Figure 1.—Correlation of ν_{N_2} and absolute intensity (A). The numbers correspond to the following compounds: 1, $Re(N_2)Cl(Me_2PhP)_4$; 2, $W(Ph_2PCH_2CH_2PPh_2)_2(N_2)_2$; 3, $Re(N_2)Cl(Ph_2PCH_2CH_2PPh_2)_2$; 4, $Mo(Ph_2PCH_2CH_2PPh_2)_2(N_2)_2$; 5, $Os(N_2)Cl_2(Et_2PhP)_3$; 6, $Os(N_2)Cl_2(Me_2PhP)_3$; 7, $Os(N_2)Br_2(Me_2PhP)_3$; 8, $Os(N_2)Br_2(Me_2PhP)_2P(OMe)_2Ph$. Intensity data for the Os(II) complexes are found in ref 2.

of π bonding from the metal increases with a decrease in nuclear charge in an isoelectronic series. At the same time there is a concomitant decrease in the N_2 stretching frequency. The larger dipole moment derivatives in the Re(I) complexes as compared with those of the Os(II) complexes are in line with the greater stability of the Re(I) species. In addition, the large value for the intensity of the N_2 stretch in $Re(Me_2PhP)_4(N_2)Cl$ is in agreement with the reactivity of the terminal nitrogen of the N_2 ligand toward Lewis acids. Electron emission spectra from the nitrogen 1s orbitals of rhenium(I)–dinitrogen complexes also suggest that the N–N bond has considerable polarity with the terminal nitrogen having a small negative charge. It is also observed in these studies that as the N_2 stretching frequency increases, this polarity of the N–N bond decreases.[11]

It is noteworthy that the intercept ($A = 0$) in Figure 1 lies close to the Raman frequency of free dinitrogen (2330 cm^{-1}).

The above discussion implies that transition metal–molecular nitrogen complexes with large infrared intensity values for the dinitrogen stretching frequency are those most likely to interact with Lewis acids. This type of interaction is expected to be very important in the reduction of the dinitrogen ligand.[3] Indeed, this interaction has been shown to be essential in the reduction of the dinitrogen ligand in cobalt[12] and iron[13] complexes.

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ards for gifts of the W(0) and Mo(0) complexes. He also thanks the Petroleum Research Fund administered by the American Chemical Society for Grant 1705-G3 which supported this research. The Arapahoe Chemical Co. is also acknowledged for its generous gift of 1,2-diphenylphosphinoethane.

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Some Rhodium(III) and Iridium(III) Hydride Complexes Obtained by Protonation with Trifluoroacetic Acid

BY PI-CHANG KONG AND D. M. ROUNDHILL*

Recently our work here has centered around the protonation of zerovalent platinum complexes and in this study we have obtained a hydride from the reaction of $Pt(PPh_3)_4$ with trifluoroacetic acid where the anion is a *dimer* of hydrogen-bonded trifluoroacetate groups.[1] In a related study we have found that the complexes $Pt(MeOPPh_2)_3$ and $Pt(BuOPPh_2)_4$ are also readily protonated by carboxylic acids but that the resulting hydride complexes are difficult to isolate in a pure state.[2] Because of phosphine exchange, several of these hydride complexes showed sharp lines in the ${}^1H$ nmr spectrum with no observable J_{P-H} coupling, and we were interested to see if this occurred with alkoxydiphenylphosphine hydride complexes of other transition metals. In this note we report our results on the protonation of the methoxydiphenylphosphinerhodium-(I) complex.

Experimental Section

Microanalyses were carried out by Chemalytics Inc., Tempe, Ariz., except for the fluorine analyses which were carried out by A. Bernhardt, Müllheim-Ruhr, Germany. Nuclear magnetic resonance spectra were obtained on a Varian T-60 spectrometer. Infrared spectra were obtained on a Perkin-Elmer Model 700 spectrometer as Nujol mulls. Far-infrared spectra were obtained on a Perkin-Elmer FIS spectrometer as vaseline mulls. Melting points were obtained on a Fischer-Johns apparatus and are uncorrected. Methoxydiphenylphosphine and n-butoxydiphenylphosphine were purchased from Arapahoe Chemicals Inc., and platinum metals as chloro salts, from Engelhard Industries Inc. Conductivity measurements were carried out as solutions in nitrobenzene using an Industrial Instruments Model RC 16B2 conductivity bridge. Chlorodicarbonylrhodium(I) dimer[3] and chlorobis(ethylene)rhodium(I) dimer[4] were prepared by previously published methods.

Dihydridocarbonyltris(triphenylphosphine)iridium(III) Hydrogen Bis(trifluoroacetate).—To a solution of hydridocarbonyltris(triphenylphosphine)iridium(I) in CH_2Cl_2 was added excess CF_3COOH. The yellow color of the solution discharged, and the addition of hexane or ether to the concentrated solution gave the *complex* as colorless crystals which were filtered, washed with hexane, and dried *in vacuo*, mp 145°. *Anal.* Calcd for $C_{59}H_{48}F_6IrO_5P_3$: C, 57.3; H, 3.92; F, 9.22; P, 7.52. Found: C, 57.5; H, 3.99; F, 9.26; P, 7.49. ν_{Ir-H} 2170, 2130 cm^{-1}; ν_{C-O} 2025 cm^{-1}; ν_{COO} 1780, 1740 cm^{-1}. The acid proton resonance in nmr is at τ −3.5.

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Chlorohydridotetrakis(methoxydiphenylphosphine)rhodium-(III) Hydrogen Bis(trifluoroacetate) (1).—To a solution of chlorodicarbonylrhodium(I) dimer or chlorobis(ethylene)rhodium(I) dimer in CH_2Cl_2 was added excess methoxydiphenylphosphine. Effervescence occurred for *ca.* 10 min, and then ether or hexane was added to the solution. Through this solution was bubbled N_2 in a rapid stream, and by trituration compound **2** was readily obtained. The melting point and ir spectra of the products from either the carbonyl or ethylene complex were identical with no bands due to a carbonyl in the 2000-cm^{-1} region of the ir spectrum. The freshly prepared air-sensitive brown solid (**2**) was recrystallized from CH_2Cl_2 and ether and then dissolved in CF_3COOH. Addition of anhydrous ether gave the *complex* as pale yellow crystals which were washed with ether and dried *in vacuo;* mp 110°.

Anal. Calcd for $C_{55}H_{34}ClF_6O_8P_4Rh$: C, 54.6; H, 4.42; F, 9.26; P, 10.0. Found: C, 55.1; H, 4.72; F, 9.30; P, 10.7. ν_{Rh-H} 2100 cm^{-1}, ν_{Rh-Cl} 304 cm^{-1}, ν_{COO} 1780, 1740 cm^{-1}. Conductivity in nitrobenzene is 21.2 ohm^{-1} cm^2 mol^{-1}. If a solution of silver nitrate in ethanol is added to a solution of the complex in the same solvent, there is no precipitate of silver chloride showing the covalent nature of the chloride group.

Chlorohydridotetrakis(methoxydiphenylphosphine)rhodium-(III) Hydrogen Dichloride-0.5-Dichloromethane (3).—Through a solution of the air-sensitive brown complex in CH_2Cl_2 was bubbled hydrogen chloride. The solution was concentrated and anhydrous ether added to give the *complex* which was washed with anhydrous ether and dried for 12 hr *in vacuo* at room temperature; mp 100°. *Anal.* Calcd for $C_{55.5}H_{55}Cl_4O_4P_4Rh$: C, 56.4; H, 4.93; Cl, 12.6; P, 11.0. Found: C, 55.7; H, 4.76; Cl, 13.0; P, 10.6. ν_{Rh-H} 2100 cm^{-1}. The ^{1}H nmr shows a resonance at τ −2.2 for the acid proton and a resonance at τ 4.7 for the CH_2Cl_2 protons, the integration corresponding to half a molecule being present for each rhodium.[5]

Chlorohydridotetrakis(methoxydiphenylphosphine)rhodium-(III) Hexafluorophosphate.—The complex $[(POMePh_2)_4Rh]PF_6$ was prepared as previously described and through a solution of this compound in CH_2Cl_2 was passed HCl gas until the color of the solution had changed from deep yellow to a very pale yellow. The passage of HCl was immediately stopped and N_2 was bubbled through the solution until the voume was about 5 ml. Anhydrous ether was added to give the complex as colorless crystals which were filtered, washed with ether, and dried *in vacuo;* yield 85%; mp 110°. *Anal.* Calcd for $C_{52}H_{53}ClF_6O_4P_5Rh$: C, 54.4; H, 4.65; P, 13.5. Found: C, 53.9; H, 4.38; P, 12.3. ν_{Rh-H} 2100 cm^{-1} (b). The ^{1}H nmr confirms the absence of CH_2Cl_2 in the complex.

Results and Discussion

The preparation of hydrido complexes by protonation with trifluoroacetic acid has been carried out by the oxidative addition reaction to low-valent compounds. The reaction of the carboxylic acid with $(PPh_3)_2IrCOCl$,[5b,6] $(PPh_3)_2IrN_2Cl$,[7] and $(PPh_3)_2PtC-(CF_3)_2NCH_3$[8] has led to the isolation of covalent hydrides where the *monomeric* trifluoroacetate group is coordinated. *Dimeric* anions such as HCl_2^- have been reported in complexes such as $[(PPh_3)_3IrCOH_2]HCl_2$,[9] and two molecules of HCN have been found to react with $(PPh_3)_3RhCl$, although in this case it is considered that one of the acid molecules is coordinated to the rhodium as an undissociated species.[5b] The reaction of $(PPh_3)_3IrCOH$ with CF_3COOH is similar to that with HCl giving a hydride where the anionic portion is a *dimer,* the formula of the complex being $[(PPh_3)_3IrCOH_2](CF_3COO)_2H$. The ^{1}H nmr spectrum is similar to that for $[(PMePh_2)_3IrCOH_2]BPh_4$ and carboxylic acid protonated species as previously re-

ported.[10–12] We have also found that chlorodicarbonylrhodium(I) dimer or chlorobis(ethylene)rhodium-(I) dimer reacts with methoxydiphenylphosphine with the liberation of carbon dioxide or ethylene to give an unstable brown solid, mp 80°, which undergoes decomposition after 12 hr even *in vacuo.* Because of this instability we have been unable to obtain satisfactory analytical data to characterize the complex, but it readily reacts with trifluoroacetic acid to yield a new complex of stoichiometry $[(POMePh_2)_4RhHCl](CF_3-COO)_2H$ (**1**). This new complex closely resembles the complexes $\{[P(OMe)_3]_4Rh\}BPh_4$ (X = Br, I) recently prepared by Haines.[13] The isolation of these iridium and rhodium complexes with the *dimeric* trifluoroacetate as anion shows that this group is quite common with ionic hydrides obtained by protonation of low-valent transition metal complexes with trifluoroacetic acid. The acid proton in the Rh complex can be observed in the ^{1}H nmr spectrum at τ −2.7 and the ir spectrum in the carboxylate region is identical with that of the triphenylphosphine platinum complex.[1] It is unlikely that the second molecule of acid is present in the coordination sphere of Rh since this would lead to a seven-coordinate Rh(III) cation. Without a crystal structure, however, we cannot completely eliminate the possibility that a molecule of free acid crystallizes in the lattice but consider it likely that the structure of the anion is analogous to that of the potassium and cesium salts of this dimer.[14]

A further interesting feature of this complex is the high-field ^{1}H nmr spectrum. It has been assumed that the stereochemistry of the complex $\{[P(OMe)_3]_4$-$RhHX\}BPh_4$ is octahedral with the four phosphine groups in the plane of the square,[13] although the hydride resonance was only poorly resolved. This stereochemistry was deduced because the ^{1}H nmr spectrum showed the absence of any 120-Hz coupling due to a phosphine trans to a hydride. We have found that compound **1** has a quite different ^{1}H nmr spectrum in that it is well resolved and clearly shows the coupling of the hydride resonance (τ 23.2) to four equivalent methoxydiphenylphosphines (J_{P-H} = 11 Hz) and ^{103}Rh (J_{Rh-H} = 19 Hz), this first-order coupling, assuming stereochemical rigidity, leading to a double quintet pattern (Figure 1). When this solution in $CDCl_3$ is allowed to stand for some time, the complex slowly changes and a new broad peak appears at τ 24.5 with a half-width comparable to that of the initial resonance. It is assumed
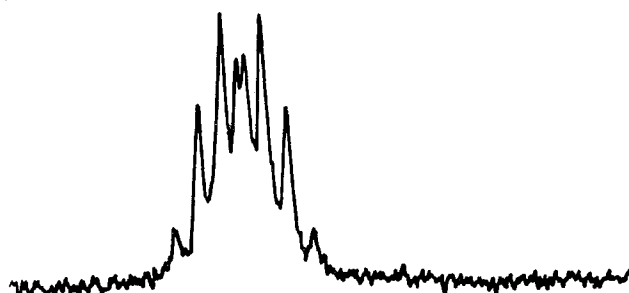

Figure 1.—The ^{1}H nmr spectrum of $[(POMePh_2)_4RhHCl]-(CF_3COO)_2H$ at room temperature.

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that this resonance is indicative of an exchange system, since if a paramagnetic Rh(II) species were being formed, its presence in solution would cause a broadening of the former resonance. After 27 hr the two resonances are of similar size, but it is noteworthy that although the initial well-resolved resonance is slowly replaced by this second broad resonance, it does not appear to become involved in the exchange since the resolution of the former peak remains unaffected. It has also been found that although compound **3** shows an ^{1}H nmr spectrum analogous to the trifluoroacetate one, this second complex shows a much more rapid conversion, the broad resonance being of comparable size after about 30 min, and essentially complete conversion occurs after 20 hr. This observation of the rapid growth of a broad resonance in the ^{1}H nmr shows that care should be taken in the interpretation of such spectra.

Although we have been unable to characterize compound **2**, it is significant that we have been able to obtain the trifluoroacetate hydride in 73% yield from this compound, and, in addition, by reaction with ammonium hexafluorophosphate, the complex [(POMe-Ph$_2$)$_4$Rh]PF$_6$ (mp 170°; conductivity in nitrobenzene 22.8 ohm^{-1} cm^2 mol^{-1}) has been obtained in 79% yield. This high yield suggests the reaction is not a disproportionation reaction of the tris compound and implies that this initial compound may be a tetrakis-phosphine complex, although we cannot discount the possibility that there is free methoxydiphenylphosphine present in the material. Because of the air sensitivity of the material we have been unable to obtain useful conductivity data but it appears unlikely that compound **2** is (POMePh$_2$)$_4$Rh$^+$Cl$^-$ because the chloro group remains coordinated after protonation with trifluoroacetic acid.

We have been unable to isolate the corresponding complex from *n*-butoxydiphenylphosphine, but since the addition of trifluoroacetic acid to a solution of the compound obtained from chlorodicarbonylrhodium(I) and the phosphine ligand shows a high-field ^{1}H nmr spectrum virtually identical with that found for compound **1**, it is likely that the compound exists in solution.

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Acid–Base Properties of the Systems AlCl$_3$–MCl (M = Li, Na, K, Cs)

BY G. TORSI[1] AND G. MAMANTOV*

We have recently reported[2] the values of the equilibrium constant for the dissociation 2AlCl$_4^-$ $\rightleftarrows$ Cl$^-$ + Al$_2$Cl$_7^-$ in molten AlCl$_3$–NaCl in the temperature range 175–400°. We now have extended these potentiometric measurements to other AlCl$_3$–MCl (M = Li, K, Cs) systems and report the results in this note.

(1) On leave of absence from Instituto di Chimica Analitica, Bari, Italy.
(2) G. Torsi and G. Mamantov, *Inorg. Chem.*, **10**, 1900 (1971)

Experimental Section

The experimental procedures have been described previously.[2] The Cl$^-$ concentration at the equivalence point of a potentiometric titration curve for a slightly basic AlCl$_3$–MCl melt (M = Li, K, Cs) with AlCl$_3$ was calculated as in ref 2. With this information, the desired equilibrium constant can be readily calculated. Only a narrow composition region near the equivalence point was studied. The electrochemical cells were made from quartz except for the Pyrex membrane separating the reference electrode compartment from the bulk melt. Reagent grade KCl was recrystallized twice from water (deionized and distilled). KCl, LiCl (Baker Analyzed reagent grade), and CsCl (99.9% pure from Alfa Inorganics) were dried in quartz tubes under reduced pressure ($\sim$2 × 10^{-2} Torr) at $\sim$400° for several hours; the tubes were then sealed and stored in the drybox.

In the measurements, particular care was taken to make sure that the asymmetry potential[2] was constant with time and temperature. In order to obtain equilibrium between the Pyrex membrane and the melts, the cell was kept at a constant temperature until there was no change in the measured voltage; this was followed by several temperature excursions until the potentials were reproducible to ±3 mV. At the end of each run, the asymmetry potentials were evaluated and corrected for by using saturated solutions of MCl in both compartments.

Results and Discussion

pK (where $K = X_{Cl^-} X_{Al_2Cl_7^-}/X_{AlCl_4^-}{}^2$) values at several temperatures are given in Table I. Data for

TABLE I
pK VALUES FOR AlCl$_3$–MCl Systems

Temp, °C	Li$^+$	Na$^+$	K$^+$	Cs$^+$
175	4.3	7.1		
250	4.0	6.3		
275			7.5	
300	3.9	5.7	7.1	
350	3.8	5.3	6.4	
400	3.8	5.0	5.8	7.4
450				6.8

the AlCl$_3$–NaCl system were reported previously.[2] It is obvious that the nature of the cation plays an important role in determining the pK value. The greater the polarizing power of the cation, the smaller is the pK at a given temperature. Plots of pK *vs.* either 1/r (where r is the cationic radius) or the cationic size (r^3) were, however, not linear. It is interesting to note that good linearity was obtained for the plot of pK *vs.* d^2 (where d is the sum of the radii of M$^+$ and AlCl$_4^-$). At this time it appears that no theoretical significance may be attached to this correlation.

From the linear plots of pK *vs.* 1/T for AlCl$_3$–LiCl (the lowest three temperatures), AlCl$_3$–NaCl, and AlCl$_3$–KCl, the ΔH's were calculated to be 4.0, 13.6, and 22.9 kcal/mol, respectively.

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Raman Intensity Measurements on and Boron–Halogen Bond Polarizability Derivatives for the Boron Trihalides

BY R. J. H. CLARK* AND P. D. MITCHELL

The observed intensity of a Raman band is given by the expression