num(II) chloride and cadmium(II) halides are indicated to be similar for phosphines with similar steric effects, and the opposite trend noted for $^1J(^{195}Pt-^{31}P)$ in previous studies is most likely due to the interplay between the electronic and steric effects.

Empirical correlations between the ^{31}P chemical shifts and other parameters for phosphine complexes of mercury(II)[7] as well as some transition metals[29] have been proposed. A linear correlation between the coordination chemical shift (δ(complex) − δ(phosphine)) and $^1J(^{199}Hg-^{31}P)$ has been noted[7,9a] for the complexes of mercury(II) halides as well as several other mercury(II) salts. On this basis, the absolute values of the coordination chemical shifts have been interpreted in terms of the strength of the metal–phosphorus bond[7] and the basicity[26] of the phosphine. Results of a recent ^{31}P NMR study[25] on the complexes of mercury(II) carboxylates have, however, shown that the proposed interpretations are very misleading. The chemical shifts and the coordination chemical shifts for the complexes of cadmium(II) halides given in Table III further show that there are no simple relationships of the coordination chemical shift with any other parameter. For a given phosphine, although the coordination chemical shift increases in the order Cl > Br ≫ I, the shift for $CdI_2(PPh_3)_2$ is, in fact, upfield instead of downfield. Unlike mercury complexes, the plots of metal–phosphorus coupling constants against coordination chemical shifts do not give straight lines except in the case of the $CdX_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$ complexes for which a straight line is obtained. For a given halide, the coordination chemical shifts for the chloro and the bromo complexes (excluding the triphenylphosphine complexes) decrease in the order of decreasing basicity of the phosphine, but for the iodo complexes the order is $P(m\text{-}CH_3C_6H_4)_3 > P[p\text{-}(CH_3)_2NC_6H_4]_3 > P(p\text{-}CH_3OC_6H_4)_3 > P(p\text{-}CH_3C_6H_4)_3 > PPh_3$.

A linear relationship[29] between the coordination chemical shift and the chemical shift of the phosphine has been found for a variety of transition-metal complexes. Such a correlation does not exist for the cadmium(II) halide complexes as shown by plots of $\Delta\delta$ against δ. Thus, despite extensive ^{31}P chemical shift data on metal–phosphine complexes, it is still very difficult to ascertain the effects of various factors on the chemical shifts.

Experimental Section

Materials. Triarylphosphines (from Strem Chemicals) were recrystallized and their purity was checked by ^{31}P NMR. Anhydrous cadmium(II) halides were reagent grade. Ethanol was refluxed over magnesium and distilled. Other solvents were reagent grade and were stored over molecular sieves.

Physical Measurements. Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ, or by Guelph Chemical Laboratories Ltd., Guelph, Ontario. Molecular weights were determined in 1,2-dichloroethane with a Hitachi Perkin-Elmer 115 vapor-phase osmometer. Infrared spectra were recorded with a Perkin-Elmer 180 spectrophotometer. Samples were prepared as mulls in Nujol and were placed between polyethylene disks. Raman spectra were measured in the solid state with a Jarrel-Ash spectrophotometer using the 5145-Å exciting line of an argon-ion laser. $^{31}P\{^1H\}$ spectra of the solutions of the complexes in dichloromethane [containing 10% $CDCl_3$ or $(CD_3)_2CO$] were recorded at ambient temperatures as well as low temperatures in the Fourier transform mode with a Bruker WP60 FT spectrometer. The chemical shifts were measured relative to 85% H_3PO_4 as external reference and are reported positive when downfield from H_3PO_4.

Preparation of the Complexes. All operations involved in the preparation and purification were carried out under an atmosphere of oxygen-free dry nitrogen. In a typical preparation, cadmium(II) halide (2 mmol) and triarylphosphine (4.2 mmol) were stirred together in refluxing ethanol (~15 mL) for ~5 h. The complex precipitated upon cooling to room temperature (concentration of the solution was sometimes necessary). After filtration it was washed with ethanol (2 × 3 mL) and benzene (2 × 5 mL) and recrystallized from a mixture of dichloromethane and hexane. Except for the losses during filtration and crystallization, yields were quantitative.

Acknowledgment. Financial assistance of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. Thanks are due to Professor D. E. Irish for Raman spectral measurements. R.C.S. thanks the University of Lucknow, India, for a leave of absence.

Registry No. $CdCl_2(PPh_3)_2$, 14494-80-5; $CdBr_2(PPh_3)_2$, 14586-73-3; $CdI_2(PPh_3)_2$, 14126-39-7; $CdCl_2[P(m\text{-}CH_3C_6H_4)_3]_2$, 77061-37-1; $CdBr_2[P(m\text{-}CH_3C_6H_4)_3]_2$, 77061-38-2; $CdI_2[P(m\text{-}CH_3C_6H_4)_3]_2$, 77061-39-3; $CdCl_2[P(p\text{-}CH_3C_6H_4)_3]_2$, 77061-40-6; $CdBr_2[P(p\text{-}CH_3C_6H_4)_3]_2$, 77061-41-7; $CdI_2[P(p\text{-}CH_3C_6H_4)_3]_2$, 77061-42-8; $CdCl_2[P(p\text{-}CH_3OC_6H_4)_3]_2$, 77061-43-9; $CdBr_2[P(p\text{-}CH_3OC_6H_4)_3]_2$, 77061-44-0; $CdI_2[P(p\text{-}CH_3OC_6H_4)_3]_2$, 77061-45-1; $CdCl_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$, 77061-46-2; $CdBr_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$, 77061-47-3; $CdI_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$, 77061-48-4.

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Temperature-Dependent Phosphite Complex Equilibria Observable with NMR and IR Techniques

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The complexes $[(OR)_3P]_2CuH_3BR'$ (R = Me, Et; R′ = H, $COOC_2H_5$) experience changes in equilibria of the type

$$L_2CuH_3BR' \overset{+L}{\rightleftharpoons} L_3CuH_3BR' \overset{+L}{\rightleftharpoons} L_4Cu^+H_3BR'$$

which are observed by NMR and IR techniques. Temperatures at which these equilibria occur and chemical shift trends are dependent on whether L is phosphine or phosphite.

Introduction

A variety of studies have been made regarding phosphine dissociation with transition-metal phosphine and phosphite complexes.[3-9] Ligand dissociation equilibria of phosphine complexes containing tetrahydroborate or its derivatives have

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Table I. Infrared Absorption (cm^{-1}) at Differing Temperature Assigned to B–H$_n$ Moieties

compd	2500–2200	2200–1900	1500–1300	1300–1000
[(MeO)$_3$P]$_2$CuBH$_4$^{a} (neat)	2380 s, 2345 sh (BH$_t$ str), 2260 w	1990 s, 1935 s (BH$_b$ str)	1390 m (bridge str)	1135 s (BH$_2$ def)
[(MeO)$_3$P]$_3$CuBH$_4$ (neat, −196 °C)	2340 s (BH$_t$ str)	2055 s (BH$_b$)	*b*	*b*
[(EtO)$_3$P]$_2$CuBH$_4$^{a} (neat)	2380 s, 2350 sh (BH$_t$ str), 2260 w	1990 s, 1930 s (BH$_b$ str)		1135 s (BH$_2$ def)
[(EtO)$_3$P]$_3$CuBH$_4$ (neat, −196 °C)	2335 s (BH$_t$ str)	2055 s (BH$_b$ str)	*b*	*b*

^{a} Reference 9; included for comparison. ^{b} Region obscured since neutral ligand peaks observed.

Table II. ^{11}B and Borane ^{1}H NMR Data for Complexes

compd	temp, °C	δ ^{1}H	δ ^{11}B^e
[(MeO)$_3$P]$_2$CuBH$_4$^{a}	ambient	+0.69^h br	30.4^h br
[(MeO)$_3$P]$_3$CuBH$_4$^{a}	−165	−0.19^h	39.0^h br
[(MeO)$_3$P]$_4$Cu$^+$BH$_4$$^-$ ^{a}	−140	+0.03^h	
[(MeO)$_3$P]$_2$CuBH$_4$,^{a} 0.04 g with 0.025 g of excess (MeO)$_3$P	ambient	+0.58^h	
	−10	+0.30^h	
	−55	+0.01^h	
	−140	−0.13^i	
	−165	−0.19^j	
[(EtO)$_3$P]$_2$CuBH$_4$^{a}	ambient	+0.65^h br	29.1^h br
[(EtO)$_3$P]$_3$CuBH$_4$^{a}	−140	−0.19^h br	40.0^h br
(MePh$_2$P)$_3$CuBH$_4$^{b}	ambient	+0.90	39.0^k
	−65	+0.71	
(MePh$_2$P)$_4$Cu$^+$BH$_4$$^-$ ^{c}	−70	+0.49^h br	
	−85	+0.17	
[(MeO)$_3$P]$_2$CuH$_3$BCOOC$_2$H$_5$^{b}	ambient	+1.02	
[(MeO)$_3$P]$_4$Cu$^+$H$_3$BCOOC$_2$H$_5$$^-$ ^{a}	ambient	+0.80	31.6^g
[(EtO)$_3$P]$_2$CuH$_3$BCOOC$_2$H$_5$^{b}	ambient	+0.88(?)	27.4(?)^g
[(EtO)$_3$P]$_4$Cu$^+$H$_3$BCOOC$_2$H$_5$$^-$ ^{a}	ambient	+0.61	31.8 sh
(Ph$_3$P)$_2$CuBH$_4$^{b,f}	−85	+1.31	29.3^k br
(MePh$_2$P)$_3$CuBH$_4$^{b,f}	ambient	+0.90	39.0^k br
KH$_3$BCO$_2$C$_2$H$_5$^{d,f,h}	ambient	+0.60, +0.71	30.7 sh

^{a} Solvent = 2:1 CH$_2$CHCl/CH$_2$CHF. ^{b} Solvent = CDCl$_3$. ^{c} Solvent = CH$_2$Cl$_2$. ^{d} Solvent = Me$_2$SO, CD$_3$OH. ^{e} Solvent = CHCl$_3$. ^{f} Included for comparison. ^{g} Sample probably has some tris or tetrakis contamination. ^{h} Quartet, br = broadened, sh = sharp. ^{i} Doublet. ^{j} Singlet. ^{k} Broad resonance with no detail.

generally been examined with use of vapor pressure osmometry and infrared techniques.[4,5,7-9] Studies on phosphite–copper(I) hydroborate complexes have indicated that a number of different phenomena may occur. The fluxional process in the complex [(MeO)$_3$P]$_2$CuBH$_4$ can be slowed upon temperature lowering in a halocarbon mixture.[10] At ambient temperature [(RO)$_3$P]$_2$CuH$_3$BCOOC$_2$H$_5$ (R = Me, Et) with an excess of phosphite results in a tris(phosphite) and then a tetrakis(phosphite).[9] The present investigation has shown that changes in equilibria in a variety of phosphite complexes can be observed, with use of IR and NMR techniques, upon lowering the temperature of the complex in the presence of excess phosphite.

Experimental Section

Infrared spectra were taken on a Beckman IR-20A. ^{1}H NMR spectra were obtained from Varian XL-100, A-60, or EM-360 spectrometers; ^{11}B NMR spectra were obtained from the Varian XL-100. Chemical shifts were based upon internal references (Me$_4$Si or known solvent for ^{1}H, BF$_3$OEt$_2$ for ^{11}B). Low-temperature ^{1}H and ^{11}B spectra were obtained from the XL-100 system with the temperature-control device calibrated by using an independent thermocouple placed within the NMR tube situated in the probe.

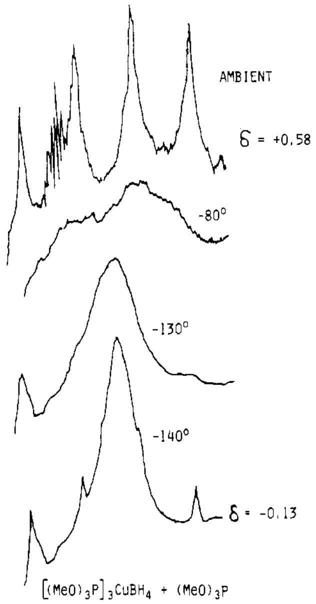

Figure 1. 100.1-MHz ^{1}H NMR spectra of [(MeO)$_3$P]$_2$CuBH$_4$ + excess (MeO)$_3$P in 2:1 CH$_2$CHCl/CH$_2$CHF upon lowering the temperatures.

Complexes were prepared by published procedures.[9,10] Infrared and NMR data are found in Tables I and II.

Discussion

L$_2$MX + L ⇌ L$_3$MX Equilibrium (L = Phosphite). Ligand dissociation equilibria of phosphine–copper tetrahydroborate complexes, studied quantitatively with use of vapor pressure osmometry, are of the general from (a) L$_2$MX ⇌ LMX + L and (b) L$_2$MX + L ⇌ L$_3$MX. Other equilibria such as (c) L$_3$MX + L ⇌ L$_4$M$^+$ + X$^-$ are not generally important at the temperatures and concentrations available with this technique. The presence of equilibrium b in the form of the equilibrium [(MeO)$_3$P]$_2$CuBH$_4$ + (MeO)$_3$P ⇌ [(MeO)$_3$P]$_3$CuBH$_4$ (the triethyl phosphite behaves similarily) was first noted in low-temperature infrared spectra upon addition of an extra equivalent of phosphite ligand to [(MeO)$_3$P]$_2$CuBH$_4$ and lowering the temperature (Table I). An argument analogous to that for the B–H absorptions for the methylidiphenylphosphine–tetrahydrobrorate bidentate and monodentate complexes can be applied here to justify the structural changes on the basis of IR.[8,11] Important features supporting the change from bidentate to monodentate coordination are the position and number of peaks in the terminal and bridging stretching region, particularly the shift of BH$_t$ to lower frequency and B–H$_b$ to higher frequency.

Low-temperature ^{1}H NMR spectra of the complex [(MeO)$_3$P]$_2$CuBH$_4$ with excess phosphine ligand support the presence of the equilibrium observed in the IR since the change in concentration of the two complexes with temperature shows up as a gradual change in chemical shift from δ +0.69 ppm

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(11) J. C. Bommer and K. W. Morse, *J. Chem. Soc., Chem. Commun.*, 137 (1977).

when no excess phosphite is present to a range of δ +0.58 ppm (ambient temperature) to −0.19 ppm (−165 °C) when excess phosphite is present. The signal is distinguishable as a quartet down to −55 °C, but between −55 and −120 °C it is a very broad doublet, making it difficult to obtain accurate δ values. Essentially complete "thermal" decoupling has taken place by −140 °C, and the signal appears as a singlet (Figure 1).

$L_3MX + L \rightleftharpoons L_4M^+ + X^-$ Equilibrium (L = Phosphite). At approximately −130 °C a second equilibrium is observed for the mixture: $[(MeO)_3P]_3CuBH_4 + (MeO)_3P \rightleftharpoons [(MeO)_3P]_4Cu^+BH_4^-$. The ionic complex begins to appear as small shoulders on the primary partially decoupled resonance at −130 °C (Figure 1), and by −140 °C the absorptions are distinguishable as reasonably sharp quartets. The −155 °C spectrum shows no noticeable relative increase in the size of this quartet. This fact, along with the fact that the quartet did not appear initially as sharp resonances but as broad absorptions which sharpened as the temperature was lowered, suggests that the appearance of these peaks is not just a result of the temperature dependence of the equilibrium constant. A logical explanation for the phenomenon is that the equilibrium becomes important at somewhat higher temperatures than does the appearance of the quartet in the NMR spectrum, but the mean lifetime for the ionic species is comparable or less than the NMR time scale. Lowering the temperature increases the mean lifetime for the tetrahydroborate anion and allows it to be observed by the resonance technique. This would account for the gradual sharpening of the quartet peaks with decrease in temperature while their relative intensity with respect to the decoupled singlet remained fairly constant. An analogous process resulting in formation of $[(EtO)_3P]_4Cu^+BH_4^-$ occurs for the triethyl phosphite complex at comparable temperatures.

The complexes $[(EtO)_3P]_2CuH_3BCOOC_2H_5$ and $[(MeO)_3P]_2CuH_3BCOOC_2H_5$ also have borane proton resonances consisting of broadened quartets at ambient temperature ($W_{1/2} \approx 30$ Hz). Only the farthest upfield resonance for the triethyl phosphite and the two upfield resonances of the trimethyl phosphite are detectable because of interfering proton resonances from the ethyl group on the (ethoxycarbonyl)trihydroborate and $(EtO)_3P$.[9] As noted in the infrared, addition of excess trialkyl phosphite ligand results in the predominance of the ionic complex $L_4Cu^+H_3BCOOC_2H_5^-$ at ambient temperature.[9] This is confirmed by the ^1H NMR's of both complex mixtures in which the somewhat broadened members of the quartet which are visible become quite sharp ($W_{1/2}$ comparable to $KH_3BCOOC_2h_5$) and shift upfield considerably (Table II) toward the value for the noncomplexed anion upon addition of excess phosphite ligand.

Equilibria When L = Phosphine. Similar dissociative equilibria are indicated when L = $MePh_2P$. Besides the presence of the dissociative equilibrium of type b between $(MePh_2P)_3CuBH_4$ and $(MePh_2P)_2CuBH_4$, the former complex also appears to undergo displacement of the anion by a fourth phosphine at low temperature in the presence of excess ligand to give $(MePh_2P)_4Cu^+BR_4^-$. The behavior is analogous to the trialkyl phosphite–tetrahydroborate complexes with the exception that the changes occur at temperatures which are considerably higher. At −65 °C, the main B–H resonance appears as a substantially decoupled peak ($W_{1/2} \approx 30$ Hz) with the two upfield peaks of the ionic BH_4^- quartet visible as weak and broad bumps. At −75 °C these upfield peaks have sharpened considerably, and at −85 °C they appear as very sharp peaks but with the same order of magnitude intensity as the "thermally" decoupled complex peak. These observations are suggestive that again what is being observed is not only a shift in equilibrium with decreasing temperature, but also a slowing down of the dynamic equilibrium process, increasing the mean lifetime of the ionic complex to one which allows observation by the NMR technique. The chemical shift of the noncoordinated BH_4^- does not appear to vary significantly with decrease in temperature.

The changes with temperature of the chemical shifts of the "thermally" decoupled complexed borane ^1H resonances may be related to the change of the equilibrium from bis(phosphine) complex toward more tris(phosphine) complex with decreasing temperature. The ^1H chemical shift for the saturated solution of tris(diphenylmethylphosphine) copper complex (ambient temperature) should be representative of a mixture of bis and tris(phosphine) complex with tris being an important species at these high concentrations according to K_{dis} values.[8] The chemical shift seems to be anomalous at first on inductive grounds as the direction is downfield (deshielded) with increasing concentration of tris complex (decreasing temperature) which is opposite to the direction of change of chemical shift for the trialkyl phosphite complexes. Changing the trialkyl phosphite ligands to aromatic phosphine ligands would be expected to have some effect upon the borane ^1H, but the inductive effects due to the greater basicity of the phosphines or due to decreased bonding interaction because of some steric effects are expected to be minimized by the intervening metal atom. On the basis of inductive effects alone, then, the trialkyl phosphite complexes would be expected to have ^1H chemical shifts similar to their triarylphosphine analogues, despite some differences in basicity of the ligands. We are led to the conclusion that the borane ^1H chemical shifts of the phosphine complexes are complicated by diamagnetic anisotropic deshielding of the borane hydrogens by the phenyl groups of the phosphine ligands on the following basis. A model on the reported crystal structure for $(Ph_3P)_2CuBH_4$[12] shows that the borane protons clearly occupy positions of deshielding relative to the phenyl groups when it is asssumed that rotation of the phosphine groups occurs in solution about the phosphorous–metal axis but that the angle of the highest probability at which the phenyl rings are "feathered" remains similar to that in the solid state because of steric barriers. One can calculate that change in screening constant for protons lying in the plane of a phenyl ring as a function of their distance from the ring:[13] $\Delta\sigma = e^2R^2/2mc^2(R + d)^3$ [R (the average diameter of the ring, taken as approximately 2.7 Å) is the distance of the deshielded hydrogen from the ring, $m = 9.108 \times 10^{-28}$ g, $c = 2.998 \times 10^{10}$ cm/s, $e = 4.803 \times 10^{-10}$ esu]. Rotation of the phosphines until the borane hydrogens were coplanar with one phenyl group at a time allowed measurement of d. (It must be emphasized that this is certainly not an attempt to determine the average deshielding environment for these hydrogens but is only to obtain an order of magnitude approximation for the effect). Under these conditions, it was found that each terminal hydrogen would be approximately 4 Å from the ring and each bridging hydrogen would be approximately 4 Å from two phenyl rings (one from each phosphine). Calculations using these values show the change in screening constant for the terminal hydrogens, $\Delta\sigma_t$, to be 0.35 ppm and the change in screening constant for the bridging hydrogens, $\Delta\sigma_b$, to be 0.70 ppm. Since the chemical shift observed is the weighted average for terminal and bridging hydrogens, the observed change in screening for the weighted average is $\Delta\sigma_{wa} = 0.53$ ppm. The observed difference in chemical shift between the bis(triphenylphosphine) complex and the bis(trialkyl phosphite) complexes is between 0.6 and 0.7 ppm, certainly of the same order of magnitude predicted for anisotropic effects by the above calculations. The difference for the (ethoxycarbonyl)trihydroborate analogues is closer to 1 ppm and

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would be expected to be higher, with assumption of similar geometry and bonding, since the weighted average for the chemical shift involves one less terminal hydrogen. These calculations show that the change in chemical shift for the borane hydrogens upon complexation to metals with phenylphosphine ligands is most likely due to a combination of inductive and anisotropic effects, since the calculations are for the probable upper limit of the anisotropic effects. This makes it difficult to assess the magnitude of the inductive effects for individual cases. The calculations do suggest, however, that the inductive effects and the metal–anion interactions are not vastly different for the bis(phosphine) complexes compared to their bis(phosphite) counterparts, a conclusion supported by the infrared spectra of these complexes. Further supporting evidence that the borane hydrogens may be experiencing an anisotropic effect comes from the neutron diffraction results on $(MePh_2P)_3CuBH_4$[14] in which one of the terminal hydrogen distances is distinctly longer than the other B–H distance, and indeed, one could envision that in solution interaction with the phenyl rings might be present.

^{11}B Chemical Shifts. The ^{11}B NMR spectra of the phosphine and phosphite complexes generally consist of a somewhat broadened quartet. Chemical shift values (Table II) indicate considerable inductive deshielding of the boron nucleus (on the assumption that the paramagnetic contribution to the chemical shift is small because of the upfield shift of some of the complexes compared to the free ligands). This may be a consequence of inductive effects through the bridging hydrogens or some direct bonding between the boron and the metal or both. Some direct Cu–B bonding has been considered as a possible explanation for the large P–Cu–P′ angle in the complex $(Ph_3P)_2CuBH_4$,[12] and neutron diffraction data on unidentate $(MePh_2P)_3CuBH_4$ suggests that the overlap pattern in the Cu–H–B bond is "closed".[14] The ^{11}B chemical shift of bis(phosphine) complexes is apparently not significantly affected by anisotropic deshielding by the phosphines, more than likely due to its distance from the phenyl rings.

Summary. We have shown that these phosphite and phosphine complexes exhibit various equilibria which are dependent on temperature, the particular phosphorus-containing ligand, and the hydroborate ligand. That the (ethoxycarbonyl)trihydroborate is completely replaceable by a phosphite even at ambient temperature is not surprising since previous studies have shown that the trihydroborate possesses a weaker M–H–B linkage than tetrahydroborate. Reduction of temperature resulting in a shift in equilibrium with a concomitant slowing down of the dynamic equilibrium process allows both the tri- and tetrahydroborate phosphite and phosphine complex equilibria to be observed. The fact that the equilibria are observed at higher temperatures for the phosphine than the phosphite may reflect the differences in basicity as well as equilibria temperature dependence.

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Registry No. $[(MeO)_3P]_2CuBH_4$, 67784-66-1; $[(MeO)_3P]_3CuBH_4$, 76986-54-4; $[(MeO)_3P]_4Cu^+BH_4^-$, 76986-53-3; $[(EtO)_3P]_2CuBH_4$, 76986-52-2; $[(EtO)_3P]_3CuBH_4$, 76986-73-7; $(MePh_2P)_3CuBH_4$, 63371-86-8; $(MePh_2P)_4Cu^+BH_4^-$, 76986-72-6; $[(MeO)_3P]_2CuH_3BCOOC_2H_5$, 76986-71-5; $[(MeO)_3P]_4Cu^+H_3BCOOC_2H_5^-$, 76986-70-4; $[(EtO)_3P]_2CuH_3BCOOC_2H_5$, 76986-69-1; $[(EtO)_3P]_4Cu^+H_3BCOOC_2H_5^-$, 76986-68-0.

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Nitrogen-14 Nuclear Quadrupole Resonance Study of Coordinated Thiocyanate[1]

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A series of twenty palladium(II) thiocyanate complexes have been synthesized and their ^{14}N nuclear quadrupole resonance (NQR) spectra recorded by using the recently developed technique of adiabatic demagnetization in the laboratory frame–double resonance level crossing (ADLF–drlc). A clearly definitive trend for determining the mode of coordination of the thiocyanate moiety, via its ^{14}N nuclear quadrupole coupling constant, has been established. The field gradients at nitrogen are found to be largest in sulfur-bound thiocyanates and smallest in nitrogen-bound thiocyanates, while ionic thiocyanates have field gradients of intermediate values. The asymmetry parameter does not vary consistently with the mode of attachment but, on the average, increases in the order $NCS^- < M\text{-}NCS < M\text{-}SCN$. These results indicate that, in general, no single nitrogen 2p orbital is occupied largely by a lone electron pair. For coordinated thiocyanate, the occupation of a single 2p orbital is greatest for the sulfur-bound complexes. These results support the resonance forms generally accepted, based on bond angle measurements from other techniques, e.g., X-ray crystal structures. Nitrogen-14 NQR via the ADLF–drlc experiment is the most unambiguous technique to date, short of a single-crystal X-ray crystal structure analysis, for the determination of the bonding mode of diamagnetic, hydrogen-containing complexes of thiocyanate in the solid state.

Introduction

Instrumental methods which depend upon nuclear properties have been employed with ever-increasing frequency in the determination of the bonding modes adopted by the ambidentate pseudohalide ions NCO^-, NCS^-, and $NCSe^-$ in coordination complexes.[3,4] Collectively, they offer significant advantages as more sensitive, unequivocal indicators of bond type. The NMR techniques utilized thus far have ranged from indirect probes, wherein nuclei external to the pseudohalides

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[1] Based on the Ph.D. dissertation of W.C.F., University of Delaware, May 1980. Presented, in part, at the 12th Middle Atlantic Regional Meeting of the American Chemical Society, Hunt Valley, MD, April 5–7, 1978 (see Abstracts, No. INOR 9).

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