light petroleum (50 ml) for 15 min. The resulting greenish yellow solution deposited yellow crystals when set aside; these were filtered off and recrystallised (hexane–EtOH) to afford the pure yellow *product* (XV) (340 mg, 71%).

(c) *With* $RhCl_3,3H_2O$. An ethanolic solution of $RhCl_3,3H_2O$ (300 mg, 1·22 mmol) and the ligand (341 mg, 2·86 mmol) was stirred at room temperature for 16 h. The yellow powder which separated was filtered off, washed with ethanol and ether, and dried *in vacuo*. The filtrate on treatment with 2,4-dinitrophenylhydrazine afforded the 2,4-DNP derivative of benzaldehyde, m.p. 236—237°.

(d) *With palladium*(II) *chloride*. Refluxing a solution of Li_2PdCl_4 (445 mg, 1·7 mmol) with the ligand (201 mg, 1·7 mmol) in methanol (50 ml) for 6 h gave a yellow-green product (XVI) which was filtered off, washed with methanol and ether, and dried (196 mg, 45%).

(e) *With* $[Ru(CO)_3Cl_2]_2$. A mixture of $[Ru(CO)_3Cl_2]_2$ (300 mg, 0·59 mmol) and benzylidenemethylamine (280 mg, 2·2 mmol) was heated at 120—140° for 3 h. Chromatography of the brown oil resulting gave a fraction (ether) which afforded a white solid, which could be recrystallised from hexane–dichloromethane. Although no analytical figures were obtained, a mass spectrum showed peaks (including a molecular ion cluster) consistent with its being $[Ru(bzm)(CO)_2Cl]_2$ (IX).

(f) *With* $Ru_3(CO)_{12}$. A solution of $Ru_3(CO)_{12}$ (300 mg, 0·515 mmol) and benzylidenemethylamine (182 mg, 1·545 mmol) in heptane (70 ml) was refluxed for 20 h. The product separated and was filtered off and recrystallised (hexane) to give pale yellow *crystals* of $Ru(bzm)_2(CO)_2$ (XI) (150 mg, 38%).

Reaction between Thallium Cyclopentadienide and Complex (XVI).—A suspension of $[(Pd(bzm)Cl]_2$ (35 mg, 0·067 mmol) and thallium cyclopentadienide (70 mg, 0·26 mmol) in diethyl ether (30 ml) was stirred overnight. After filtration, the orange filtrate was evaporated, and the residue recrystallised (hexane–diethyl ether) to give dark red *crystals* of $Pd(bzm)(\pi\text{-}C_5H_5)$ (XVII) (25 mg, 64%).

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