Complexes with Rhodium–Boron Bonds

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SEVERAL adducts of Lewis-type acids (BH_3, BF_3, BCl_3, $AlMe_3$) with transition-metal complexes have been described such as $[H_3B–Mn(CO)_4PPh_3]^{-1}$ or $(\pi\text{-}C_5H_5)_2WH_2\cdot BF_3$.[2] Lewis basicity is also demonstrated by the square planar d^8 complexes of the type $(R_3P)_2M(CO)X$ (M = Rh or Ir; X = Cl or Br) as shown by the ready addition of SO_2 to give a five-co-ordinated species $(Ph_3P)_2Ir(CO)Cl\cdot SO_2$[3] or of HCl, the halogens, CH_3I and H_2 to yield six-co-ordinate M^{III} complexes.[4–7]

We have shown that the rhodium compounds $L_2Rh(CO)X$ add BCl_3 and BBr_3 in benzene solution at room temperature forming derivatives of the composition $L_2Rh(CO)X\cdot BY_3$ in 60—95% yield. The BBr_3 -adducts are thermally rather stable. They decompose on melting at temperatures appreciably higher than the starting materials (see the Table). They can be recrystallized from a mixture of benzene and pentane. On the other hand the BCl_3 derivatives lose the boron halide rather readily in a vacuum or on recrystallisation.

Although we expected that the products would be six-co-ordinate containing Y_2B-groups bonded to the metal, the present evidence points to Lewis-acid–base adducts. Thus pyridine displaces BBr_3 from $(Ph_3P)_2Rh(CO)Br\cdot BBr_3$ as $C_5H_5N\cdot BBr_3$, and three equivalents of bromide ions are formed on basic hydrolysis, conditions under which the complexes $(Ph_3P)_2Rh(CO)X$ are not attacked. Also the ^{11}B chemical shifts (doublets, see Table) suggest four-co-ordinate boron.†

The carbonyl stretching frequencies in the infrared spectra of the adducts are shifted by about 20—70 cm.$^{-1}$ to higher wave numbers compared with the parent compounds. Apart from the main carbonyl absorption, a weak band at 2100 cm.$^{-1}$ was also observed. In Nujol mulls the pattern of absorptions was sometimes more complicated, possibly on account of crystal field interactions, as this resolved into a strong sharp band at *ca.* 2000 cm.$^{-1}$ and a weak one at *ca.* 2100 cm.$^{-1}$ in chloroform solution.

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† $Ph_3P\cdot BBr_3$ shows the same ^{11}B chemical shift and J_{B-P} as observed in $(Ph_3P)_2Rh(CO)Br\cdot BBr_3$. We therefore cannot completely rule out the possibility of decomposition of the product into this compound in solution. On the other hand the products can be recrystallized several times without change in composition, and furthermore the *X*-ray powder patterns of the rhodium complex and $Ph_3P\cdot BBr_3$ are quite distinct.

TABLE

	m.p.[a] (°c)	colour	νCO (cm.$^{-1}$)[f]	$\delta^{11}B$ (p.p.m.)[b]	J(RhB) (c./sec.)
$(Ph_3P)_2Rh(CO)Cl$	195—200	yellow	1968s	—	—
$(Ph_3P)_2Rh(CO)Br$	187—193	yellow	1969s	—	—
$(Ph_3As)_2Rh(CO)Cl$	250—253	orange	1967s	—	—
$(Ph_3P)_2Rh(CO)Cl{\cdot}BCl_3$	210[c]	yellow	1991s[d]	−3·7	146
$(Ph_3P)_2Rh(CO)Cl{\cdot}BBr_3$	260—270	light brown	1990s	−4·4[e] ?	—
			2098w	+1·3	146
				+7·3	149
				+14·3	146
$(Ph_3As)_2Rh(CO)Cl{\cdot}BBr_3$	261—265	orange brown	2047s	—	—
			2101m		
$(Ph_3P)_2Rh(CO)Br{\cdot}BCl_3$	193—198	yellow	—	—	—
$(Ph_3P)_2Rh(CO)Br{\cdot}BBr_3$	271—276	light brown	1985s	+14·4	145
			1998s		
			2049m		
			2102w		

[a] All compounds melt with decomposition.
[b] BF_3–ether complex as external standard.
[c] Decomposition temperature; melting starts at 260°.
[d] In $CHCl_3$ solution.
[e] These doublets can only be accounted for if halogen exchange has taken place. The formula therefore gives only the gross composition of the compound which is not actually a pure BBr_3 adduct.
[f] In Nujol mulls.

Since Shriver *et al.*[8] have not been able to obtain $(Ph_3P)_2Rh(CO)Cl{\cdot}BF_3$; this fact and our results show that towards the bases $L_2Rh(CO)X$ acidity of the boron halides increases in the series $BF_3 \rightarrow BBr_3$ as expected.

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