

Figure 2. ^{31}P NMR spectrum of $\text{mer}-(\text{OC})_3\text{Mo}(\text{dpm})_2$ in CD_2Cl_2 , chemical shifts in ppm relative to 85% H_3PO_4 , with negative values downfield from reference. Coupling constants are $|^2J_{ab}| = 64.4$ Hz, $|^2J_{bc}| = 25.6$ Hz, $|^2J_{bd}| = 72.4$ Hz, $|^2J_{cd}| = 24.4$ Hz.

compared to the coordinated phosphorus atom of monodentate dpm. We have observed the same trend in other dpm complexes of molybdenum and iron.⁸ In contrast, it is well established that chemical shifts of phosphorus atoms in five-membered chelate rings show a large downfield shift relative to unchelated coordinated phosphorus.^{9,10}

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Registry No. $\text{fac}-(\text{OC})_3\text{Mo}(\text{dpm})_2$, 56009-06-4; $\text{mer}-(\text{OC})_3\text{Mo}(\text{dpm})_2$, 56085-32-6; $(1-6-\eta\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3$, 12125-77-8; ^{31}P , 7723-14-0.

References and Notes

- (1) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).
- (2) D. M. Adams, "Metal-Ligand and Related Vibrations", Edward Arnold, London, 1967, p 101.
- (3) J. R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, **1**, 287 (1967).
- (4) J. M. Jenkins, J. R. Moss, and B. L. Shaw, *J. Chem. Soc. A*, 2796 (1969).
- (5) R. B. King, "Organometallic Syntheses", Vol. 1, Academic Press, New York, N.Y., 1965, p 125.
- (6) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).
- (7) T. W. Beall and L. W. Houk, *J. Organomet. Chem.*, **56**, 261 (1973).
- (8) E. E. Isaacs, Ph.D. Thesis, University of Alberta, 1974.
- (9) S. O. Grim, W. L. Briggs, R. C. Barth, C. A. Tolman, and J. P. Jesson, *Inorg. Chem.*, **13**, 1095 (1974); S. O. Grim, J. D. Gaudio, R. P. Molenda, C. A. Tolman, and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 3416 (1974).
- (10) J. A. Connor, J. P. Day, E. M. Jones, and G. K. McEwen, *J. Chem. Soc., Dalton Trans.*, 347 (1973).

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The Interaction of HCN with $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$

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The rearrangement of N-bound imidazole to the C-bound form when it is ligated to $\text{Ru}(\text{II})$ and the labilization of the trans position by the C-bound form¹ prompted the present study which is concerned with the formation of the HCN complex of $\text{Ru}(\text{II})$, and with the subsequent reactions of the species. Some observations on the complex when it is formed as product of the decomposition of $[\text{Ru}(\text{NH}_3)_5\text{NCBH}_3]^+$ have been reported by Ford.² These observations have been amplified and modified by this work in which the instability of the ion $[\text{Ru}(\text{NH}_3)_5\text{HCN}]^{2+}$ is attributed to intramolecular rearrangement of the N-bound to the C-bound, resulting in labilization of the trans ammonia and subsequent polymerization.

Experimental Results and Discussion

A solid of composition $\text{Ru}(\text{NH}_3)_5(\text{HCN})(\text{PF}_6)_2$ (I) was prepared by the following procedure. Oxygen-free HCN was bubbled through $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ in 6 M trifluoroacetic

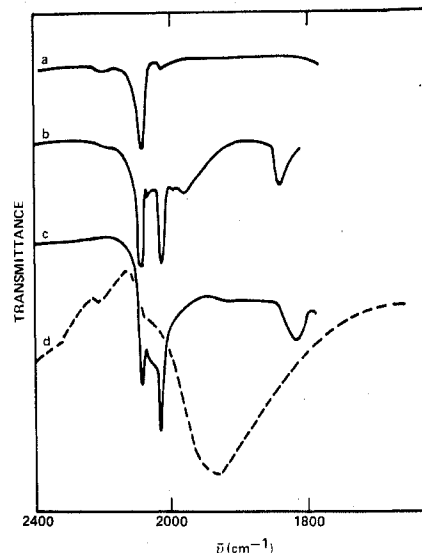


Figure 1. Infrared spectra in the region $2000\text{--}1800\text{ cm}^{-1}$ for the rearrangement of $[\text{Ru}(\text{NH}_3)_5\text{NCH}](\text{PF}_6)_2$ (KBr pellets): (1a) freshly prepared (6 M acid); (1b and 1c) 1 and 0.1 M acid, respectively; (1d) after addition of NH_3 to I and reprecipitation. Similar spectra were obtained when I was aged for periods of days.

Table I. Infrared Frequencies ($\nu(\text{C}\equiv\text{N})$) for Free and Coordinated Nitriles

Compd	$\nu(\text{CN})$, cm^{-1}	Ref
CH_3CN	2254	2
HCN	2097	2
NaCN	2080	3
$[\text{Ru}(\text{NH}_3)_5\text{NCCH}_3](\text{BF}_4)_2$	2239	2
$[\text{Ru}(\text{NH}_3)_5\text{NCH}](\text{ClO}_4)_2$	1960 vs. b	2
$[\text{Ru}(\text{NH}_3)_5\text{NCH}](\text{PF}_6)_2$	2085	This work
$[\text{Ru}(\text{NH}_3)_5\text{CN}]\text{PF}_6$	1998	This work

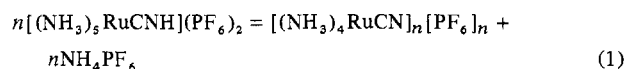
acid for 15 min, resulting in a pale yellow solution. On addition of excess NH_4PF_6 a light yellow solid was precipitated in high yield, ca. 70%. Elemental analysis of the solid was consistent with the formulation $[\text{Ru}(\text{NH}_3)_5(\text{NCH})](\text{PF}_6)_2$. Calcd: C, 2.39; H, 3.20; N, 16.69. Found: C, 2.50; H, 3.17; N, 16.16.

The infrared spectra recorded for the salt $[\text{Ru}(\text{NH}_3)_5\text{NCH}](\text{PF}_6)_2$ are shown in Figure 1. Different nitrile stretching frequencies were found depending on the conditions used for the preparation. When I is freshly prepared (the freshly prepared material only will hereinafter be designated as I) under strict exclusion of oxygen in strongly acidic conditions (ca. 6 M acid), the spectrum shown in Figure 1a is obtained ($\nu(\text{CN})$ 2080 cm^{-1}). Figures 1b and 1c show the spectra obtained when the preparation was carried out under less acidic conditions (less than 1 M acid). Aging of I resulted in a progression of absorption bands similar to those shown in Figures 1b, 1c, and 1d. When a solution of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ is treated with an equimolar solution of sodium cyanide, the solid, precipitated as a PF_6^- salt, shows one strong, sharp band, $\nu(\text{CN})$ 1998 cm^{-1} . Table I summarizes the infrared frequencies ($\nu(\text{CN})$) for free and coordinated nitriles, including results reported by Ford.²

The behavior described taken together with consideration of the conditions for the preparation of I imply that the compound is the N-bound HCN complex, analogous to the acetonitrile complex of $\text{Ru}(\text{II})$. This supposition is supported by the fact that I shows a band maximum at 238 nm ($\log \epsilon \sim 4$) which can be compared with the band maximum for $[\text{Ru}(\text{NH}_3)_5\text{NCCH}_3]^{2+}$ at 229 nm ($\log \epsilon$ 4.2).³

The immediate product of the reaction of $\text{Ru}(\text{NH}_3)_5\text{NCBH}_3^+$ with 2 M HCl is reported² to have an absorption band with a maximum at 241 nm and with $\epsilon \sim 4$, in good agreement with our measurements for the ion we

believe to be $[\text{Ru}(\text{NH}_3)_5\text{NCH}]^{2+}$. Our results and those described by Ford differ on the matter of the infrared absorption of the solid. Ford reports for the solid purported to be $[\text{Ru}(\text{NH}_3)_5\text{NCH}](\text{ClO}_4)_2$ a strong broad band at 1960 cm^{-1} which according to our observations represents a late decomposition product of I. We take the intermediate species which has a sharp maximum at 2020 cm^{-1} arising from I on aging of the solid to be the C-bound HCN complex, and, on the basis of results to be described, the material giving the broad final absorption (Figure 1d) to be a polynuclear CN-bridged species arising from the decomposition reaction



Species I is unstable in solution and its decomposition (as measured by the disappearance of the band at 229 nm) accelerates as the acidity decreases. Approximate values for the specific rate of this reaction as a function of pH (acetate buffer) are: $k_{\text{obsd}} \times 10^2, \text{ sec}^{-1} = 1, 4, 7, 17, >70$ at pH's of 3.6, 4.5, 4.8, 5.5, 7.0, respectively. We take the decomposition reaction, at least in its first stages, to involve isomerization of N-bound HCN to a C-bound form, a reaction which it is reasonable to suppose will take place more readily for the deprotonated ligand than for the protonated.

When the reaction is studied with isonicotinamide (isn) present, the reaction course is simple, and a product is formed which has an absorption maximum at 415 nm. Similar absorption spectra were obtained for $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{CN}(\text{isn})]^+$ starting with $[\text{Ru}(\text{NH}_3)_5\text{NCH}]^{2+}$ or $[\text{Ru}(\text{NH}_3)_5\text{CN}]^+$ and isonicotinamide at pH 8.3. Since $[\text{Ru}(\text{NH}_3)_5(\text{isn})]^{2+}$ has a maximum at 480 nm, the reaction leading to product is not substitution of CN^- by isn. From the kinetic behavior and in analogy to observations^{1a} made on the labilization of trans ammonia by C-bound imidazole, we take the reaction product to be $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{CN}(\text{isn})]^+$ (II).

The rate of formation of II from I was found to be independent of pH in the range 5 to 7.3, and of [isn] over the range 0.01 to 0.1 M. The specific rate calculated for the reaction is $5.3 \times 10^{-3} \text{ sec}^{-1}$. The results just described, compared with those on rearrangement, show that the formation of the isn product is slow compared with the rearrangement of cyanide. We conclude, therefore, that the step governing the rate of formation of II is the release of trans NH_3 from the C-bound form of $\text{Ru}(\text{NH}_3)_5\text{CN}^+$. Comparison with the literature value⁵ for the release of NH_3 from $\text{Ru}(\text{NH}_3)_6^{2+}$ shows that replacing NH_3 by CN^- enhances the rate of trans ammonia release by a factor of 3×10^3 . The effect of CN^- is almost as great as that of SO_3^{2-} where the corresponding labilizing factor is found⁶ to be 6×10^3 .

Aging the solid for a period of days or adding I to $\sim 2\text{ M}$ NH_3 and immediately reprecipitating it produced spectrum 1d. In view of the labilization of the trans position noted above, it is reasonable to suppose that the substance giving rise to 1d is the product of polymerization of $\text{Ru}(\text{NH}_3)_4\text{CN}^+$. An analysis was not obtained for the solid, but the conclusion that the species is polymeric is supported by the fact that it is not eluted from a cation exchange column by 1.5 M LiCl. For this interpretation to be accepted, a great decrease in the affinity of NH_3 for Ru(II) when CN^- is coordinated must be assumed, in line with the increased lability already documented for the trans ammonia.

An incidental conclusion which follows from the rate profiles, k vs. pH, for the decomposition (rearrangement) reaction and the formation of II is that while $\text{Ru}(\text{NH}_3)_5\text{NCH}^{2+}$ is still largely protonated at pH 5.5, $\text{Ru}(\text{NH}_3)_5\text{CNH}^{2+}$ is fully deprotonated at this pH.

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Registry No. $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$, 21393-88-4; $[\text{Ru}(\text{NH}_3)_5(\text{NCH})](\text{PF}_6)_2$, 55822-60-1; $[\text{Ru}(\text{NH}_3)_5\text{CN}]\text{PF}_6$, 55822-62-3; $\text{trans-}[\text{Ru}(\text{NH}_3)_4\text{CN}(\text{isn})]^+$, 55822-63-4.

References and Notes

- (1) (a) R. J. Sundberg, R. E. Shepherd, and H. Taube, *J. Am. Chem. Soc.*, **94**, 6558 (1972); (b) R. J. Sundberg, R. F. Bryan, I. F. Taylor, and H. Taube, *ibid.*, **96**, 381 (1974).
- (2) P. C. Ford, *Chem. Commun.*, 7 (1971).
- (3) P. C. Ford, *Coord. Chem. Rev.*, **5**, 79 (1970).
- (4) For N-bound to C-bound cyanide rearrangements on other metal ions, see: (a) J. Halpern and S. Nakamura, *J. Am. Chem. Soc.*, **87**, 3002 (1965); (b) J. Espenson and J. Birk, *ibid.*, **87**, 3280 (1965); (c) J. Guttenberger, *Chem. Ber.*, **101**, 403 (1968).
- (5) R. E. Shepherd and H. Taube, *Inorg. Chem.*, **12**, 1392 (1973). Note that allowance must be made for the statistical value of 6 in making comparisons with the present work.
- (6) S. Isid and H. Taube, *Inorg. Chem.*, **13**, 1545 (1974).

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The Hydrolysis of Methyl(phosphino)germanes. Evidence for Ge-H Bond Lability in Methylgermoxanes¹

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It has been reported that instead of rapidly cleaving the germanium-phosphorus bond of GeH_3PH_2 to form phosphine and germanol and/or germoxane products, water promotes the redistribution of germyl and hydrido groups on phosphorus to yield phosphine, digermylphosphine, and trigermylphosphine.³ Prompted by our interests in redistribution reactions as routes to new germanium-phosphorus bonded compounds⁴⁻⁶ we have examined reactions that the methyl-(phosphino)germanes, $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$, $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$, and $(\text{CH}_3)_3\text{GePH}_2$, undergo with water. Our results are reported below.

Experimental Section

Apparatus and Materials. All manipulations were carried out in standard vacuum-line apparatus.⁷ Proton magnetic resonance data were obtained using a Varian A-60A spectrometer. Proton chemical shift values are reported relative to internal $(\text{CH}_3)_4\text{Si}$ (negative δ downfield). Infrared spectra were obtained with a Perkin-Elmer Model 337-G spectrometer. Mass spectra were obtained with a Varian MAT CH-5 spectrometer operating at an ionizing voltage of 70 eV. The $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$, $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$, and $(\text{CH}_3)_3\text{GePH}_2$ were prepared as described previously.⁸ Dimethoxyethane (monoglyme) was distilled from LiAlH_4 prior to use. Distilled water was used in hydrolysis reactions.

Hydrolysis Reactions. Typically, the methyl(phosphino)germanes and water, and in some cases monoglyme, were condensed into heavy-walled NMR tubes or Pyrex bulbs and allowed to react as shown in Table I. Examples in the table are bulb reactions unless specified otherwise. Products from bulb reactions were removed and separated by fractional condensation and/or sublimation techniques. Reaction materials were identified by comparison of their reported spectral properties with literature values as: PH_3 (ir^9 and $^1\text{H NMR}^{10}$), $(\text{CH}_3)_2\text{GeH}_2$ (ir^{11} and $^1\text{H NMR}^{12}$), $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$ ($^1\text{H NMR}^8$), $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)_2$ ($^1\text{H NMR}^8$), $(\text{CH}_3)_3\text{GePH}_2$ ($^1\text{H NMR}^8$), $[(\text{CH}_3)_3\text{Ge}]_2\text{O}$ ($^1\text{H NMR}^{13}$), and $[(\text{CH}_3)_2\text{GeO}]_{3,4}$ ($^1\text{H NMR}^{14}$). In experiments 2 and 3, the reported quantities of $[(\text{CH}_3)_2\text{GeO}]_{3,4}$ are those obtained after purification of the products by sublimation along a horizontal gradient-heated sublimation tube. The $[(\text{CH}_3)_2\text{GeH}]_2\text{O}$ in experiment 4 was separated crudely from other reactants by fractional condensation. Extraction of the crude material into diethyl ether followed by removal of the ether in vacuo resulted in pure $[(\text{CH}_3)_2\text{GeH}]_2\text{O}$ in about 50% yield.

In a separate series of experiments, $(\text{CH}_3)_2\text{Ge}(\text{PH}_2)\text{H}$ and H_2O in a 10:1 ratio in monoglyme in an NMR tube were allowed to react at room temperature while reaction progress was periodically