



Figure 1. Plot of the pseudo-first-order rate constant for the formation of (acetonitrile)pentaammineruthenium(III) trifluoromethanesulfonate from (trifluoromethanesulfonato)pentaammineruthenium(III) in sulfolane as a function of the initial concentration of acetonitrile (at 37 °C).

obtained some kinetics data that are useful in predicting rates of reactions for synthetic purposes.

The substitution reactions of Ru(III) ammine complexes are notoriously slow, and few kinetic data are available for such reactions. The hydrolysis rate for $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ has been reported to be $3.1 \times 10^{-6} \text{ s}^{-1}$ at 35 °C¹⁵ and $3.6 \times 10^{-6} \text{ s}^{-1}$ at 37.3 °C¹⁶ while that for $[\text{Ru}(\text{NH}_3)_5\text{Br}]^{2+}$ has been reported to be $4.0 \times 10^{-6} \text{ s}^{-1}$ at 37.3 °C.¹⁶ The trifluoromethanesulfonate ligand is a much better leaving group, as shown by the hydrolysis rate of $[\text{Ru}(\text{NH}_3)_5(\text{CF}_3\text{SO}_3)]^{2+}$, $9.3 \times 10^{-2} \text{ s}^{-1}$ at 25 °C.¹⁴ The complex $[\text{Ru}(\text{NH}_3)_5(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)_2$ is a relatively labile precursor for synthesis of a wide variety of ligands when used in the inert solvent sulfolane at moderate temperatures. Figure 1 shows the dependence of the rate of formation of (acetonitrile)pentaammineruthenium(III) at 37 °C on the concentration of CH_3CN . The calculated second-order rate constant for this reaction is $6.4 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. Comparable rate constants were obtained for other neutral ligands: $3.2 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for the formation of (1-adamantanecarbonitrile)pentaammineruthenium(III) at 37 °C and $0.19 \text{ M}^{-1} \text{ s}^{-1}$ for formation of (4-phenylpyridine)pentaammineruthenium(III) at 48 °C. The formation rate for the bromide complex, $[\text{Ru}(\text{NH}_3)_5\text{Br}]^{2+}$, is considerably greater, $6.7 \text{ M}^{-1} \text{ s}^{-1}$ at 30 °C and $9.5 \text{ M}^{-1} \text{ s}^{-1}$ at 40 °C. This result is consistent with the favorable formation of an ion pair prior to the substitution step. Reactions with iodide ion are rapid. Even at a KI concentration of $5 \times 10^{-4} \text{ M}$, the formation of $[\text{Ru}(\text{NH}_3)_5\text{I}]^{2+}$ was complete on mixing. This rapid reaction of iodide ion with the Ru(III) complexes has been previously observed by Ford and co-workers¹⁷ and Taube and co-workers¹⁸ and has been attributed to the ability of I^- to reduce Ru(III) to produce labile Ru(II) intermediates. Unfortunately, catalytic substitution of $[\text{Ru}(\text{NH}_3)_5(\text{CF}_3\text{SO}_3)]^{2+}$ in the presence of I^- is not a useful synthetic procedure since I^- coordinates preferentially in the presence of other potential ligands (i.e., in the presence of excess CH_3CN , $[\text{Ru}(\text{NH}_3)_5\text{I}]^{2+}$ is formed predominantly), the I^- is thereby sequestered, and $[\text{Ru}(\text{NH}_3)_5\text{I}]^{2+}$ is inert.

Our results indicate that $[\text{Ru}(\text{NH}_3)_5(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)_2$ can be made readily, is stable for months with minor precautions (storage in a common desiccator over P_2O_5), and is useful for a variety of synthetic applications. Rates of reaction can be reliably estimated. The preliminary kinetic data indicate that this complex may be useful for establishing the nature of substitution reactions of Ru(III) and for comparing with data available for other robust ions such as Co(III), Rh(III), and Ir(III).¹⁹

Acknowledgment. We gratefully acknowledge support of the National Institutes of Health (Grant Nos. GM 27179 and RR 08176), the Petroleum Research Fund, administered by the American Chemical Society, and the CUNY PSC-BHE grants program for support of this work.

Registry No. $[\text{Ru}(\text{NH}_3)_5(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)_2$, 84278-98-8; $[\text{Ru}(\text{NH}_3)_5\text{Cl}]_2$, 18532-87-1; $[\text{Ru}(\text{NH}_3)_5\text{I}](\text{CF}_3\text{SO}_3)_2$, 90245-34-4; $[\text{Ru}(\text{NH}_3)_5\text{Br}](\text{CF}_3\text{SO}_3)_2$, 90245-35-5; $[\text{Ru}(\text{NH}_3)_5\text{Cl}](\text{CF}_3\text{SO}_3)_2$, 53195-19-0; $[\text{Ru}(\text{NH}_3)_5\text{L}](\text{CF}_3\text{SO}_3)_3$ (L = acetonitrile), 90245-38-8; $[\text{Ru}(\text{NH}_3)_5\text{L}](\text{CF}_3\text{SO}_3)_3$ (L = benzonitrile), 90245-39-9; $[\text{Ru}(\text{NH}_3)_5\text{L}](\text{CF}_3\text{SO}_3)_3$ (L = *o*-dicyanobenzene), 90245-41-3; $[\text{Ru}(\text{NH}_3)_5\text{L}](\text{CF}_3\text{SO}_3)_3$ (L = *m*-dicyanobenzene), 90245-42-4; $[\text{Ru}(\text{NH}_3)_5\text{L}](\text{CF}_3\text{SO}_3)_3$ (L = *p*-dicyanobenzene), 90245-43-5; $[\text{Ru}(\text{NH}_3)_5\text{L}](\text{CF}_3\text{SO}_3)_3$ (L = 1-adamantanecarbonitrile), 90245-44-6; Ru, 7440-18-8; pyridine, 110-86-1; (1,4-dicyanobicyclo[2.2.2]octane)-bis(pentaammineruthenium(III) trifluoromethanesulfonate), 90245-37-7; ((1,4-dicyanobicyclo[2.2.2]octane)pentaammineruthenium(III))aquotetraamminecobalt(III) trifluoromethanesulfonate, 86542-42-9; ((*m*-dicyanobenzene)pentaammineruthenium(III))aquotetraamminecobalt(III) trifluoromethanesulfonate, 90245-48-0; ((*p*-dicyanobenzene)pentaammineruthenium(III))aquotetraamminecobalt(III) trifluoromethanesulfonate, 90245-50-4; ((*trans*-1,4-dicyanocyclohexane)pentaammineruthenium(III))aquotetraamminecobalt(III) trifluoromethanesulfonate, 90245-46-8.

Contribution from the Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322

$[(\text{Ph}_2\text{MeP})_3\text{Cu}(\text{NC})_2\text{BH}_2]$ and $\text{P}^3\text{Cu}(\text{NC})_2\text{BH}_2$ ($\text{P}^3 = 1,1,1\text{-Tris}(\text{diphenylphosphino})\text{methyl} \text{ethane}$): The First Metal Complexes of Dicyanodihydroborate

Paul G. Egan, David G. Holah,¹ and Karen W. Morse*

Received June 21, 1983

The synthetic and structural chemistry of the cyanotrihydroborate anion, H_3BCN^- , with several transition-metal complexes is known.² Depending upon reaction conditions, it has been found that either the cyano alone may coordinate to the metal or the cyano and hydroborate may both coordinate, resulting in a H_3BCN^- bridging ligand.^{2a,b} The recent success of McPhail and Spielvogel in synthesizing the new substituted hydroborate, dicyanodihydroborate, $(\text{H}_2\text{B}(\text{CN})_2)^-$,³ allowed us to investigate the Cu(I) complexes of this interesting ligand. The dicyanodihydroborate offers the possibilities, by analogy with the cyanohydroborate, that only one cyano will coordinate or that a cyano and hydrogen will coordinate. In addition, the second cyano group offers additional interesting possibilities for coordination.

- (1) On sabbatical leave from Department of Chemistry, Lakehead University, Thunder Bay, Ontario, Canada.
- (2) Examples include: (a) Melmed, K. M.; Li, T.; Mayerle, J. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1974**, *96*, 69. (b) Lippard, S. J.; Welcker, P. S. *J. Chem. Soc. D* **1970**, 515; *Inorg. Chem.* **1972**, *11*, 6. (c) Segal, B. G.; Lippard, S. J. *Ibid.* **1974**, *13*, 822; **1977**, *16*, 1623. (d) Holah, D. G.; Hughes, A. N.; Hui, B. C.; Wright, K.; *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 835. (e) Drummond, A.; Kay, J. F.; Morris, J. H. *Reed, D. J. Chem. Soc., Dalton Trans.* **1980**, 284. (f) Kay, J. F.; Morris, J. H.; Reed, D. *Ibid.* **1980**, 1917. (g) Purcell, K. F.; Yeh, S. M.; Eck, J. S. *Inorg. Chem.* **1977**, *16*, 1708. (h) Purcell, K. F.; Zapeta, J. P. *J. Chem. Soc., Chem. Commun.* **1978**, 497.
- (3) (a) Spielvogel, B. F.; McPhail, A. T.; et al., submitted for publication in *J. Org. Chem.* (b) Our purification procedure differed from that of Spielvogel and McPhail. The crude product (5 g) was placed in water and allowed to stand for 1 h. The water was removed and the solid recrystallized from THF/dioxane and dried under vacuum. Anal. Calcd for $\text{NaBH}_2(\text{CN})_2 \cdot 0.65(\text{dioxane})$: C, 38.0; H, 4.96; N, 19.3. Found: C, 38.3; H, 5.00; N, 19.3. This gave an air-stable, nonhygroscopic material. (c) See also: Emri, J.; Gyori, B. *J. Chem. Soc., Chem. Commun.* **1983**, 1303.

- (15) Broomhead, J. A.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1964**, *3*, 826.
- (16) Eliades, T.; Harris, R. O.; Reinsalu, P. *Can. J. Chem.* **1969**, *47*, 3823.
- (17) Marchant, J. A.; Matsubara, T.; Ford, P. C. *Inorg. Chem.* **1977**, *16*, 2160.
- (18) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1979**, *18*, 549.
- (19) Swaddle, T. *Can. J. Chem.* **1977**, *55*, 3166; *Coord. Chem. Rev.* **1974**, *14*, 217; *Inorg. Chem.* **1980**, *19*, 3203.

We have been successful in providing the first of the above possibilities, coordination of one cyano to copper, by synthesizing the first dicyanodihydroborate complexes, $(\text{Ph}_2\text{MeP})_3\text{Cu}(\text{NC})_2\text{BH}_2$ and $\text{P}^3\text{Cu}(\text{NC})_2\text{BH}_2$ ($\text{P}^3 = 1,1,1$ -tris((diphenylphosphino)methyl)ethane). $(\text{Ph}_2\text{MeP})_3\text{Cu}(\text{NC})_2\text{BH}_2$ is formed from the reaction of 0.72 mmol of $(\text{Ph}_2\text{MeP})_3\text{CuCl}$ in 20 mL of CH_2Cl_2 and approximately 0.73 mmol of $\text{Na}(\text{NC})_2\text{BH}_2 \cdot 0.65(\text{dioxane})^{3b}$ 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 $(\text{Ph}_2\text{MeP})_3\text{Cu}(\text{NC})_2\text{BH}_2$ may be compared with those of the corresponding tetrahydroborate, $(\text{Ph}_2\text{MeP})_3\text{CuBH}_4$,⁴ and cyanohydroborate, $(\text{Ph}_2\text{MeP})_3\text{CuNCBH}_3$,^{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 $\text{P}^3\text{CuBH}_2(\text{CN})_2$ 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 $\text{C}\equiv\text{N}$ 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 $\nu_{\text{BH}} = 2410$ (s), 2392 (s), 2380 (m) cm^{-1}). There are two bands assigned in the $\text{C}\equiv\text{N}$ stretching region, one at 2192 cm^{-1} and one at 2210 cm^{-1} . The peak at 2192 cm^{-1} is decreased from the $\text{C}\equiv\text{N}$ stretching band in sodium dicyanodihydroborate and is assigned to the terminal $\text{C}\equiv\text{N}$, while the peak at 2210 cm^{-1} is assigned to the bridging $\text{C}\equiv\text{N}$ stretch. Corresponding peaks for the P^3 complex are $\nu_{\text{B—H}} = 2382$ cm^{-1} and $\nu_{\text{C}\equiv\text{N}} = 2198$ 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 $\delta_{\text{CH}} = 1.56$, $\delta_{\text{CH}} = 2.39$, and $\delta_{\text{Ph}} = 7.17$, 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 complexes⁴⁻⁶ 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 donation 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 ($\delta_{\text{Ph}_2\text{MeP}} = -28$, $\delta_{\text{P}^3} = -26.9$) 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 $(\text{Ph}_3\text{P})_3\text{CuNCBH}_3$, 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.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Registry No. $(\text{Ph}_2\text{MeP})_3\text{Cu}(\text{NC})_2\text{BH}_2$, 90148-91-7; $\text{P}^3\text{Cu}(\text{NC})_2\text{BH}_2$, 90148-92-8; $(\text{Ph}_2\text{MeP})_3\text{CuCl}$, 36386-10-4; P^3CuCl , 37701-76-1.

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024^{1a}

Studies of Ion Pairing for Salts of $[\text{M}_3(\mu\text{-H},\mu\text{-CO})(\text{CO})_{10}]^-$ (M = Fe, Ru)

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

Received August 16, 1983

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 $[\text{RFe}(\text{CO})_4]^-$ 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

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

(5) This includes ¹¹B results obtained in our laboratory on $(\text{Ph}_2\text{MeP})_3\text{CuH}_3\text{BCN}$, which is analogous to $(\text{Ph}_3\text{P})_3\text{CuH}_3\text{BCN}$.^{2b} Both have H_3BCN^- bound to the copper through the nitrogen.

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

(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.