fin moieties, upon adduct formation, are less striking in the C_2H_4 than in the C_2F_4 unit, which is explained in terms of the weaker metal to olefin π bonding in the Rh–C_2H_4 than in the Rh–C_2F_4 bond.[27] On the other hand, X-ray analyses show that $IrBr(CO)(PPh_3)_2(TCNE)$,[15] $IrH(CO)(PPh_3)_2(FN)$,[28] and $IrCl(CO)(AsPh_3)_2(TCNE)$[29] adopt trigonal-bipyramidal configurations with the cyanoolefins coordinated rigidly and that the degrees of distortion of their geometries, upon adduct formation, indicate strong π-bonding interactions between the iridium atoms and the cyanoolefins. No evidence for the free rotation of the cyanoolefins around the coordination bond is reported for these compounds.[1]

Comparison of **1a** and **1b** with **2a** and **2b**, respectively, shows that the replacement of the two isocyanides with two triphenylphosphines in the parent complexes has produced a change in the bonding behavior of TCNE toward the rhodium atom, from nonrigid to rigid. It is well known that the tertiary phosphines have more σ-donor and less π-acceptor capacity compared with the isocyanides.[30] Thus an expected increase in the transition metal basicity of $[Rh(RNC)_2(PPh_3)_2]ClO_4$ compared with that of $[Rh(RNC)_4]X$, which is evidenced from a comparison of their $\nu(N{\equiv}C)$ data (Table II), seems to cause formation of the rigid adducts **2a** and **2b**. In addition, $[Rh(RNC)_2(PPh_3)_2]ClO_4$ can react with FN (electron affinity of 0.78 eV[25]), and in the adducts formed (**6a** and **6b**) the FN is rotating. This result suggests that a moderate π-bonding interaction between the more basic Rh(I) substrate and a rather weak π acid FN yields the nonrigid adducts.

Although Raman spectra of some of these compounds were measured, they were unfortunately too complicated to assign the $\nu(C\overset{\cdots}{-}C)$ of the coordinated olefins with confidence, precluding a quantitative comparison of the π-bonding interaction. In connection with $[Rh(RNC)_2(PPh_3)_2(olefin)]ClO_4$ (olefin = TCNE or FN), it is suggestive that the analogous iridium compounds $[Ir(p\text{-}CH_3C_6H_4NC)_2(PPh_3)_2(olefin)]ClO_4$ (olefin = TCNE, FN, or maleic anhydride) synthesized by us recently[31] are found to have trigonal-bipyramidal configurations with the rigidly bonded olefins. In view of the generally stronger basicity of a certain Ir(I) complex than that of an analogous Rh(I) complex,[2] the stronger π-bonding interactions between the iridium atom and the olefins have probably resulted in the rigid adducts even for the FN and maleic anhydride.

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Registry No. **1a**, 51567-54-5; **1b**, 36682-31-2; **1c**, 36620-24-3; **1d**, 51567-56-7; **1e**, 36620-25-4; **2a**, 51567-62-5; **2b**, 51567-63-6; **3a**, 51567-58-9; **3b**, 51567-60-3; **4**, 51567-61-4; **5a**, 51635-58-6; **5b**, 51635-59-7; **6a**, 51635-61-1; **6b**, 51635-63-3; $[Rh(CH_3NC)_4]BPh_4$, 34742-53-5; $[Rh(p\text{-}CH_3OC_6H_4NC)_4]ClO_4$, 14075-09-3; $[Rh(p\text{-}CH_3C_6H_4NC)_4]ClO_4$, 43093-67-0; $[Rh(o\text{-}CH_3C_6H_4NC)_4]ClO_4$, 51567-65-8; $[Rh(CH_3NC)_2(PPh_3)_2]I$, 51743-55-6; $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]I$, 51567-66-9; $[Rh(p\text{-}CH_3OC_6H_4NC)(PPh_3)_2]Cl$, 51567-67-0; $[Rh(CH_3NC)_2(PPh_3)_2]ClO_4$, 51703-33-4; $[Rh(p\text{-}CH_3OC_6H_4NC)_2(PPh_3)_2]ClO_4$, 51567-69-2.

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Interaction of Four-Coordinate Rhodium(I) Complexes with Boron-Containing Lewis Acids

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The interaction of Lewis acids with $RhCl(PPh_3)_3$, $RhClCO(PPh_3)_2$, $[Rh(diphos)_2]BPh_4$, $RhClC_8H_{12}PPh_3$, and $[RhC_8H_{12}(PPh_3)_2]PF_6$ is reported. The Lewis acid complexes were characterized by stoichiometry, molecular weight, medium- and far-infrared, and ^{11}B, ^{31}P, ^{19}F, ^{1}H, and ^{103}Rh nmr data. Several types of reactions involving metal basicity, halide basicity, and phosphine abstraction were observed.

Of major interest in the study of platinum metal complexes have been their reactions with simple substrates such as O_2, SO_2, C_2H_4, HX, RX, H_2, CO, and C_2H_2.[1] These reactions generally involve synergic bonding between the platinum metal and the substrate, while substrates that can complex solely as σ-electron acceptors, such as group III Lewis acids, have not been as extensively studied. Those platinum metal complexes that have been investigated with Lewis acids have usually led to the formation of metal base–Lewis acid adducts.[1i,2-8] Studies involving Lewis acids with other metal

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Table I. Nmr Spectral Parameters for Rhodium Complexes and Related Compounds of Interest

	^{103}Rh[a]	^{31}P[a]			^{11}B[a]			^{19}F[a]
Compd	δ(Rh), ppm	δ(P), ppm	J_{Rh-P}, Hz	J_{P-P}, Hz	δ(B), ppm	J_{Rh-B}, Hz	J_{P-B}, Hz	δ(F), ppm
$Ph_3P \cdot BCl_3$		5.2			14.6		147	
$Ph_3P \cdot BF_3$		11.8			15.6		*c*	26.0[c,d]
diphos·$2BCl_3$		−4.2			15.5		147	
BF_3Cl^- [b]					16.6			−2
$[Rh(diphos)_2]BPh_4$		−57.3	136		*e*			
$[Rh(diphos)_2]BPh_4 \cdot 2BCl_3$	−1203	−51.0	93		15.0[e]	153		
$[Rh(diphos)_2]BPh_4 \cdot 2BF_3$		−56.7	132		18.7[e]	*c*		31.9
$RhCl(PPh_3)_3$		−31.5	142	39				
		−48.3	192	39				
$RhCl(PPh_3)_3$ [f]	−1291	−31.5	142	38				
		−48.0	189	38				
$RhCl(PPh_3)_3 \cdot 2BCl_3$		−44.1	129		12.2			
$RhCl(PPh_3)_3 \cdot 2BF_3$		−32.5	168		17.2			28.4
		−49.5	194					
$RhClC_8H_{12}PPh_3$	−1741	−30.4	149					
$RhClC_8H_{12}PPh_3 \cdot BCl_3$		*g*			14.8		155	
$RhClC_8H_{12}PPh_3 \cdot BF_3$		−28.6	149		15.9[d]	*c*		28.8[d]
$RhClCO(PPh_3)_2$ [f]	−1003	−29.1	−124					
$RhClCO(PPh_3)_2 \cdot BCl_3$		−25.6	149		15.0	154		
		−33.9	149					
$RhClCO(PPh_3)_2 \cdot BF_3$ [h]		−29.7	151		20.5	*c*		29.2[d]

[a] All spectra were recorded at room temperature in CH_2Cl_2 unless otherwise noted. The chemical shifts are calculated from $\delta(X) = [(\nu_r - \nu_s)/\nu_r] \times 10^6$, where ν_r and ν_s are the resonant frequencies of the reference and sample, respectively, at a field strength such that the proton signal from TMS would be observed at 90 MHz. For δ(Rh), ν_r is the frequency of rhodium metal (2.840104 MHz); for δ(P), ν_r is the frequency for 85% H_3PO_4; for δ(B), ν_r is the frequency for $B(OCH_3)_3$; and for δ(F), ν_r is the frequency for BF_3. [b] This ion has been postulated as an intermediate in halide-exchange reactions involving BCl_3: J. S. Hartman and G. J. Schrobilgen, *Inorg. Chem.*, 11, 940 (1972). [c] We were unable to detect any coupling. [d] Very broad. [e] The δ(B) for BPh_4^- was not determined. [f] Value from T. H. Brown and P. J. Green, *J. Amer. Chem. Soc.*, 92, 2359 (1970). [g] Not determined. [h] Run in 1,2-dichloroethane.

complexes have demonstrated that a variety of reactions can occur. These include ligand abstraction,[9-12] ligand bridging,[13,14] ligand exchange,[15,16] and metal basicity.[1c] In the present study this wide variety of reactions has been demonstrated for the first time for a series of seemingly closely related square-planar rhodium(I) complexes.

Experimental Section

Since the materials used are air sensitive in solution, all work was performed using Schlenk, drybox, or high-vacuum line techniques.[17] The stoichiometries of the Lewis acid–metal complex adducts were determined by elemental analysis (Galbraith Laboratories, Inc., Knoxville, Tenn.), tensimetric titrations, net acid uptake experiments, and back-reaction of the isolated adducts with $(CH_3)_3N$. The adducts were characterized by cryoscopic molecular weight determinations in an air-free apparatus[18] and infrared (Beckman IR-9 and IR-11) and nmr (Brucker HFX-90) spectra. All nmr spectra were obtained on 10-mm sample tubes that were sealed off under vacuum. The nmr spectral data are summarized in Table I. Rhodium frequencies were determined in two cases by a triple irradiation experiment in which the proton-decoupled phosphorus spectrum was repeatedly scanned while irradiating at 100-Hz intervals in the rhodium frequency range of 2.830–2.850 MHz. The large Rh–P and Rh–B coupling constants made it impossible to decouple most of the phosphorus and boron spectra with the power available in the rhodium frequency range. There was no ^1H nmr evidence of hydride formation in any of the adducts. The infrared data were only useful to indicate the presence of a four-coordinate Lewis acid and therefore are only mentioned in special cases. Purification of the Lewis acids has been described previously.[5] All the metal complexes were prepared according to standard literature methods: $[Rh(diphos)_2]BPh_4$,[19] $RhCl(PPh_3)_3$,[20] $RhClC_8H_{12}PPh_3$,[21] $RhClCO(PPh_3)_2$,[22] $[RhC_8H_{12}(PPh_3)_2]PF_6$,[23] and $Rh_2Cl_2(CO)_4$.[24] Solvents were refluxed over P_2O_5, distilled under nitrogen, and stored over an appropriate drying agent under vacuum or in a nitrogen atmosphere.

Results and Discussion

$[Rh(diphos)_2]BPh_4$.[25] The tensimetric titration of $[Rh(diphos)_2]BPh_4$ with BF_3 (in C_6H_5Cl at −45°) or BCl_3 (in CH_2Br_2 at 0°) gave stoichiometries of 1.97 and 2.06 mol of acid/mol of rhodium complex, respectively. In addition, a back-reaction of the BF_3 adduct with excess $(CH_3)_3N$ gave a stoichiometry of 2.06 BF_3 per rhodium, while an elemental analysis of the BCl_3 adduct gave the following results. *Anal.* Calcd for $RhC_{70}H_{66}B_3Cl_6P_4$: Rh, 7.1; C, 62.9; H, 4.7; B, 2.2; Cl, 14.7. Found: Rh, 7.1; C, 62.9; H, 5.1; B, 2.8; Cl, 15.6.

The nmr data for $[Rh(diphos)_2]BPh_4$ and its BF_3 and BCl_3 adducts are summarized in Table I. The ^{11}B nmr spec-

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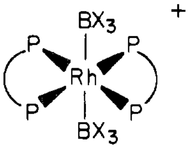
Table II. Molecular Weights of the Rhodium Complexes and Their Adducts

Compd	Solvent	Calcd molality for soln × 10^3	Av obsd mol wt	Formula wt
$RhCl(PPh_3)_3$[a]	Benzene		950 ± 40	925
$RhCl(PPh_3)_3$	1,2-Dichloroethane	2.71	970	925
$RhCl(PPh_3)_3 + 2BCl_3$	1,2-Dichloroethane	2.71	1070	1159
$RhClC_8H_{12}PPh_3$	1,2-Dichloroethane	8.83	510	509
$RhClC_8H_{12}PPh_3 + BCl_3$	1,2-Dichloroethane	8.83	415	626
$RhClC_8H_{12}PPh_3 + BF_3$	1,2-Dichloroethane	21.73	883	578
$RhClC_8H_{12}PPh_3 + BF_3$	Benzene	6.39	860	578
$RhClCO(PPh_3)_2$	Benzene	2.88	685	691
$RhClCO(PPh_3)_2 + BCl_3$	Benzene	2.88	797	808

[a] Average for four determinations; concentration range (2.39-5.85) × 10^{-3} *m*.

tra for both adducts indicate that both BCl_3 and BF_3 are four-coordinate and are equivalent on the nmr time scale.[26] In addition, the BCl_3 adduct exhibits a doublet due to boron-rhodium ($S = {}^1/_2$) coupling. Rhodium-BF_3 coupling was not observed in any of the BF_3 complexes studied, presumably owing to BF_3 exchange. The ^{31}P nmr spectra of $[Rh(diphos)_2]BPh_4$, Figure 1a, and $[Rh(diphos)_2]BPh_4{\cdot}2BCl_3$, Figure 1b, each consist of a doublet and thus show that all four phosphorus atoms are equivalent. Formation of diphos·$2BCl_3$ can be eliminated since its ^{31}P signal occurs at −4.2 ppm or approximately 50 ppm upfield. That all four phosphorus atoms are still attached to the rhodium in $[Rh(diphos)_2]{\cdot}2BCl_3$ is demonstrated by the ability to rhodium decouple the phosphorus spectrum, Figure 1c. The ^{31}P spectrum for the BF_3 adduct, Figure 1d, is similar to the BCl_3 adduct except that BF_3 does not lower the J_{Rh-P} appreciably. The nmr equivalence of the boron and phosphorus atoms in both adducts suggests the structure shown in 1.



1

$\overset{\frown}{P\ P}$ = diphos
X = F, Cl

A tensimetric titration of $[Rh(diphos)_2]BPh_4$ with diborane at −78° in CH_2Cl_2 indicated that no reaction occurs.

$RhCl(PPh_3)_3$. The initial molecular weight and kinetic data of Wilkinson and coworkers suggested that $RhCl(PPh_3)_3$ was completely dissociated in solution according to the reaction[1f]

$$RhCl(PPh_3)_3 \rightleftharpoons RhCl(PPh_3)_2 + PPh_3$$

A reinvestigation of the molecular weight was prompted when the addition of BCl_3 to solutions of $RhCl(PPh_3)_3$ failed to produce the very stable adduct $Ph_3P{\cdot}BCl_3$. The molecular weight data, Table II, reveal that little dissociation occurs when oxygen is rigorously excluded from the solution,[27] and low dissociation has been confirmed by other techniques.[28]

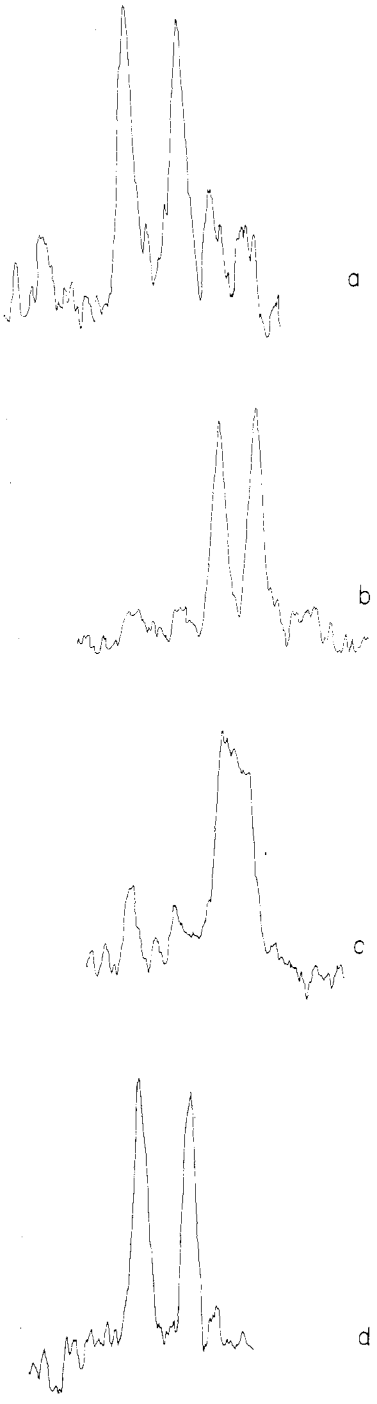


Figure 1. ^{31}P spectra of (a) $[Rh(diphos)_2]BPh_4$, (b) $[Rh(diphos)_2]BPh_4{\cdot}2BCl_3$, (c) $[Rh(diphos)_2]BPh_4{\cdot}2BCl_3$ rhodium decoupled at 2.843520 MHz, and (d) $[Rh(diphos)_2]BPh_4{\cdot}2BF_3$. *H* increases to the right.

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[26] Four-coordinate BCl_3 appears in the range of +10 to +16 ppm, while three-coordinate BCl_2X appears in the range of −38 to −20 ppm. Four-coordinate BF_3 appears from +14 to +21 ppm, while three-coordinate BF_2X is usually in the range of −10 to +8 ppm (chemical shifts relative to $B(OCH_3)_3$). See G. R. Eaton and W. H. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969, pp 436-507.

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When an excess of BCl_3 was added to a CH_2Br_2 solution of $RhCl(PPh_3)_3$ and stirred for 30 min at room temperature, a stoichiometry of 2.10 BCl_3 per rhodium was found based on the recovered, unreacted BCl_3. *Anal.* Calcd for $RhC_{54}H_{45}B_2Cl_7P_3$: Rh, 8.9; C, 55.9; H, 3.90; B, 1.9; Cl, 21.4. Found: Rh, 8.1; C, 56.0; H, 4.00; B, 2.6; Cl, 22.7. This 2:1 interaction was further demonstrated by a tensimetric titration at 0° in CH_2Cl_2.

Tensimetric titration of $RhCl(PPh_3)_3$ with BF_3 at 0° in $CHCl_3$ revealed a stoichiometry of 1.89 BF_3 per rhodium complex and a back-reaction of the isolated BF_3 adduct with $(CH_3)_3N$ gave 2.00 BF_3 per rhodium.[29]

Despite a wealth of data on both of these adducts, their structures remain obscure. A molecular weight determination of the BCl_3 adduct, Table II, indicates that no dissociation occurs in solution. A comparison of the ^{31}P nmr spectra of $RhCl(PPh_3)_3$, Figure 2a, $RhCl(PPh_3)_3 + 1\ BCl_3$, Figure 2b, and $RhCl(PPh_3)_3 + 2\ BCl_3$, Figure 2c, clearly shows that a 1:1 adduct is not formed. The distinct presence of both parent and 2:1 adduct in Figure 2b also demonstrates that intermolecular exchange of BCl_3 is not occurring on the nmr time scale. The simple doublet observed in $RhCl(PPh_3)_3 \cdot 2BCl_3$, Figure 2c, shows that phosphines are equivalent. This conclusion holds over the temperature range −90 to +30°.[30] The absence of a ^{31}P nmr signal for $Ph_3P \cdot BCl_3$ agrees with the molecular weight evidence that extensive dissociation of $RhCl(PPh_3)_3$ does not occur. The presence of $Ph_3P \cdot BCl_3$ is detected, however, if the samples are allowed to stand for several days. Apparently the rate of attack of BCl_3 on the metal complex is much faster than that of phosphine dissociation. Any proposed structure for this adduct must explain the equivalent non-temperature-dependent phosphine ^{31}P nmr spectrum, the singlet in the ^{11}B spectrum, the lack of formation of a 1:1 adduct, and a molecular weight that indicates no dissociation. We considered that $B_2Cl_7^-$ might be formed as either a discrete ion or a ligand. The possibility that this hitherto unisolated ion[31] might be stabilized by a large cation was explored by tensimetric titrations of Ph_4AsCl and Bu_4NCl with BCl_3 at 0°. In both instances only a 1:1 interaction was observed, thereby casting doubt on the existence of $B_2Cl_7^-$ in the rhodium adduct. We have been unable to arrive at another reasonable structure involving a single species.

The data available for the $RhCl(PPh_3)_3 \cdot 2BF_3$ system do not assist in the structural characterization of the BCl_3 adduct, since they closely resemble those obtained for the BCl_3 system. Aside from BX_3 frequencies, medium- and far-infrared bands are very similar for the two boron halide adducts. A single ^{11}B nmr resonance also was observed in both cases, Table I. One difference, however, is that the ^{31}P nmr spectrum of $RhCl(PPh_3)_3 \cdot 2BF_3$ shows two sets of doublets with chemical shifts and coupling constants which indicate that the phosphine and halide arrangement of the parent is preserved in the adduct.[30]

A tensimetric titration of $RhCl(PPh_3)_3$ with $B(CH_3)_3$ in CH_2Cl_2 at −45° does indicate a weak interaction. The adduct, however, evolves $B(CH_3)_3$ at room temperature.

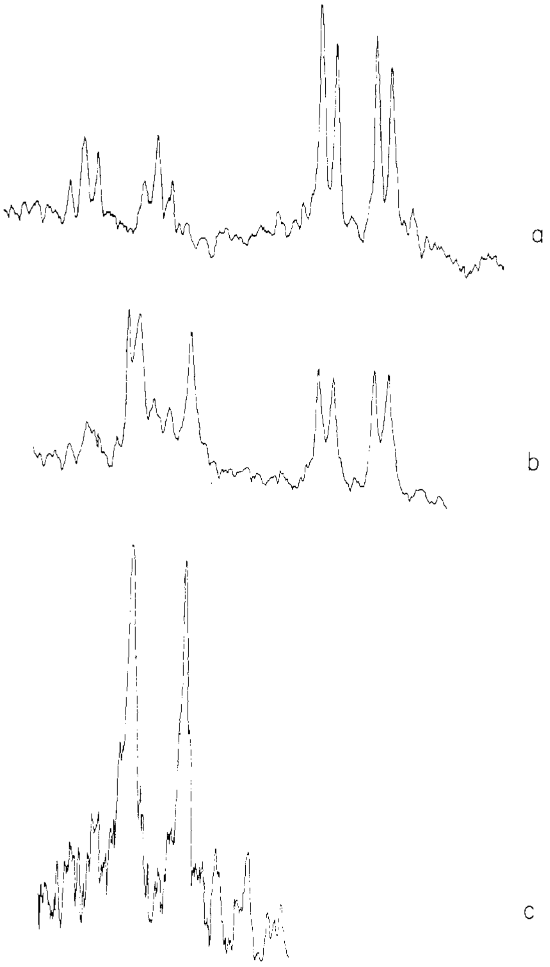

Figure 2. ^{31}P spectra of (a) $RhCl(PPh_3)_3$, (b) $RhCl(PPh_3)_3 + 2\ BCl_3$, and (c) $RhCl(PPh_3)_3 + 1\ BCl_3$. *H* increases to the right.

$RhClC_8H_{12}PPh_3$. A tensimetric titration of $RhClC_8H_{12}PPh_3$ with BCl_3 in C_6H_5Cl at 25° gave a stoichiometry of 1.07 BCl_3 per rhodium. From molecular weight data, Table II, it is apparent that extensive dissociation occurs upon adduct formation. Two compounds, identified by infrared data, were obtained when the adduct was treated with hexane: a white, hexane-insoluble material, $Ph_3P \cdot BCl_3$, and an orange, hexane-soluble material, $[RhCl(C_8H_{12})]_2$.[21] The overall reaction can be written as

$$2RhClC_8H_{12}PPh_3 + 2BCl_3 \rightarrow [RhClC_8H_{12}]_2 + 2Ph_3P \cdot BCl_3$$

To our knowledge, this is the first reported example of a phosphine abstraction by a Lewis acid from a stable metal complex.

A phosphine abstraction reaction is not observed, however, when BF_3 is added to $RhClC_8H_{12}PPh_3$. In this case, addition of excess BF_3 to a stirred solution of $RhClC_8H_{12}PPh_3$ in CH_2Cl_2 at room temperature yielded a stoichiometry of 0.97 BF_3 per rhodium, and tensimetric titration at −78° in CH_2Cl_2 gave a ratio of 1.16. Interestingly, the molecular weight data, Table II, suggest association rather than dissociation. The ^{11}B and ^{19}F nmr signals are both very broad, presumably owing to BF_3 exchange. The ^{31}P spectra of $RhClC_8H_{12}PPh_3$ and its BF_3 adduct show that a 2-ppm upfield shift occurs in the phosphine doublet upon addition of BF_3, but no change occurs in J_{Rh-P}. There is no evidence for either $Ph_3P \cdot BF_3$ or BF_3Cl^- in the various nmr spectra.

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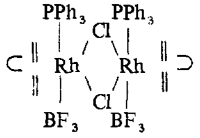
(29) The elemental analyses of the BF_3 adducts in this study were consistently very low in fluoride and high in chloride. The spectroscopic evidence, however, clearly shows the presence of BF_3 and routine checks of the recovered BF_3 failed to show the presence of chloride.

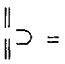
(30) By contrast, the phosphorus spectrum of $RhClH_2(PPh_3)_3$ is very temperature dependent: C. A. Tolman, private communication.

(31) Its existence has been postulated as an intermediate in halide-exchange reactions involving BCl_3: J. S. Hartman and G. J. Schrobilgen, *Inorg. Chem.*, 11, 940 (1972).

The available data suggest, but by no means prove, that the predominant species in solution is **2**.



2

 = 1,5-cyclooctadiene

$RhClCO(PPh_3)_2$. Powell and Noth previously reported a BCl_3 adduct of $RhClCO(PPh_3)_2$,[2] but further characterization of this complex seemed warranted because of the close similarity of the ^{11}B nmr spectrum of the adduct with that of $Ph_3P \cdot BCl_3$, the small observed increase in ν_{CO} upon adduct formation,[4,32,33] and the failure of related $IrClCO(PPh_3)_2$ to form a simple BCl_3 adduct.[7,34]

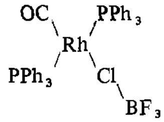
The 1:1 stoichiometry $RhClCO(PPh_3)_2 \cdot BCl_3$ was confirmed from the net uptake of BCl_3 by a benzene solution of $RhClCO(PPh_3)_2$. A molecular weight determination, Table II, shows that dissociation does not occur upon BCl_3 addition, demonstrating that $Ph_3P \cdot BCl_3$ is not formed. In addition to ^{11}B nmr data which agree with those of Powell and Noth, we obtained a ^{31}P nmr spectrum, Table I, which indicates that the two phosphines are not equivalent. The infrared spectrum of the adduct shows the same increase in ν_{CO} from 1969 to 1989 cm^{-1} that was reported.[2] In addition, absorptions at 298, 681, and 720 cm^{-1} that are characteristic of four-coordinate BCl_3[35] and a 5-cm^{-1} increase in ν_{Rh-Cl} (320 cm^{-1}) are observed. The presence of an unperturbed BCl_4^- is ruled out by the lack of an absorption at 250 cm^{-1}.[36] This additional work supports the original formulation of $RhClCO(PPh_3)_2 \cdot BCl_3$ as a metal base-Lewis acid adduct.

Prior to the work of Powell and Noth, Scott had found that BF_3 does not form an isolable adduct with $RhClCO(PPh_3)_2$ in benzene or toluene.[34] However, when 1,2-dichloroethane is used as a solvent, a stoichiometric adduct can be isolated. The dependence of the stoichiometry on the solvent is unique to this system.

When a large excess of BF_3 reacted overnight at room temperature with a 1,2-dichloroethane solution of $RhClCO(PPh_3)_2$, a stoichiometry of 1.01 BF_3 per rhodium was found, based on recovered, unreacted BF_3. A back-reaction of the isolated adduct with excess $(CH_3)_3N$ gave a stoichiometry of 1.1 BF_3 per rhodium. The infrared spectrum of $RhClCO(PPh_3)_2 \cdot BF_3$ has only two changes from the spectrum of the parent: a very small decrease in ν_{CO} from 1969 to 1963 cm^{-1} (this is the first report of a decrease in ν_{CO} for adducts of $RhClCO(PPh_3)_2$) and absorptions due to four-coordinate BF_3 (1170-1050 and 850 cm^{-1}).[37] The nmr data summarized in Table I for $RhClCO(PPh_3)_2 \cdot BF_3$ resemble those of the parent. The ^{11}B and ^{19}F spectra allow the elimination of $Ph_3P \cdot BF_3$ and BF_3Cl^- as possible products. This series of minor changes in the nmr and infrared spectra leads us to postulate that the BF_3 bonds to chloride, as shown in **3**.

Table III. Summary of the Basic Sites in Rhodium Complexes Studied

	BCl_3	BF_3
$[Rh(diphos)_2]BPh_4$	Rhodium	Rhodium
$RhCl(PPh_3)_3$	Chloride	Chloride or rhodium
$RhClC_8H_{12}PPh_3$	Phosphine	Rhodium?
$RhClCO(PPh_3)_2$	Rhodium	Chloride



3

Miscellaneous Reactions. The addition of a large excess of BF_3 to a chlorobenzene solution of $[RhC_8H_{12}(PPh_3)_2]PF_6$ at 0° gave a stoichiometry of 1.1 BF_3 per rhodium, based on recovered, unreacted BF_3. The volatiles also contained PF_5 and an infrared examination of the solid revealed the presence of BF_4^- but not PF_6^-. The overall reaction is therefore

$$[RhC_8H_{12}(PPh_3)_2]PF_6 + BF_3 \rightarrow [RhC_8H_{12}(PPh_3)_2]BF_4 + PF_5$$

No reaction was observed when excess BCl_3 was added to a benzene solution of $Rh_2Cl_2(CO)_4$ at room temperature. Both reactants were recovered unchanged.

Summary

The basic sites on the Rh(I) complexes studied here are summarized in Table III. Metal-boron bonding is indicated for three adducts: $RhClCO(PPh_3)_2 \cdot BCl_3$, $[Rh(diphos)_2^+] \cdot 2BCl_3$, and $[Rh(diphos)_2^+] \cdot 2BF_3$. Phosphine abstraction was established in the reaction of BCl_3 with $RhCl(C_8H_{12})PPh_3$. The other systems are more ambiguous but halide attachment is probable for some or all of these. Clearly subtle changes in the metal complex lead to significantly different reactions with BF_3 and BCl_3. Furthermore, the most convenient tools for the study of these reactions, B-X stretching frequencies and ^{11}B nmr spectra, are often not symptomatic of the mode of interaction.

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Registry No. $[Rh(diphos)_2]BPh_4$, 15007-81-5; $[Rh(diphos)_2]BPh_4 \cdot 2BCl_3$, 51716-80-4; $[Rh(diphos)_2]BPh_4 \cdot 2BF_3$, 51716-82-6; $RhCl(PPh_3)_3$, 14694-95-2; $RhCl(PPh_3)_3 \cdot 2BCl_3$, 51795-64-3; $RhCl(PPh_3)_3 \cdot 2BF_3$, 51795-63-2; BCl_3, 10294-34-5; BF_3, 7637-07-2; $RhClC_8H_{12}PPh_3$, 31781-57-4; $RhClC_8H_{12}PPh_3 \cdot BCl_3$, 51795-62-1; $RhClC_8H_{12}PPh_3 \cdot BF_3$, 51716-85-9; $RhClCO(PPh_3)_2$, 15318-33-9; $RhClCO(PPh_3)_2 \cdot BCl_3$, 51716-83-7; $RhClCO(PPh_3)_2 \cdot BF_3$, 51716-84-8; Rh, 7440-16-6; P, 7723-14-0; ^{11}B, 14798-13-1.

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(32) For example, ν_{CO} increases by 65, 100, and 70 cm^{-1} for $RhClCO(PPh_3)_2 \cdot SO_2$,[33] $IrClCO(PPh_3)_2 \cdot 2BF_3$,[4] and $IrClCO(PPh_3)_2 \cdot SO_2$,[4] respectively.

(33) K. W. Muir and J. A. Ibers, *Inorg. Chem.*, 8, 1921 (1969).

(34) R. N. Scott, Ph.D. Thesis, Northwestern University, Evanston, Ill., 1968.

(35) D. F. Shriver and B. I. Swanson, *Inorg. Chem.*, 10, 1354 (1971).

(36) J. A. Creighton, *J. Chem. Soc.*, 6589 (1965).

(37) B. Swanson and D. F. Shriver, *Inorg. Chem.*, 9, 1406 (1970).