from the metal site and this interaction is unlikely to account for the rather substantial difference between the two metalloporphyrins. Rather, we believe that the charges at the periphery appreciably influence the size of the molecular orbitals containing the π electrons and hence the delocalization of the electron density off the metal center. We have in he past noted significant differences in the spectral, acid–base, aggregation, ligation, and substitution properties of water-soluble meso-substituted porphyrins which could be correlated with the charge type at the periphery of the molecule and the resultant influence on the π cloud of the porphyrin moiety.[3–5,20–22] We now see a dramatic effect of peripheral charge on the ease of reduction of the metal center; relative to the positively charged peripheries, the negative periphery leads to a concentration of electron density near the porphyrin core and makes the liganded metal ion more resistant to reduction.

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Registry No. $Co^{III}P(H_2O)_2$, 51405-04-0; $Ru(NH_3)_6^{2+}$, 19052-44-9; $CoP(H_2O)(SCN)^{4+}$, 57808-60-3; $CoP(H_2O)(N_3)^{4+}$, 57808-61-4; Cl^-, 16887-00-6; SCN^-, 302-04-5; $Co^{II}P(H_2O)_2$, 58188-34-4.

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Redistribution Reactions of Organometallic Complexes. Carbonyl, Halogen, and Organophosphine Exchange between Coordinately Unsaturated Rhodium(I) and Iridium(I) Complexes[1]

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Halide, carbon monoxide, and organophosphines undergo intermolecular exchange between four-coordinate species of the type $MCOXL_2$ [M = Rh, X = Cl, Br, L = PPh_3, $P(m\text{-}CH_3C_6H_4)_3$, PPh_2Et, $PPhEt_2$, PEt_3, PPh_2Me, $AsPh_3$, $Sb(o\text{-}CH_3C_6H_4)_3$, $P(OPh)_3$; M = Ir, X = Cl, Br, L = PPh_3, $PPhEt_2P(OPh)_3$]. Exchange of CO and X appears to be random. Exchange of organophosphines between rhodium complexes is random whereas phosphine–phosphite exchange between Rh and Ir strongly favors the mixed species $MCOCl[PR_3][P(OR')_3]$. Exchange of CO and X is proposed to occur through four-center associative mechanisms whereas organophosphine exchange is proposed to occur via a dissociative process. No CO exchange was observed between $Rh^{13}COCl(PPh_3)_2$ and $RhCOCl_3(PPh_3)_2$.

Introduction

Transition metal organometallic redistribution reactions have received only a fraction of the extensive study given to redistributions between main group inorganic compounds.[3] Although the square-planar, coordinately unsaturated rhodium(I) and iridium(I) complexes $MCOX(PR_3)_2$ have been extensively studied in oxidative addition reactions[4–6] and more specifically as hydrogenation and hydroformylation catalysts,[7] little is known about intermolecular interactions between these complexes in solution. We have, therefore, investigated intermolecular redistribution of ligands using infrared and phosphorus-31 NMR spectroscopy.

Experimental Section

^{31}P spectra were recorded in 5-mm o.d. tubes using the Fourier transform technique at 40.5 MHz on a Varian XL-100 spectrometer. All spectra were obtained under the conditions of white noise proton decoupling. Pulse delay times at 30° were typically 7.5 sec. Chemical shifts are given with respect to external 85% H_3PO_4, downfield shifts being negative. Line widths were typically 1 Hz.

Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer, values of $\nu(CO)$ being good to ± 2 cm^{-1}. All infrared and NMR samples were prepared under an atmosphere of argon. $RhCOClL_2$, L = PPh_nEt_{3-n}, n = 3–0, PPh_2Me, $P(m\text{-}CH_3C_6H_4)_3$, and $AsPh_3$, were prepared by addition of the appropriate ligand to hexane solutions of $Rh_2Cl_2(CO)_4$. $RhCOCl[Sb(o\text{-}CH_3C_6H_4)_3]_2$,[8] $RhCOCl_3(PPh_3)_2$,[9] $IrCOCl(PPh_3)_2$,[10] and $Rh_2Cl_2(COD)[P(OPh)_3]_2$[11] (COD = cyclooctadiene) were prepared by literature methods. Bromides were prepared by metathesis with LiBr in acetone.

$IrCOClL_2$, L = $PPhEt_2$, $P(OPh)_3$. The insoluble blue powder which results from bubbling CO through a $CHCl_3$ solution of $[IrCl(COT)_2]_2$ (COT = cyclooctene) was suspended in benzene and a benzene solution of L was added dropwise until the blue suspension became a clear yellow solution. Excess L was removed by elution through an acid alumina column with chloroform. The resulting solution was reduced in volume and ethyl ether added to induce precipitation. The yellow crystalline solids thus obtained were washed with ethyl ether and dried under vacuum. The products exhibited satisfactory elemental analyses and infrared and ^{31}P spectra.

Results and Discussion

Carbon Monoxide Exchange. Basolo et al. proposed that the instantaneous exchange of labeled CO with RhCOCl-

Table I. Infrared Data for Rh(I) and Ir(I) Complexes

	$\nu(^{12}CO)$, cm^{-1}	$\nu(^{13}CO)$, cm^{-1}	$\nu(^{13}CO)$-(theor), cm^{-1}
$RhCOCl(PPh_3)_2$	1962	1917	1918
$RhCOacac(PPh_3)$	1983	1936	1939
$RhCOCl((o\text{-}CH_3C_6H_4)_3Sb)$	1955	1908	1910
$RhCONCS(PPh_3)_2$	1983	1936	1939
$RhCOCl_3(PPh_3)_2$	2100		
$IrCOCl(PPh_3)_2$	1953	1907	1909
$IrCONCS(PPh_3)_2$	1974	1927	1930

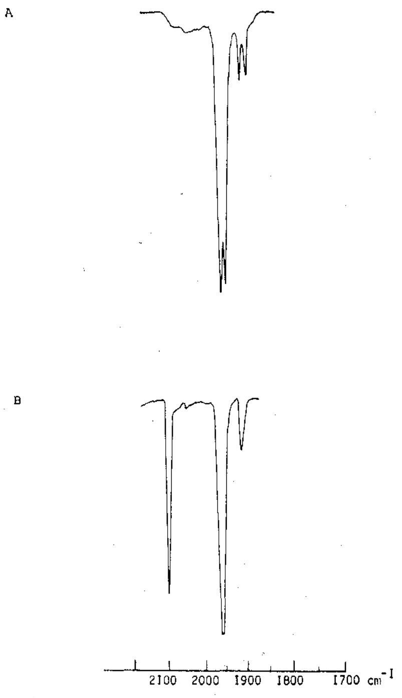

Figure 1. Infrared spectra: (A) $Ir(CO)Cl(PPh_3)_2$ + $Rh(^{13}CO)Cl(PPh_3)_2$; (B) $Rh(CO)Cl_3(PPh_3)_2$ + $Rh(^{13}CO)Cl(PPh_3)_3$.

$(PPh_3)_2$ occurs by an SN2 process through the five-coordinate intermediate $Rh(CO)_2Cl(PPh_3)_2$.[12,13] Exchange of CO with $RhCOCl_3(PPh_3)_2$ was found to be more complex.[14] The rate of exchange was ca. 10^{-5} s^{-1} and independent of the CO concentration. It was proposed that CO exchanged by an SN1 process involving the five-coordinate intermediate $RhCl_3(PPh_3)_2$.

To determine whether intermolecular exchange of CO occurs between complexes, carbon-13-enriched $RhCOCl(PPh_3)_2$ was allowed to react at room temperature with several rhodium(I) and iridium(I) complexes. In ≤60 s the intensity of the ^{13}CO ir absorption due to $RhCOCl(PPh_3)_2$ and the ^{13}CO absorption due to the other reactant species were of equal intensity indicating a random redistribution had occurred. Values for $\nu(^{13}CO)$ and $\nu(^{12}CO)$ are given in Table I.[15] Figure 1A shows the infrared spectrum obtained from the reaction of $Rh^{13}COCl(PPh_3)_2$ with $IrCOCl(PPh_3)_2$.

The interaction of ^{13}C-enriched $RhCOCl(PPh_3)_2$ with $RhCOCl_3(PPh_3)_2$ for 4 h gave the infrared spectrum shown in Figure 1B, indicating that CO exchange had not occurred. The lack of exchange between the Rh(I) and Rh(III) complexes suggests that coordinative unsaturation is a prerequisite for fast carbonyl exchange under these conditions.

Exchange of CO can occur by associative or dissociative mechanisms (Figure 2). A dissociative process should result in the precipitation of insoluble $[RhCl(PPh_3)_2]_2$ with the evolution of CO; however this dimer was not observed even in a refluxing acetone solution under a rapid flow of nitrogen.

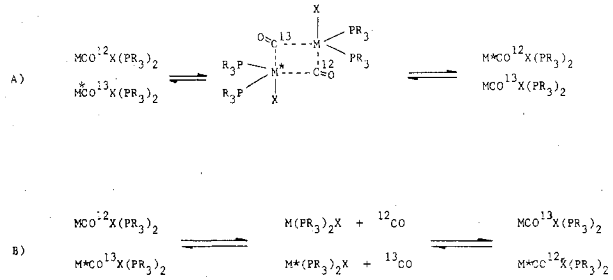

Figure 2. Possible mechanisms for carbon monoxide exchange: (A) associative; (B) dissociative.

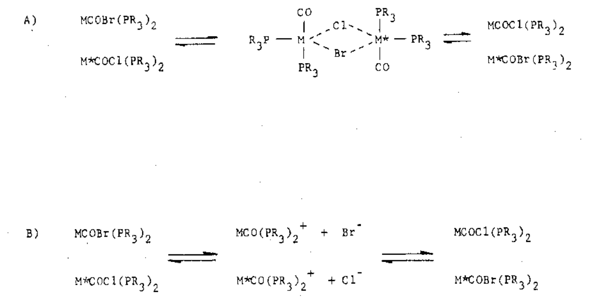

Figure 3. Possible mechanisms for halide exchange: (A) associative; (B) dissociative.

Halide Exchange. Since rapid intermolecular exchange with labeled chloride has been observed for complexes of the type $RhCOCl(PPh_3)_2$,[16] it was of interest to examine halide exchange between such complexes.[17] A ^{31}P spectrum of equimolar quantities of $RhCOBr(PPh_3)_2$ and $IrCOCl(PPh_3)_2$ at 30° in methylene chloride or benzene exhibited four resonances of equal intensity due to $RhCOCl(PPh_3)_2$, $RhCOBr(PPh_3)_2$, $IrCOCl(PPh_3)_2$, and $IrCOBr(PPh_3)_2$, indicating random redistribution of the halides had occurred. The redistribution was complete in ≤180 s. Similar random halide exchanges were observed for numerous rhodium–rhodium systems. The halide exchanges can be effectively slowed and at −75° a mixture of $RhCOBr(PPh_2Et)_2$ with $RhCOCl(PPhEt_2)_2$ showed no sign of exchange within 15 min. Halide exchange can occur by either an associative or a dissociative mechanism (Figure 3). An associative mechanism would involve a doubly five-coordinate bridging halide intermediate in the intermolecular transfer. The ionic intermediate in the dissociative process is less likely for exchanges in benzene.

Organophosphine Exchange. General detection of organophosphine redistributions was facilitated by phosphorus-31 NMR. However, in some instances ABX spectra were obtained because of small chemical shift differences. When the $\delta(P)$ values were <5 ppm apart, the outer four peaks ("wings") of the eight-line AB pattern were of very low intensity. Observation of the X portion of an ABX spectrum is necessary to calculate J_{AX} and J_{BX} and thus only $^2J_{AB}$ could be determined by observation of the AB portion of the spectra.

Stephenson et al.[18] have reported that $RhCOCl(PPh_3)(L)$ can be isolated from the reaction of $[RhCOCl(PPh_3)]_2$ with a variety of ligands (L = PPh_2Me, $P(C_6H_{11})_3$, $AsPh_3$). When the reaction was carried out using $PPhEt_2$, $PPhMe_2$, or $AsEt_3$ only *trans*-$RhCOCl(PPh_3)_2$ and *trans*-$RhCOCl(L)_2$ were isolated. They proposed that equilibrium 1 lay predominantly

$$2RhCOCl(PPh_3)(L) \rightleftharpoons RhCOCl(PPh_3)_2 + RhCOCl(L)_2 \qquad (1)$$

to the left for all L and that the isolation of either $RhCOCl(PPh_3)L$ or $RhCOCl(L)_2$ depends upon "preferential precipitation".

The ^{31}P spectra of $RhCOCl(PPh_3)(L)$, L = PPh_2Et, $AsPh_3$, prepared by the method of Stephenson and the corresponding ^{31}P spectra of equimolar mixtures of $RhCOCl(PPh_3)_2$ and $RhCOCl(L)_2$ are identical. Analyses of these spectra verify the existence, in solution, of the three proposed species.

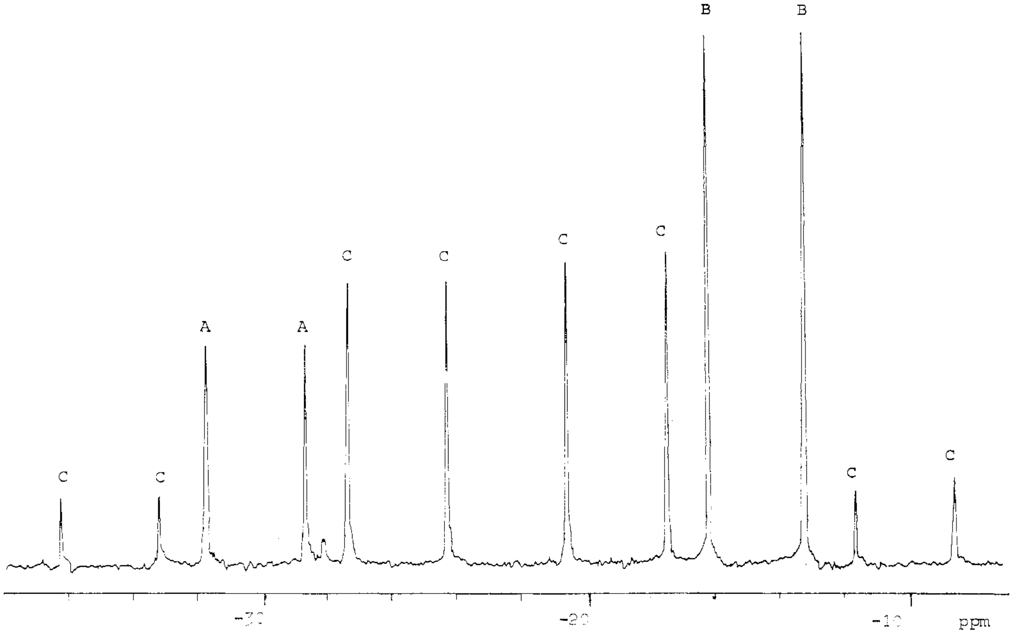

Figure 4. The 40.5-MHz ^{31}P spectrum of 1.6:1 $Rh(CO)Cl(PPh_2Me)_2$:$Rh(CO)Cl(\textit{m}\text{-}CH_3C_6H_4)_3P)_2$: (A) $RhCOCl((\textit{m}\text{-}CH_3C_6H_4)_3P)_2$; (B) $RhCOCl(PPh_2Me)_2$; (C) $RhCOCl(PPh_2Me)(\textit{m}\text{-}CH_3C_6H_4)_3P$.

Reaction of $RhCOCl(PPh_2Me)_2$ with $RhCOCl[P(\textit{m}\text{-}CH_3C_6H_4)_3]_2$, $RhCOCl(PPh_2Et)_2$, $RhCOCl(PPhEt_2)_2$, or $RhCOCl(PEt_3)_2$ at 30° in benzene or methylene chloride results in an ABX spectrum due to $RhCOCl(PPh_2Me)(L)$, in addition to resonances due to the starting complexes. All organophosphine redistributions are random as evidenced by the $RhCOClL_2$:$RhCOClLL'$:$RhCOClL'_2$ ratio of 1:2:1 when equimolar quantities of the complexes are mixed. For the reactions involving $RhCOCl(PPh_2Me)_2$ all eight lines of the AB portion of the spectra were obtained, giving $^2J_{P_1P_2}$ values between 361.8 and 344.3 Hz (Table II, Figure 4). These are the first such trans phosphorus–phosphorus coupling constants reported for rhodium(I) complexes. The complexes $RhCOCl(PR_3)L$, L = $AsPh_3$ and $Sb(\textit{o}\text{-}CH_3C_6H_4)_3$, exhibit lower $\delta(P)$ and larger J_{Rh-P} values than observed for the mixed phosphine complexes (Table II).

In order to obtain J_{Rh-P} in the mixed species, chemical shift difference between $RhCOCl(PR_3)_2$ and $RhCOCl(PR'_3)_2$ must be large. Such would be the case for a mixed phosphine–phosphite complex. We therefore sought to prepare a phosphite complex of the type $RhCOCl[P(OR)_3]_2$ and study its exchange characteristics with analogous phosphine complexes. The ^{31}P spectrum (CH_2Cl_2) of the yellow solid obtained from the reaction of $Rh_2Cl_2(CO)_4$ with $P(OMe)_3$ indicates the presence of two species—$Rh_2Cl_2[P(OMe)_3]_4$ (19%) [$\delta(P)$ −141.7, J_{Rh-P} = 294.3 Hz] and $RhCOCl[P(OMe)_3]_2$ (81%) [$\delta(P)$ −130.5, J_{Rh-P} = 195.0 Hz]. $[P(OPh)_3]_2RhCl_2Rh(COD)$ [$\delta(P)$ −117.0, J_{Rh-P} = 311 Hz] was synthesized to aid in the identification of these species.

The iridium phosphite analogs, $IrCOCl[P(OR)_3]_2$, proved easier to prepare. Such complexes have been prepared by addition of L to $IrCO_3X$.[19] We find that the iridium phosphite complexes can be obtained from the more accessible starting material $[IrCl(COT)_2]_2$[20] (see Experimental Section). Figure 5 shows the ^{31}P spectrum obtained from the reaction of $IrCOCl[P(OPh)_3]_2$ with $RhCOCl(PPhEt_2)_2$ (12 h, 30°, CH_2Cl_2). The six possible products are observed.

Table II. ^{31}P Data for Rh(I) and Ir(I) Mixed Phosphine Complexes

Complex	δ,[a] ppm	J_{Rh-P}, Hz	$^2J_{PP}$, Hz
$RhCOCl(PPh_3)_2$	−28.9	129.4	
$RhCOBr(PPh_3)_2$	−27.6	125.8	
$RhCOCl(P(\textit{m}\text{-}CH_3C_6H_4)_3)_2$	−29.4	127.6	
$RhCOCl(PPh_2Et)$	−27.1	124.0	
$RhCOBr(PPh_2Et)$	−26.0	122.8	
$RhCOCl(PPhEt_2)$	−24.6	121.1	
$RhCOBr(PPhEt_2)$	−22.9	119.7	
$RhCOCl(PEt_3)_2$	−23.6	117.1	
$RhCOCl(PPh_2Me)_2$	−14.4	122.3	
$RhCOCl[P(OPh)_3]_2$	−115.2	217.4	
$(P(OPh)_3)_2RhCl_2Rh(COD)$	−117.0	311.5	
$RhCOCl(P(OMe)_3)_2$	−130.5	195.0	
$Rh_2Cl_2(P(OMe)_3)_4$	−141.7	294.3	
$RhCO_2Cl(PPh_3)$	−24.8	130.2	
$RhCOacac(PPh_3)$	−48.5	175.3	
$RhCl(COD)(PPh_3)$	−30.8	152.4	
$IrCOCl(PPh_3)_2$	−23.9		
$IrCOBr(PPh_3)_2$	−22.4		
$IrCOCl(PPhEt_2)_2$	−21.9		
$IrCOCl(P(OPh)_3)_2$	−103.9		
$RhCOCl(PPh_3)(AsPh_3)$	−31.45	152.1	
$RhCOCl(PPhEt_2)(Sb(\textit{o}\text{-}CH_2C_6H_4)_3)$	−33.31	157.9	
$RhCOCl(PPh_2Me)(PPh_3)$			361.8
$RhCOCl(PPh_2Me)(P(\textit{m}\text{-}CH_3C_6H_4)_3)$			360.7
$RhCOCl(PPh_2Me)(PPh_2Et)$			352.4
$RhCOCl(PPh_2Me)(PPhEt_2)$			348.3
$RhCOCl(PPh_2Me)(PEt_3)$			344.3
$RhCOCl(PPhEt_2)(P(OPh)_3)$	−26.3,[b] −119.0[c]	119.5,[b] 215.2[c]	537.8
$IrCOCl(PPhEt_2)(P(OPh)_3)$	−21.4,[b] −110.5[c]		531.3

[a] In CH_2Cl_2 vs. 85% H_3PO_4. [b] Phosphine. [c] Phosphite.

Accurate calculation of the position of equilibria from observation of room-temperature ^{31}P spectra of mixed phosphine–phosphite complexes necessitates knowledge of the T_1 relaxation time and NOE of such complexes. The greater distance of protons on phosphite ligands from phosphorus nuclei should result in longer T_1 times and smaller nuclear Overhauser enhancements.[21] This is observed in Figure 5 where the phosphite resonances of $IrCOCl(PPhEt_2)[P(OPh)_3]$ and $RhCOCl(PPhEt_2)[P(OPh)_3]$ are of somewhat lower intensity than the phosphine resonances. This spectrum does however show that formation of mixed phosphine–phosphite products is strongly favored. This is consistent with the infrared observation[22] that $IrCOCl(PPh_3)_2$ and $IrCOCl[P(OPh)_3]_2$ react in toluene at 25°, to give $IrCOCl(PPh_3)[P-$

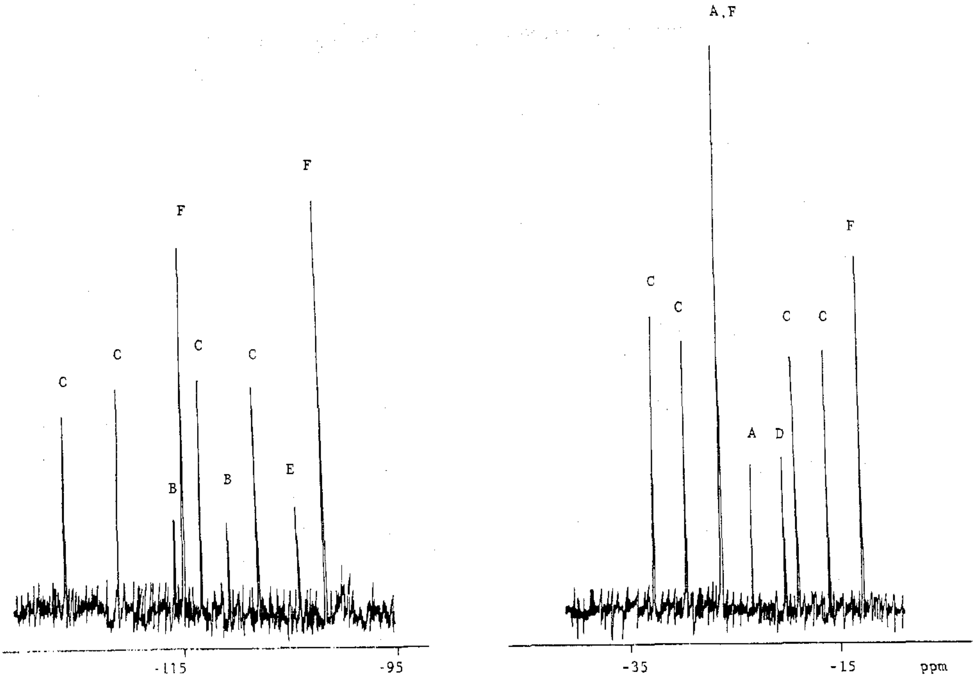

Figure 5. The 40.5-MHz ^{31}P spectrum of $Rh(CO)Cl(PPhEt_2)_2$ + $Ir(CO)Cl(P(OPh)_3)_2$: (A) $Rh(CO)Cl(PPhEt_2)_2$; (B) $Rh(CO)Cl(P(OPh)_3)_2$; (C) $Rh(CO)Cl(PPhEt_2)(P(OPh)_3)$; (D) $Ir(CO)Cl(PPhEt_2)_2$; (E) $Ir(CO)Cl(P(OPh)_3)_2$; (F) $Ir(CO)Cl(PPhEt_2)(P(OPh)_3$.

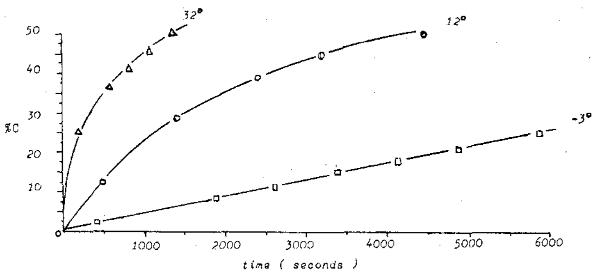

Figure 6. Temperature dependence of the reaction of $Rh(CO)Cl(PPhEt_2)_2$ with $Rh(CO)Cl(PPh_2Et)_2$. C = $Rh(CO)Cl(PPhEt_2)(PPh_2Et)$.

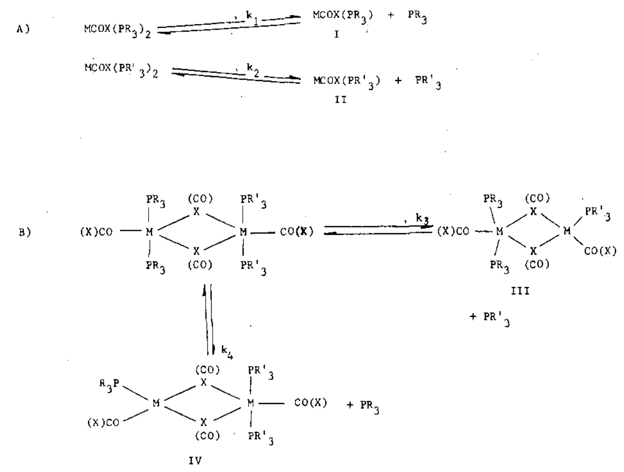

Figure 7. Possible mechanisms for organophosphine exchange: (A) dissociation of monomers; (B) dissociation of proposed halide- or (carbon monoxide)-bridged dimers.

$(OPh)_3]$ exclusively.[23] The J_{Rh-P} and $^2J_{P_1P_2}$ values obtained from analysis of Figure 5 are given in Table II. The $^2J_{P_1P_2}$ values of 537.8 and 531.3 Hz for $RhCOCl(PPhEt_2)[P(OPh)_3]_2$ and $IrCOCl(PPhEt_2)[P(OPh)_3]$, respectively, are the first trans phosphine–phosphite coupling constants reported for Rh(I) or Ir(I) complexes.

The mechanism of intermolecular phosphine exchange between four-coordinate, 16-electron rhodium(I) and iridium(I) species is of great interest. Phosphine exchange by an associative, bridging-phosphine mechanism is unlikely. Exchange must therefore be occurring by a dissociative process.

Although a thorough kinetic study of the exchanges was not made, some useful qualitative observations were. The reactions proceeded slightly faster in methylene chloride than in benzene. The rates also vary with the concentration of both reactants. When catalytic amounts of free phosphine were added (1:100 molar ratio), all of the redistributions were complete in ≤ 180 s. Reactions involving $RhCOCl(PEt_3)_2$ were particularly air sensitive. Presumably decomposition causes liberation of free phosphine, which then gives anomalously fast reaction rates. Figure 6 depicts the temperature dependence of the rates for the reaction of $RhCOCl(PPh_2Et)_2$ with $RhCOCl(PPhEt_2)_2$.

Of great interest is the rate of exchange of PPh_3 for the well-known catalyst $RhCOCl(PPh_3)_2$. Reaction of $RhCOCl(PPh_3)_2$ with any other organophosphine complex achieved statistical redistribution in ≤ 180 s. It was first suspected that the $RhCOCl(PPh_3)_2$ was contaminated by excess PPh_3; however exchange using samples prepared by the reaction of $Rh_2Cl_2(CO)_4$ with a deficit of PPh_3 gave the same anomalous results.

Two mechanisms are possible as shown in Figure 7. In mechanism A, dissociation of PR_3 from $MCOCl(PR_3)_2$, M = Rh, Ir, would result in 14-electron, three-coordinate intermediates (I, II) which would then react with PR_3 or PR'_3. The rate of the overall reaction would be dependent on the slower dissociation rate. In mechanism B, dissociation can occur from the dimeric carbonyl- or halide-bridged intermediates proposed for CO and halide exchange. III or IV could then react rapidly with PR_3 or PR'_3. The overall reaction rate would depend on the relative rates of k_3 and k_4.

The latter mechanism would be consistent with Tolman's proposals[24] concerning 16- and 18-electron intermediates; however, there is evidence that 14-electron compounds may also be reasonable.[25-27]

Registry No. CO, 630-08-0; $RhCOCl(PPh_3)_2$, 13938-94-8; $RhCOacac(PPh_3)$, 25470-96-6; $RhCOCl(Sb(o\text{-}CH_3C_6H_4)_3)_2$, 52527-04-5; $RhCONCS(PPh_3)_2$, 57636-57-4; $IrCOCl(PPh_3)_2$, 14871-41-1; $IrCONCS(PPh_3)_2$, 57636-58-5; $RhCOBr(PPh_3)_2$, 14056-79-2; $RhCOCl(AsPh_3)_2$, 14877-90-8; $RhCOCl(PEt_3)_2$, 14871-47-7; $RhCOCl(PPh_2Et)_2$, 14875-00-4; $RhCOBr(PPh_2Et)_2$, 15134-27-7; $RhCOCl(PPhEt_2)_2$, 29553-46-6; $RhCOBr(PPhEt_2)_2$, 57636-59-6; $RhCOCl(PPh_2Me)_2$, 52611-29-7; $RhCOCl(P(m\text{-}CH_3C_6H_4)_3)_2$, 24554-72-1; $RhCOCl(P(OPh)_3)_2$, 25780-71-6; $RhCOCl(P(OMe)_3)_2$, 57587-14-1; $IrCOBr(PPh_3)_2$, 14970-06-0; $IrCOCl(PPhEt_2)_2$, 27488-97-7; $IrCOCl(P(OPh)_3)_2$, 15682-63-0; $(P(OPh)_3)_2RhCl_2Rh(COD)$, 31781-80-3; $Rh(CO)_2Cl(PPh_3)$, 35679-01-7; $RhCl(COD)(PPh_3)$, 31781-57-4; $Rh_2Cl_2(P(OMe)_3)_4$, 49634-27-7; $RhCOCl(PPh_3)(AsPh_3)$, 34347-94-9; $RhCOCl(PPhEt_2)(Sb(o\text{-}CH_3C_6H_4)_3)$, 57587-15-2; $RhCOCl(PPh_2Me)(PPh_3)$, 39194-72-4; $RhCOCl(PPh_2Me)(P(m\text{-}CH_3C_6H_4)_3)$, 57587-16-3; $RhCOCl(PPh_2Me)(PPh_2Et)$, 57587-17-4; $RhCOCl(PPh_2Me)(PPhEt_2)$, 57587-18-5; $RhCOCl(PPh_2Me)(PEt_3)$, 57587-19-6; $RhCOCl(PPhEt_2)(P(OPh)_3)$, 57587-20-9; $IrCOCl(PPhEt_2)(P(OPh)_3)$, 57587-21-0; ^{31}P, 7723-14-0.

References and Notes

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1,2- and 1,7-Dicarba-*closo*-dodecaborane(12)–Iridium(I) Complexes Formed through Metal–Carbon σ Bonds: Synthesis and Characterization. Unusual Stereochemistry of the Oxidative Addition Reaction of Hydrogen

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A series of new stable iridium(I) complexes of the type *trans*-$[(C_6H_5)_3P]_2Ir(CO)(\sigma\text{-carb})$, where carb is 2-R-1,2-$B_{10}C_2H_{10}^-$ (R = H, CH_3) and 7-R'-1,7-$B_{10}C_2H_{10}^-$ (R' = H, CH_3, C_6H_5), has been prepared. Their infrared spectra are discussed. An analogous carborane complex containing $CH_3(C_6H_5)_2P$ has also been prepared for NMR structural purposes. These complexes are isoelectronic and isostructural with the Vaska's complex but differ from this in two principal aspects: (a) the reaction with hydrogen is irreversible; (b) it occurs yielding three different isomers of cis addition as a result of solvent dependence of the hydrogen uptake. One of these isomers is not stable in solution and isomerizes, the type of the reaction product depending on the solvent used. The stereochemistry of the octahedral dihydrido derivatives obtained has been assigned by a combination of ir and ^1H NMR spectroscopy. Evidence supporting the kinetic control of the hydrogen addition is also reported.

Introduction

In the course of our research on the synthesis, characterization, and reactions of transition metal complexes containing 1,2- and 1,7-dicarba-*closo*-dodecaborane(12) formed through metal–carbon σ bonds,[1-6] we have prepared a series of stable uncharged iridium(I)–carborane complexes of general formula *trans*-$[(C_6H_5)_3P]_2Ir(CO)(\sigma\text{-carb})$, where carb is 2-R-1,2-$B_{10}C_2H_{10}^-$ (R = H, CH_3) and 7-R'-1,7-$B_{10}C_2H_{10}^-$ (R' = H, CH_3, C_6H_5).

In spite of the remarkable interest concerning the properties and reactivities of various halogen and phosphine analogs of the Vaska complex, *trans*-$[(C_6H_5)_3P]_2Ir(CO)Cl$, only very few stable organometallic derivatives of these iridium(I) complexes have been reported.[7-9]

We wish to report here the preparation and characterization of some neutral iridium(I)–carborane complexes containing stable metal–carbon σ bonds. The reactions of these complexes with molecular hydrogen are also reported together with a study of their stereochemical course.

Results and Discussion

Preparation and Characterization of the Iridium(I)–Carborane Complexes. Compounds of general formula *trans*-$[(C_6H_5)_3P]_2Ir(CO)(\sigma\text{-carb})$, carb = $B_{10}C_2H_{10}R^-$, were obtained by treating a benzene suspension of *trans*-$[(C_6H_5)_3P]_2Ir(CO)Cl$ with an excess of 1-Li-2-R-1,2-$B_{10}C_2H_{10}$ (R = H, CH_3) or 1-Li-7-R'-1,7-$B_{10}C_2H_{10}$ (R' = H, CH_3, C_6H_5) in diethyl ether (eq 1). In a similar manner

$$\textit{trans}\text{-}[(C_6H_5)_3P]_2Ir(CO)Cl + Li(carb) \rightarrow \textit{trans}\text{-}[(C_6H_5)_3P]_2Ir(CO)(\sigma\text{-carb}) + LiCl \qquad (1)$$

the complex *trans*-$[(C_6H_5)_2CH_3P]_2Ir(CO)(\sigma\text{-carb})$, where carb = 7-$C_6H_5$-1,7-$B_{10}C_2H_{10}^-$, was also prepared. Table I lists the complexes obtained with pertinent analytical and ir (ν_{CO}) data. Complexes I–VI (Table I) are stable under inert