We have been successful in providing the first of the above possibilities, coordination of one cyano to copper, by synthesizing the first dicyanodihydroborate complexes, $(Ph_2MeP)_3Cu(NC)_2BH_2$ and $P^3Cu(NC)_2BH_2$ (P^3 = 1,1,1-tris((diphenylphosphino)methyl)ethane). $(Ph_2MeP)_3Cu(NC)_2BH_2$ is formed from the reaction of 0.72 mmol of $(Ph_2MeP)_3CuCl$ in 20 mL of CH_2Cl_2 and approximately 0.73 mmol of $Na(NC)_2BH_2\cdot 0.65$(dioxane)[3b] in 10 mL of absolute ethanol (conditions analogous to those used in making tetrahydroborate and cyanotrihydroborate complexes).[2] After the solid formed in the reaction was filtered out, crystals were obtained from the filtrate by adding equal volumes of ethanol and pentane and cooling. Reduction of the volume was necessary in some cases to obtain crystals. These were washed with Et_2O and dried under vacuum. The composition of the complex $(Ph_2MeP)_3Cu(NC)_2BH_2$ may be compared with those of the corresponding tetrahydroborate, $(Ph_2MeP)_3CuBH_4$,[4] and cyanohydroborate, $(Ph_2MeP)_3CuNCBH_3$,[2b] complexes. In all three cases the hydroborate coordinates to a single copper. Analysis supports the designated composition. Anal. Calcd: C, 67.54; H, 5.62; Cu, 8.72; B, 1.51. Found: C, 67.42; H, 5.75; Cu, 8.63; B, 1.57. MP: 128–129 °C. The P^3 complex was made similarly and analysis supports the $P^3CuBH_2(CN)_2$ formulation. Anal. Calcd: C, 68.57; H, 5.85; Cu, 8.44; B, 1.96. Found: C, 68.32; H, 5.55; Cu, 8.35; B, 1.67. MP: 195–197 °C.

The IR spectra of both complexes (Nujol mulls) support the proposed formulation. Characteristic B—H and $C\equiv N$ bands are found in the 2000–2500-cm^{-1} region. For the Ph_2MeP complex strong absorptions at 2410 and 2360 cm^{-1} are assigned to the B–H stretching vibrations (free ligand ν_{BH} = 2410 (s), 2392 (s), 2380 (m) cm^{-1}). There are two bands assigned in the $C\equiv N$ stretching region, one at 2192 cm^{-1} and one at 2210 cm^{-1}. The peak at 2192 cm^{-1} is decreased from the $C\equiv N$ stretching band in sodium dicyanodihydroborate and is assigned to the terminal $C\equiv N$, while the peak at 2210 cm^{-1} is assigned to the bridging $C\equiv N$ stretch. Corresponding peaks for the P^3 complex are $\nu_{B-H} = 2382\ cm^{-1}$ and $\nu_{C\equiv N}$ = 2198 and 2220 cm^{-1}.

The proton NMR of the Ph_2MeP complex (in $CDCl_3$) shows the presence of the phosphorus ligand in the complex with peaks at 1.53 and 7.34 ppm (referenced to Me_4Si) corresponding to the methyl protons and the phenyl protons respectively. The relative intensities of the peaks are 9.5:3 as compared to an expected ratio of 10:3. The absence of the B–H proton resonances is consistent with the fast quadrupole relaxation by the boron. Analogous peaks for the P^3 complex are $\delta_{CH} = 1.56$, $\delta_{CH} = 2.39$, and δ_{Ph} = 7.17, 7.40.

The boron NMR supports the coordination of the dicyanodihydroborate ligand by a cyano nitrogen rather than a B–H hydrogen. The spectra of both the Ph_2MeP and P^3 complexes consist of a 1:2:1 triplet, resulting from splitting by two equivalent hydrogens and centered at –41.3 ppm, J = 95.3 Hz (Ph_2MeP complex, CH_3CN), and –40.8 ppm, J = 95.3 Hz (P^3 complex, CH_3CN) (referenced to boron trifluoride etherate). The peaks are sharp compared to those of most metal hydroborate complexes[4–6] but slightly broadened compared to those of the free dicyanodihydroborate salt. The center of the multiplet is shifted downfield from sodium dicyanodihydroborate (–42.1 ppm, CH_3CN). This slight downfield shift upon coordination indicates only a very small donaton of electron density from the boron on formation of the N–M bond and is consistent with the small shift in the B–H stretching frequency on coordination (6 cm^{-1}). These facts suggest that the boron does not donate very much electron density to the coordinate bond and that the B–H hydrogens are not involved in coordination to the metal.

As was found with the proton NMR, the phosphorus NMR supports the existence of phosphine ligand in each complex. A singlet is observed at –17.4 ppm for the Ph_2MeP complex and at –25.8 ppm for the P^3 complex (referenced to 85% phosphoric acid). In each case the peak is found downfield from the free ligand ($\delta_{Ph_2MeP} = -28$, $\delta_{P^3} = -26.9$) consistent with coordination of the phosphine to the metal.

The osmometric molecular weight (37 °C) of the Ph_2MeP complex was 290 ($CHCl_3$) (P^3 complex 559, CH_2Cl_2). As with other methyldiphenylphosphine complexes,[4,6] this is lower than the expected value of 728.5 (P^3 complex 694). The much lower value for the monodentate ligand is attributed to the dissociation of the phosphine ligand, a common observance with copper(I) phosphine complexes (for $(Ph_3P)_3CuNCBH_3$, see ref 2b).

All the physical data are consistent with one nitrogen of one CN group being attached to copper(I). Studies are continuing with this anion to investigate the possibilities of additional or different kinds of coordination by changing reaction conditions, the phosphine ligand, and the metal.

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Registry No. $(Ph_2MeP)_3Cu(NC)_2BH_2$, 90148-91-7; $P^3Cu(NC)_2BH_2$, 90148-92-8; $(Ph_2MeP)_3CuCl$, 36386-10-4; P^3CuCl, 37701-76-1.

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(4) Bommer, J. C.; Morse, K. W. *Inorg. Chem.* **1980**, *19*, 587.

(5) This includes ^{11}B results obtained in our laboratory on $(Ph_2MeP)_3CuH_3BCN$, which is analogous to $(Ph_3P)_3CuH_3BCN$.[2b] Both have H_3BCN^- bound to the copper through the nitrogen.

(6) Bommer, J. C. Ph.D. Thesis, Utah State University, 1977.

Contribution from the Department of Chemistry
and Biochemistry, University of California,
Los Angeles, California 90024[1a]

Studies of Ion Pairing for Salts of $[M_3(\mu\text{-}H,\mu\text{-}CO)(CO)_{10}]^-$ (M = Fe, Ru)

K.-P. Schick, N. L. Jones, P. Sekula, N. M. Boag,
J. A. Labinger,[1b] and H. D. Kaesz*

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It was of interest to determine the extent of ion pairing in salts of metal-cluster anions as a first step toward understanding their reactivity in stoichiometric and catalytic reactions. Collman et al.[2a] have shown that Li^+ accelerates alkyl migration in $[RFe(CO)_4]^-$ more than does Na^+; the migration is slowed 170-fold if the Na^+ is complexed by dicyclohexyl-18-crown-6.[2b–d]

Infrared spectroscopy has been shown to be a useful technique for the study of ion pairing with mononuclear carbonyl metalates.[3] In clusters, ion-pairing phenomena may be more

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(1) (a) Work performed at UCLA under a Cooperative Research Agreement with the Occidental Research Corp. (b) Occidental Research Corp., Irvine, CA 92713.

(2) (a) Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 4766–4772. The importance of alkali metal ion assistance in the migration reaction has been further demonstrated in crown-ether-attached metal complexes. See: (b) Powell, J.; Kuksis, A.; May, C. J.; Nyburg, S. C.; Smith, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 5941–5943. (c) Powell, J.; Gregg, M.; Kuksis, A.; Meindl, P. *Ibid.* **1983**, *105*, 1064–1065. (d) McLain, S. J. *Ibid.* **1983**, *105*, 6355–6357.

0020-1669/84/1323-2204$01.50/0

Table I. Bridging Carbonyl IR Absorptions (1750-1600 cm^{-1})

C^+	added salt	solvent[a]	$\nu_{C=O}$, cm^{-1}		
		$[C][Fe_3H(CO)_{11}]$			
NEt_4^+		CH_2Cl_2		1718[b]	
		THF	1747	1725	
Na^+		THF	1747	1690[c]	
Li^+		THF	1747	1670[c]	
PPN^+		THF	1747		
		Et_2O	1752	1736	
NEt_3H^+		CH_2Cl_2		1650[b]	
		THF	1747	1728	
		$[C][Ru_3H(CO)_{11}]$			
NEt_4^+		CH_2Cl_2		1696[d]	
		THF	1733	1708	
	LiBr	THF	1733	1708	1653
		THF-d_8	1732	1708	
		Me_2THF	1736	1701	
	LiBr	Me_2THF	1736	1698	1656
		p-dioxane		1692	
	LiBr	*p*-dioxane		1692	1634
		Et_2O		1694	
		DME	1730	1711	
		Me_4THF	1720	1693	
	LiBr	Me_4THF	1720	1693	1653
Na^+		THF	1733	1678	
Li^+		THF	1733	1653	
PPN^+		THF	1733		
		Et_2O	1736	1722	
		$[Na][Ru_3H(^{13}CO)_{11}]$			
		THF	1732, 1692	1678, 1644	

[a] THF = tetrahydrofuran; DME = 1,2-dimethoxyethane. [b] Reference 6. [c] Reference 9. [d] Cf. 1691 cm^{-1}.[5]

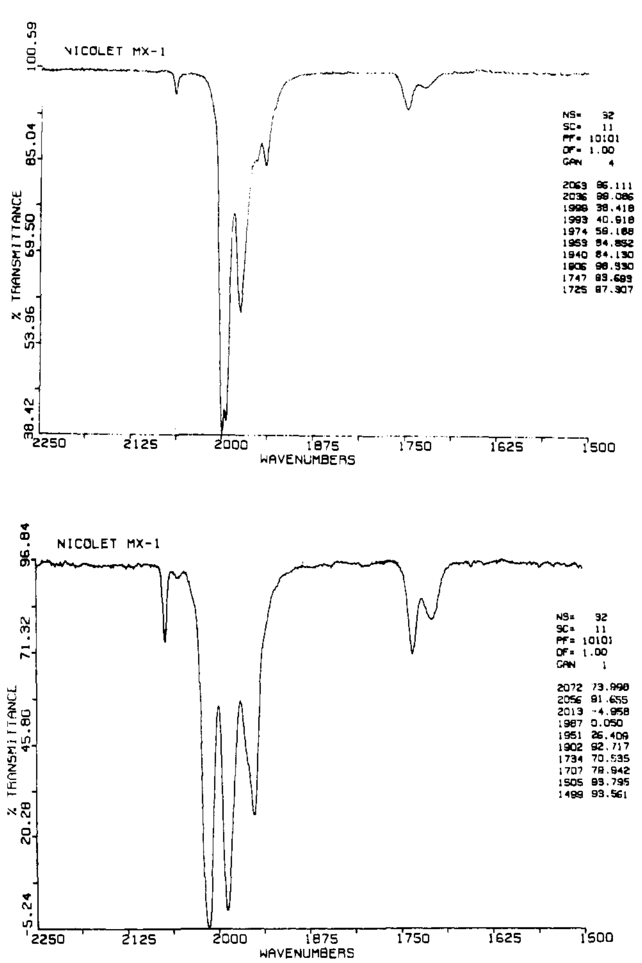
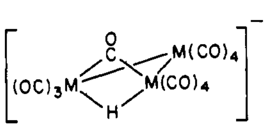


Figure 1. Absorptions in the carbonyl stretching region (THF solution): top, $[NEt_4][Fe_3H(CO)_{11}]$; bottom, $[NEt_4][Ru_3H(CO)_{11}]$.

difficult to interpret owing to the greater complexities in their vibrational spectra. For initial study the anions $[M_3H(CO)_{11}]^-$ ($\mathbf{1}^-$) were selected since their structures have been determined for $[NEt_3H][\mathbf{1a}]$[4] and $[PPN][\mathbf{1b}]$[5] ($PPN^+ = N(PPh_3)_2^+$). In both anions one edge of the metal triangle is bridged by a hydride and by one CO group.[4,5] IR studies[5,6] show that the structures of these two anions are also similar in solution. The bridging carbonyl group in the trinuclear anions is expected to provide a unique site for ion pairing, on the basis of two previous studies. The first is an IR study of the interactions of polynuclear carbonyl derivatives with Lewis acids[7a] reporting that the Lewis acid is attached at the oxygen atom of a bridging carbonyl group. Similarly, in the second case, alkylation of carbonyl anions takes place at the oxygen atom of the bridging carbonyl group.[5,7b,8]



$\mathbf{1a}^-$, M = Fe
$\mathbf{1b}^-$, M = Ru

Results

Bridging Carbonyl Absorption(s) in the IR Spectra for Salts of $\mathbf{1a}^-$ and $\mathbf{1b}^-$. A survey was undertaken to find an appropriate solvent for ion-pairing studies. Only one bridging carbonyl absorption is reported for each of the salts in CH_2Cl_2 (Table I). The broadness ($\Delta\nu_{1/2} \sim 46$ cm^{-1}) of these carbonyl absorptions makes CH_2Cl_2 an unsuitable solvent for the study of ion pairing. In Et_2O the two NEt_4^+ salts are practically insoluble and their bridging carbonyl absorptions are very broad and barely perceptible. Solutions in tetrahydrofuran, THF, give rise to sharp IR bands. Their spectra contain *two* absorptions in the bridging carbonyl region (Table I and Figure 1). To eliminate the possibility that the second band arises from the solvent, spectra of $[NEt_4][\mathbf{1b}]$ were also obtained in THF-d_8, 2,5-Me_2THF, and 2,2,5,5-Me_4THF. Two bands with very little shift in position are seen in the spectra of each of these solutions (see Table I); the spectrum of $[NEt_4][\mathbf{1b}]$ in THF-d_8, is shown in Figure 2a (supplemental).

Two bands in the bridging carbonyl region are also observed in THF for the Li^+ or the Na^+ salts[9] (Table I and Figure 3 (supplemental)). To establish that these bands arise from the carbonyl metalate a sample of ^{13}C-enriched $[Na][\mathbf{1b}]$ was prepared from ^{13}C-enriched $Ru_3(CO)_{12}$ and $NaBH_4$. The spectrum of the product contains two new bands at 1692 and 1644 cm^{-1} (Table I and Figure 2b (supplemental)), the maxima of which agree well with the expected isotopic shifts.

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(3) (a) Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hanckel, J. R.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521-1530. (b) Darensbourg, M. Y.; Darensbourg, D. J.; Burns, D.; Drew, D. A. *Ibid.* **1976**, *98*, 3127-3136.

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(7) (a) Alich, A.; Nelson, N. J.; Strope, D.; Shriver, D. F. *Inorg. Chem.* **1972**, *11*, 2976-2983. (b) Hodali, H. A.; Shriver, D. F. *Ibid.* **1979**, *18*, 1236-1241.

(8) Observations of the influence of counterion on CO absorptions have been made for the triruthenium anion[5] and for the cluster anion $[H_2Ru_4(CO)_{12}]^{2-}$: Inkrott, K. E.; Shore, S. G. *Inorg. Chem.* **1979**, *18*, 2817-2821.

(9) Similar observations have been independently made for the Li^+, Na^+, K^+, Rb^+, and Cs^+ salts of $[Fe_3H(CO)_{11}]^-$. Cf.: Cheng, C.-H.; Chen, C. *Inorg. Chem.* **1983**, *22*, 3378. These workers conclusively demonstrate that the lower energy absorption arises from a contact-ion-paired species by titration of $[K][Fe_3H(CO)_{11}]$ with crown ether. The lower energy band decreases in intensity as the higher energy band increases.

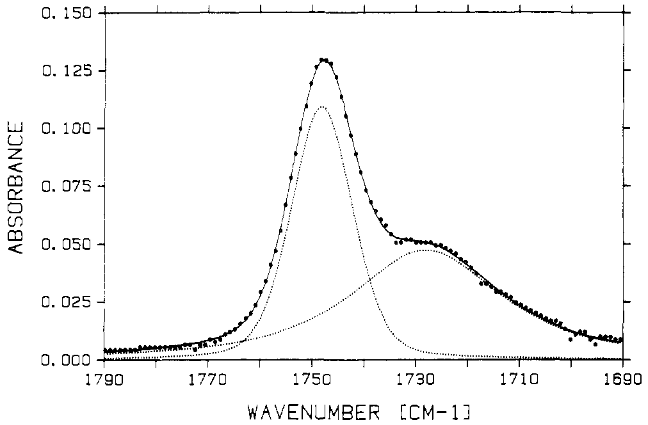

Figure 4. Deconvolution of the bridging carbonyl absorption for $[NEt_3H][Fe_3H(CO)_{11}]$.

The high-energy band occurs at the same frequency regardless of cation (cm^{-1}): **1a**, 1747; **1b**, 1733. This may therefore be assigned to a less associated species in solution while the lower energy band is assigned to a contact-ion-paired species.[9] The shift of this maximum to lower energy in going from $[NEt_3H]$[**1a**] and the NEt_4^+ salts to the Na^+ and then to the Li^+ salts reflects the increasing strength of interaction of the cation with the oxygen atom of the bridging carbonyl group. The two-band pattern is also observed for $[NEt_4]$[**1b**] in DME but not in Et_2O, CH_2Cl_2, or *p*-dioxane (Table I). In these weakly solvating agents only contact ion pairs exist. For the PPN^+ salts only a single maximum arising from a less associated anion is observed in THF, but in less solvating diethyl ether a two-band pattern is observed.

Effects of Ion pairing on the Terminal Carbonyl Absorptions. Where the bridging carbonyl region indicates the presence of a single type of species, i.e. for [PPN][**1b**], the terminal carbonyl absorptions are sharp (Figure 3, supplemental). Where more than one species is indicated in the bridging carbonyl region, the other carbonyl absorptions are broadened as in Figure 1. Where a strong interaction with the cation is indicated by a large separation of the two absorptions in the bridging carbonyl region, i.e. for [Li][**1b**], the highest energy terminal carbonyl absorption is resolved into two maxima, 2079 and 2072 cm^{-1} (Figure 3 (supplemental)) while distinct shoulders can be discerned for the other bands.

Concentration Studies of IR Intensity of the Two Bridging Carbonyl Absorptions. These studies were undertaken to elucidate the nature of the equilibria in this system. The absorption in the bridging carbonyl region was deconvoluted into two overlapping bands as shown in Figure 4 for $[NEt_3H]$[**1a**]. IR spectra were measured of THF solutions of $[NEt_3H]$[**1a**], $[NEt_4]$[**1a**], and $[NEt_4]$[**1b**] at varying concentrations. Although the ratio of the integrated intensities of the two bands shows a concentration dependence, the total area under the peaks in the bridging carbonyl region for these salts obeys the Lambert–Beer law, showing linearity over the range 1×10^{-3} through 4×10^{-2} M (Figure 5 and Table II (supplemental)). The extinction coefficients of the two bands representing two (or more) species in solution are thus equal within experimental error in both salts. The data cannot be fit by a single dissociation such as represented by K_1 but indicate that three species are involved[10] obeying the relationships

$$K_1 = [A][C]/[AC] \qquad K_2 = [A][C]/[ASC]$$

$$K_3 = [ASC]/[AC] = K_1/K_2$$

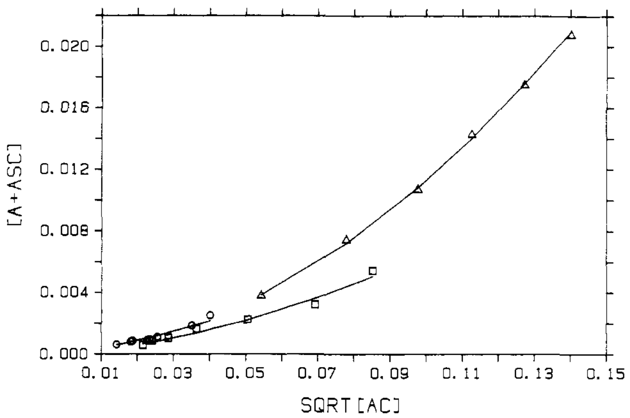

Figure 6. Least-squares fit of data to eq 2 for $[NEt_3H][Fe_3H(CO)_{11}]$ (squares), $[NEt_4][Fe_3H(CO)_{11}]$ (circles), and $[NEt_4][Ru_3H(CO)_{11}]$ (triangles).

Table III. Equilibrium Constants

	10^4K_1/M	10^4K_2/M	K_3
$[NEt_3H]$[1a]	4.65 (2)	10.48 (5)	0.444 (1)
$[NEt_4]$[1a]	12.92 (2)	28.78 (8)	0.449 (1)
$[NEt_4]$[1b]	4.33 (9)	4.70 (10)	0.922 (2)

where A = free anion, C = free cation, AC = contact ion pair, and ASC = solvent-separated ion pair.

The data may be treated in tems of α, eq 1. When [A] = [C] in K_1, $[A] = (K_1[AC])^{1/2}$, and we obtain eq 2. Least-squares fit of the data to eq 2 is shown in Figure 6, and the values of the equilibrium constant are given in Table III.

$$\alpha = [A + ASC]/[T] \qquad ([T] = [A + AC + ASC]) \quad (1)$$

$$\alpha[T] = (K_1[AC])^{1/2} + K_3[AC] \quad (2)$$

Comparison of the data for the NEt_4^+ salts of **1a**$^-$ and **1b**$^-$ shows significantly greater dissociation for the triiron salt, indicating greater charge dispersion in this anion. There is less dissociation for $[NEt_3H]$[**1a**], indicating some added interactions, perhaps of the type noted in the structure determination of $[NEt_3H][Co(CO)_4]$.[11]

Competition Studies Between LiBr and $[NEt_4]$[1b]. Routine precautions to exclude air and moisture were not adequate to carry out concentration studies on Li^+ or Na^+ salts of **1b**$^-$. Instead, varying quantities of LiBr were added to a THF solution of $[NEt_4]$[**1b**]. This resulted in a decrease in the intensity of the IR band at 1708 cm^{-1} accompanied by appearance of a band at 1653 cm^{-1} (eq 3). The total area under all three bands however does not obey the Lambert–Beer law (supplemental Table IV). Equilibrium constants can not be calculated from such data owing to too many unknown variables.

$$[NEt_4][\mathbf{1b}] + [Li][Br] = [Li][\mathbf{1b}] + [NEt_4][Br] \quad (3)$$

$$[PPN][\mathbf{1b}] + [Li][Br] = \text{no change} \quad (4)$$

By contrast, addition of LiBr to a THF solution of [PPN][**1b**], eq 4, produces no change in the IR spectrum, even with a large excess of LiBr. The driving force for reaction 3 is the greater ion-pairing tendency of $[NEt_4]$[Br] compared to that of [Li][Br].[12] In the case of the PPN^+ salt, despite greater ion pairing expected for [Li][**1b**], the tighter ion pairing in [Li][Br] as compared to that of [PPN][Br] is not overcome and no reaction is observed. The analogous **1a**$^-$ salts behave

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(10) Edgell, W. In "Ions and Ion Pairs in Organic Reactions"; Szwarc, M., Ed.; Wiley: New York, 1972; Vol. I, p 153.

(11) Calderazzo, F.; Fachinetti, F.; Marchetti, F.; Zanazzi, P. F. *J. Chem. Soc., Chem. Commun.* **1981**, 181.

(12) Paralleling the smaller dissociation constant in THF observed for $[NBu_4][BPh_4]$ as compared to that for $[Li][BPh_4]$: Bhattacharyya, D. N.; Lee, C. L.; Smid, J.; Szwarc, M. *J. Phys. Chem.* **1965**, *69*, 608–611.

similarly upon reaction with LiBr.

Conclusion

The trinuclear carbonyl anions are found to be relatively weakly paired to unipositive cations; the dissociation constants observed in THF are 1–2 orders of magnitude larger than those determined by conductivity measurements for the mononuclear anions $[CpMo(CO)_3]^-$ and $[Mn(CO)_5]^-$.[3]

Experimental Section

Tetrahydrofuran (THF), *p*-dioxane and diethyl ether (Mallinckrodt), 2,5-Me_2 THF and 2,2,5,5-Me_4 THF (Aldrich), 1,2-dimethoxyethane (DME; Matheson Coleman and Bell (MCB)) were freshly distilled from sodium/benzophenone under prepurified dinitrogen. Dichloromethane was distilled from P_2O_5. Tetrahydrofuran-d_8 (Aldrich) was degassed and used without further purification. All procedures were performed under dinitrogen in standard Schlenk-type glassware.[13] Lithium bromide (MCB) was dried at 130 °C under vacuum for a minimum of 24 h. All syringes and the IR cells (CaF_2, 0.1 mm; KCl, 0.5 mm) were flushed with dinitrogen prior to use. All infrared spectra were recorded for solutions under an atmosphere of dinitrogen on a Nicolet MX-1 FT-IR spectrometer. Data were transferred to a VAX computer through an interface developed by B. S. Seiler in these laboratories. THF solutions of $LiBEt_3H$ and $LiB(s\text{-}Bu)_3H$ (Aldrich) were used as received, as were the salts $LiBH_4$ (Aldrich) and $LiOH{\cdot}H_2O$ (MCB). $Ru_3(CO)_{12}$ was used as purchased (Strem). Literature procedures were used to prepare the Na^+, NEt_4^+, and PPN^+ salts of $[Ru_3H(CO)_{11}]^-$ (**1b**$^-$)[5] and $[PPN][Fe_3H(CO)_{11}]$ ([PPN][**1a**]).[14] $[NEt_3H]$[**1a**] and $[NEt_4]$[**1a**] were prepared by adaptation from the preparation of [PPN][**1a**].

Data Acquisition and Handling. Infrared spectra were obtained on a Nicolet MX-1 FT-IR spectrometer and transferred to an LSI (DEC) microprocessor. For the representation of IR bands we chose the "restricted" Cauchy–Gauss sum function described by R. N. Jones[15] and obtained very satisfactory fits by keeping the half-bandwidths of the two functions equal. For minimization of the sum of weighted least-squares we used the subroutine CURFIT.[16]

Attempted Preparations of Pure [Li][1b]. In a typical experiment $Ru_3(CO)_{12}$ (30 mg, 0.047 mmol) is dissolved in 5–10 mL of THF. A THF or Et_2O solution of $LiBR_3H$ (1–10 equiv) is then added by syringe (R = H, 25 °C; R = Et, 0 °C; R = *s*-Bu, −78 °C). The initially orange solution turns deep red with stirring. Reaction progress is followed by infrared spectroscopy. Attempts to isolate solids by solvent removal lead to unidentified decomposition products.

In a second attempt, a flask containing a solution of $Ru_3(CO)_{12}$ (30 mg, 0.047 mmol) in 5 mL of THF is flushed with CO. A solution of $LiOH{\cdot}H_2O$ (0.02 g, 0.42 mmol) in 1 mL of distilled, degassed H_2O is then added by syringe. The system is flushed with CO again and stirred at room temperature for 1 h. The solvents are stripped off under vacuum; the residue is dried under vacuum and then redissolved in THF. IR spectra confirm the presence of [Li][**1b**]; however, any further experimental manipulations lead to decomposition.

Dilution Studies. For $[NEt_3H]$[**1a**] and $[NEt_4]$[**1a**], THF solutions at the varying concentrations shown in Table II (supplemental) were made by adding successive increments of the salt to an initial dilute solution. For $[NEt_4]$[**1b**] a 30 mg/mL stock solution was prepared in THF. Solutions of lower concentration (see Table II (supplemental)) were prepared by successive dilutions of the initial stock solution.

Competition Study between $[NEt_4][Ru_3H(CO)_{11}]$ and LiBr in THF. A stock solution of $[NEt_4][Ru_3H(CO)_{11}]$ and a stock solution of LiBr (1 mg/mL) were prepared as described above. Infrared spectra were obtained of solutions containing the lithium salts and the ruthenium anion as shown in Table IV (supplemental).

Acknowledgment. Partial support of this work from NSF Grant CHE 81-11332 to H.D.K. and discussions with Dr. Joel S. Miller of Occidental Research Corp. are gratefully acknowledged.

Registry No. $[NEt_4^+]$[**1a**], 55976-22-2; $[Na^+]$[**1a**], 87145-37-7; $[Li^+]$[**1a**], 87145-36-6; $[PPN^+]$[**1a**], 23254-21-9; $[NEt_3H^+]$[**1a**], 56048-18-1; $[NEt_4^+]$[**1b**], 12693-45-7; $[Na^+]$[**1b**], 71936-71-5; $[PPN^+]$[**1b**], 85781-92-6; $[PPN^+]$[**1b**], 71936-70-4; ^{13}C, 14762-74-4; LiBr, 7550-35-8.

Supplementary Material Available: Figures 2 and 3 (IR spectra), Figure 5 (a Lambert–Beer plot), Table II (data for concentration studies), and Table IV (data for competition studies) (4 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Windsor, Windsor, Ontario, Canada N9B 3P4

Iridium Complexes of (Diphenylphosphino)ethanethiol. Crystal and Molecular Structure of $[IrH(SCH_2CH_2PPh_2)(HSCH_2CH_2PPh_2)(CO)]^+Cl^-$: A New and Novel Example of Thiol Coordination

Douglas W. Stephan

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Transition-metal complexes of thiolates and thioethers have received considerable attention because of their involvement in both enzymatic[1] and nonbiological catalytic processes.[2,3] The chemistry of phosphine complexes, on the other hand, forms the basis for a variety of catalytic reactions.[4,5] The development of these two fields of research led to the recent interest in mixed-donor phosphorus–sulfur ligands. Phosphine–thioether chelates have been studied by the research groups of Meek,[6,7] Clark,[8] Roundhill,[9] Sanger,[10] and others.[11–14] The chemistry of phosphine–thiol ligands has received lesser attention.[15–18] In this paper we report our initial investigations of the chemistry of one such phosphine–thiol chelate, (diphenylphosphino)ethanethiol, $Ph_2PCH_2CH_2SH$ (PSH). The reactions of PSH with *trans*-$Ir(PPh_3)_2(CO)Cl$ (**1**) are described. The resulting new Ir(III) and Ir(I) species are characterized. An X-ray crystallographic investigation reveals that reaction of **1** with excess ligand yields a new and novel complex in which thiol and thiolate coordination occurs. The results and implications of this chemistry are discussed below.

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