sulting in an increase in the basicity of the ruthenium(II)-ligand species and a decrease in the acidity of the chromium(III) ion compared to the protonated nicotinamidechromium(III) ion.

The intense visible absorption band characteristic of pentaammineruthenium(II) complexes with a heterocyclic ligand and the greater basicity of pyrazinepentaammineruthenium(II) compared to uncoordinated pyrazine have been accounted for on the basis of ruthenium-to-ligand charge transfer.[12] The present work offers further evidence for significant metal-to-ligand back-donation in ruthenium(II) complexes with heterocyclic ligands.

Acknowledgment. R. W. C. is grateful for a Non-Service Fellowship supported by the University of Tennessee.

Registry No. I, 50639-78-6; Cr^{2+}, 22541-79-3; (ruthenium(II) nicotinamide)chromium(III) ion, 50639-79-7.

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Cobaloxime Nitrosyl. Reaction with Molecular Oxygen and Formation of Coordinated Nitrato Complexes

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Reaction of coordinated nitrosyl with molecular oxygen has been observed to produce coordinated nitro groups.[1,2] Formation of coordinated nitrate is restricted to a few ruthenium complexes.[3,4] The most extensive study of the reaction of nitrosyl complexes with oxygen has been carried out by Clarkson and Basolo,[1] who studied principally complexes of the general type Co(L)NO, where L is a quadridentate dinegative Schiff base chelate or two bidentate dialkyldithiocarbamate ligands. These complexes react most readily in the presence of monodentate ligands, B, such as pyridine (py) and tri-*n*-butylphosphine (Bu_3P). From the determination of the dependence of the rate of reaction on [B], it was concluded that BCo(L)NO complexes were formed. The low formation constants prevented spectral characterization of BCo(L)NO. This complex most likely reacts with oxygen to form $BCo(L)NOO_2$, where NOO_2 is angular O-N-O-O coordinated through N.[1] This peroxy intermediate then reacts with another BCo(L)NO complex to produce $BCo(L)NO_2$ complexes.

During the course of an investigation of cobaloximes containing ligands with high trans effects, we had occasion to prepare cobaloxime nitrosyl $Co(DH)_2NO$ (where DH is the monoanion of dimethylglyoxime). The general interest in the activation of small molecules by transition metals and recent interest in the oxidation of nitrosyls led us to investigate the reaction of cobaloxime nitrosyl with oxygen. It has been previously reported that in the absence of added ligands, B, the nitro complex $(H_2O)Co(DH)_2NO_2$ is formed.[2]

We have found that the major product of the oxidation of $BCo(DH)_2NO$ in CH_2Cl_2 is usually the O-bonded nitrato compound, $BCo(DH)_2NO_3$, found in amounts greater than 50% when B = *t*-Bu(py), CNpy, Me(IMD), and $P(C_6H_5)_3$.[5] The second major product is the expected nitro compound formed in amounts less than 50%. The reaction was not clean in that small amounts of side products which could not be identified were also formed (<10%). After discovery of this reaction, we began preliminary studies to determine the mechanism. However, the product distribution, while being little dependent on a variety of factors such as the nature and concentration of B, the solvent, and the total complex concentration, was not exactly reproducible. The product ratio of nitrato to nitro also did not change significantly on addition of a variety of cobalt(II) catalysts[6,7] or of chelating agents such as bipyridine. In every case (over 50 reactions) the nitrato product was formed and in amounts greater than the nitro product.

The ratio of products was also independent of added nitrate or nitro products after subtraction of the contribution of product initially added. In this connection, we observed that the nitrato complex does not react with the nitrosyl complex in the presence of added B.

Because of the above difficulties and the rapidity of the reaction (complete in *ca.* 15 sec), we have not been able to determine the reaction mechanism. However, the formation of nitrato complexes from oxidation of nitrosyl compounds has only been observed for ruthenium complexes. These may react through dioxygen complex intermediates.[3,4] We report here our observations substantiating nitrate formation for one ligand, *t*-Bu(py), and one solvent, CH_2Cl_2. We also report several observations on the spectral properties of cobaloxime nitrosyl.

Results

A methylene chloride solution (*ca.* 0.01 *M*) of $Co(DH)_2NO$[2] under nitrogen exhibits a pmr signal at τ 7.58 assignable to the four equivalent bis(dimethylglyoximato) methyl groups. Addition of base, B, causes an upfield shift of the signal. The chemical shift depends on B in a manner consistent with eq 1. The observation of only one bis(dimethylglyoximato) methyl resonance for the nitrosyl complexes

$$Co(DH)_2NO + B \rightleftharpoons BCo(DH)_2NO \qquad (1)$$

when [complex]/[B] > 1 and the variation in chemical shift of the ligand resonances (such as the *t*-Bu groups in *t*-Bu(py)) are consistent with eq 1 being rapid on the pmr time scale. For example, only an average *t*-Bu resonance is observed for coordinated and free *t*-Bu(py) (when [complex] > [*t*-Bu(py)], the *t*-Bu resonance occurs at τ 8.79 and shifts to a limiting low-field value of τ 8.68 when [complex] << [*t*-Bu(py)]).

In the presence of excess *t*-Bu(py), the bis(dimethyl-

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(1) S. G. Clarkson and F. Basolo, *Inorg. Chem.*, 12, 1528 (1973), and references therein.

(2) M. Tamaki, I. Masada, and K. Shinra, *Bull. Chem. Soc. Jap.*, 45, 171 (1972).

(3) K. R. Laing and W. R. Roper, *Chem. Commun.*, 1568 (1968).

(4) K. R. Grundy, K. R. Laing, and W. R. Roper, *Chem. Commun.*, 1500 (1970).

(5) Abbreviations used are *t*-Bu(py) = 4-*tert*-butylpyridine, CNpy = 4-cyanopyridine, and Me(IMD) = 1-methylimidazole. Chemical shifts observed for the methyloxime resonances for nitrato and nitro, respectively, are as follows: CNpy, τ 7.62 and 7.72; Me(IMD), τ 7.60 and 7.72; $(C_6H_5)_3P$, τ 7.95 and 8.04. The last compound has been reported previously. The high-field positions of the $(C_6H_5)_3P$ compounds are the result of anisotropic shielding of the phenyl groups and the resonances are split by phosphorus, J = 0.7 Hz (NO_3) and 1.5 Hz (NO_2).

(6) L. G. Marzilli, J. G. Salerno, and L. A. Epps, *Inorg. Chem.*, 11, 2050 (1972).

(7) K. G. Caulton, *J. Amer. Chem. Soc.*, 95, 4076 (1973).

glyoximato) methyl resonance occurs at τ 7.82. Introduction of air into the solutions described above rapidly yields (*ca.* 15 sec) the final nitro and nitrato products. When more concentrated solutions were employed, the pmr spectrum indicated the existence of the starting and product complexes and there were no resonances attributable to intermediates. Furthermore, the ratio of nitrato to nitro complex was similar to that found after complete oxidation.

The identity of the products in most instances was inferred primarily by the pmr spectrum since the order of chemical shifts of $BCo(DH)_2X$ complexes is not altered greatly by changing B.[8] When B = *t*-Bu(py), the complexes *t*-Bu(py)$Co(DH)_2NO_2$[8] and *t*-Bu(py)$Co(DH)_2NO_3$ were added to product solutions resulting in increases of the signals at τ 7.72 and 8.79 and at τ 7.60 and 8.81, respectively. The nitrato complex was isolated (40% yield) from a preparative-scale reaction in CH_2Cl_2 and the ir spectrum (KBr pellet) contained nitrato peaks at 1512 (m), 1504 (m), 1275 (s), and 980 (s) cm^{-1} identical with that of the known complex and consistent with the coordinated nitrato group.[9] More soluble fractions of the reaction contained primarily *t*-Bu(py)$Co(DH)_2NO_2$ (contaminated with *t*-Bu(py)$Co(DH)_2NO_3$) as evidenced by ir bands at 1420, 1315, and 815 cm^{-1}. Bands in this region have previously been attributed to the nitro group[1,2] and the *t*-Bu(py)$Co(DH)_2NO_2$ compound prepared directly using $NaNO_2$ also contains these bands.

Cobaloxime nitrosyl exhibits interesting ir behavior. In the solid, the material prepared by the original preparative method[2] has a strong band at 1635 cm^{-1} (KBr) which corresponds to the band at 1641 cm^{-1} (Nujol).[2] This band has been assigned to the NO stretch.[2] The only strong band which can be assigned to this stretch in CH_2Cl_2 appears at 1710 cm^{-1}. The product gives low carbon analyses and on heating (110° *in vacuo*) acceptable analyses are obtained and a band at 1710 cm^{-1} appears (KBr). Caulton has reported that $(CH_3OH)Co(DH)_2NO$ has ν_{NO} 1710 cm^{-1} ($HCCl_3$) and 1639 cm^{-1} (KBr).[7] The methanol is not coordinated in solution.[7] These results strongly suggest that the product originally reported as $Co(DH)_2NO$ is in fact $(H_2O)Co(DH)_2NO$.

Addition of ligands, B, to CH_2Cl_2 solutions of cobaloxime nitrosyl caused a decrease in size of the band at 1710 cm^{-1} and the appearance of a new band at $\sim$1645 cm^{-1} (dependent on B). This band disappears on introduction of air. The position of the band for B = Bu_3P, *t*-Bu(py), $(CH_3O)_3P$, and $(C_6H_5)_3P$ was 1628, 1634, 1648, and 1661 cm^{-1}, respectively. This shift is consistent with donation of electron density into the NO π-antibonding orbitals. The formation constants for eq 1 seemed much higher than for the complexes studied by Clarkson and Basolo and a titration of $Co(DH)_2NO$ with pyridine in acetone (at 25°, 6000 Å, $[Co] = 3 \times 10^{-3}\ M$) gave a value of about 25 M^{-1} compared to values of about 1 M^{-1} for other Co(L)NO complexes.[1]

Discussion

Cobaloxime nitrosyl clearly differs from other complexes of the type Co(L)NO in that nitrate formation is observed. The solid-state ir spectra of several cobalt nitrosyls of the type Co(L)NO have been compared by Basolo[1] and the NO stretching frequencies fall in the range 1624–1654 cm^{-1}. The X-ray structure of some of these[1] has shown that Co–N–O is nonlinear and it has been concluded that bent bonding occurs in all these systems.

Our work and that of Caulton[7] place ν_{NO} at 1710 cm^{-1} for cobaloxime nitrosyl. Thus this band for the five-coordinate complex is *ca.* 60 cm^{-1} higher than those five-coordinate complexes which yield exclusively nitro products.[1] It would be interesting to determine if the NO stretching frequency can be used to predict whether NO_2 or NO_3 will be formed on oxidation. Since most BCo(L)NO complexes have low formation constants, ν_{NO} values have not been measured, but we would anticipate that ν_{NO} would be below 1600 cm^{-1} for the complexes studied previously.[1] The ν_{NO} for one of the dioxygen-ruthenium complexes which yield NO_3 products has been reported as 1765 cm^{-1}.[3] Thus the ν_{NO} of nitrosyl complexes might prove to be a useful criterion for predicting whether NO_3 or NO_2 will be formed.

Comparisons of Schiff base complexes and cobaloximes have been made previously primarily because both systems stabilize cobalt–carbon bands. Cobaloximes have higher formation constants than Schiff base complexes.[10] Therefore, more complex is in the reactive form (BCo(L) or BCo(L)NO). Cobaloximes also undergo oxidation reactions more readily.[10] Although we have not performed rate studies, cobaloxime nitrosyl reacts very rapidly with oxygen. Finally, the dioximes appear to be better electron-withdrawing ligands.[11] This property, which may involve π bonding, explains the higher frequency of ν_{NO} and the greater affinity for a sixth ligand of cobaloxime nitrosyl as compared to Co(L)NO. No further work on these oxidation reactions is planned.

Experimental Section

Materials and Instruments. Solvents acetone and CH_2Cl_2 were reagent grade and used without further purification. Nitrogen ligands were purchased from Aldrich and phosphorus ligands from Strem. Pmr spectra were recorded either on MH100 (Jeol) or A60 (Varian) instruments. Ir spectra were recorded on a Perkin-Elmer 457 grating instrument and visible spectra on a Cary 14 spectrophotometer.

Cobaloxime Nitrosyl. This compound was prepared several times using published methods or variation of published methods.[2] The product contains traces of cobalt(II) impurities as evidenced by ligand-exchange reactions[6] after aerial oxidation, although conceivably aerial oxidation could have led to the formation of the catalysts. The product was also prepared by the method of Caulton[7] but using CH_2Cl_2 as solvent. The material was not isolated by this procedure but oxidation also gave nitrato products. The material isolated from methanol reactions was washed with water as directed.[2] However, it is quite soluble in water. This washing step probably introduces water by exchange with $(CH_3OH)Co(DH)_2NO$.[7] Methanol was never observed in the pmr spectrum of any of the preparations. However, low carbon values were obtained unless the material was dried (110° *in vacuo*). *Anal.* Calcd for $C_8CoH_{14}N_5O_5$: C, 30.10; H, 4.43; Co, 18.46. Found: C, 29.9; H, 4.3; Co, 18.3.

***t*-Bu(py)$Co(DH)_2NO_3$ from Cobaloxime Nitrosyl.** Cobaloxime nitrosyl (1.0 g, 0.003 mol) was suspended in CH_2Cl_2 (50 ml) and *t*-Bu(py) (0.43 ml, 0.003 mol) added over 5 min with stirring. After the solution was allowed to air oxidize for 1 hr, it was filtered to remove a small amount of undissolved material and evaporated to dryness with a rotary evaporator. The residue was redissolved in CH_2Cl_2 (15 ml) and diethyl ether (100 ml) added slowly with stirring. The brown product was collected and washed with diethyl ether–CH_2Cl_2 (50:50, 5 ml) and dried (110° *in vacuo*); yield 0.6 g, 40%. This material was shown to be *t*-Bu(py)$Co(DH)_2NO_3$ by spectral comparison to authentic samples. It is extremely readily

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(8) R. Stewart and L. G. Marzilli, unpublished results.

(9) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley-Interscience, New York, N. Y., p 171.

(10) For example cobal(II)oxime complexes are usually five-coordinate in solution, but Schiff base complexes have measurable formation constants: L. G. Marzilli, P. A. Marzilli, and J. Halpern, *J. Amer. Chem. Soc.*, 93, 1374 (1971).

(11) R. M. McAllister and J. H. Weber, *J. Organometal. Chem.*, 55, C85 (1973).

hydrolyzed to [t-Bu(py)Co(DH)$_2$(H$_2$O)]NO$_3$ which is poorly soluble in CH$_2$Cl$_2$. The filtrate from above was allowed to evaporate to dryness and spectral characterization showed the residue to be primarily t-Bu(py)Co(DH)$_2$NO$_2$ with some t-Bu(py)Co(DH)$_2$NO$_3$.

t-Bu(py)Co(DH)$_2$NO$_3$ by Direct Preparation. To a solution of t-Bu(py)Co(DH)$_2$Cl[6] (3.0 g, 0.0067 mol) in methanol (75 ml), silver nitrate (1.28 g, 0.0075 mol) was added. The suspension was warmed and stirred for 2 hr and let stand overnight. After filtration, water (75 ml) was added to the filtrate in an open beaker. After 2 days the solution had evaporated (to ~30 ml) and the crystals which had formed were collected and washed with water (5 ml) and diethyl ether (90 ml). The product [t-Bu(py)Co(DH)$_2$-(H$_2$O)]NO$_3$ (2.15 g, 60% yield) was dehydrated (110° *in vacuo*) to give t-Bu(py)Co(DH)$_2$NO$_3$ quantitatively. *Anal.* Calcd for $C_{17}CoH_{27}N_6O_7$: C, 42.0; H, 5.6; Co, 12.2. Found: C, 42.4; H, 5.4; Co, 11.9.

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Registry No. Cobaloxime nitrosyl, 36509-25-8; (t-Bu(py))Co-(DH)$_2$NO$_3$, 50276-21-6.

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Trifluorosilylpentaboranes

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The prospect of making (fluorinated silyl)pentaboranes was encouraged by the results of an attack by SiF$_2$ upon B$_5$H$_9$ in a cocondensation process performed by Dr. David Solan in these laboratories. His crude product was separated from resinous nonvolatiles, and the unstable volatiles were allowed to decompose until it became possible to isolate 0.013 mmol of a slightly volatile liquid (vapor tension near 1 mm at 0°) having infrared and ^{11}B nmr spectra suggesting 1-HSiF$_2$B$_5$H$_8$.

Accordingly, a direct synthesis of SiF$_3$B$_5$H$_8$ was attempted, using LiB$_5$H$_8$ with excess SiF$_4$ in ether at $-78°$ or lower. The volatile product was almost exclusively 2-SiF$_3$B$_5$H$_8$, convertible by a difficult catalysis to its isomer 1-SiF$_3$B$_5$H$_8$.

Syntheses. An ether solution of LiB$_5$H$_8$ was made from B$_5$H$_9$ and LiC$_2$H$_5$,[1] rather than LiC$_4$H$_9$,[2] because the evolved ethane could be isolated easily, as a measure of the formation of LiB$_5$H$_8$. The reaction occurred in a vertical 350 mm long tube (25 mm wide), attached to the high-vacuum manifold. For complete conversion to LiB$_5$H$_8$, 12 hr at $-78°$ usually sufficed, but sometimes temperatures as high as $-40°$ were allowed. Small excesses of B$_5$H$_9$ seemed not to harm the subsequent process.

The ether solution of LiB$_5$H$_8$ was covered by a layer of fresh ether (distilled in slowly at $-78°$); then SiF$_4$ in 3:1 ratio to LiB$_5$H$_8$ was forced into this ether layer (at $-78°$ or as low as $-120°$), from above. The reaction was started by sudden mixing of the layers at $-78°$ or lower, using a magnetic plunger as a stirrer. The mixture was allowed to stand for 12 hr at $-78°$, and then all volatiles were drawn off *in vacuo* during slow warming, finally to 60°.

This procedure led to yields of 2-SiF$_3$B$_5$H$_8$ representing as much as 45% of the LiB$_5$H$_8$. For example, 3.280 mmol of LiB$_5$H$_8$ and 9.717 mmol of SiF$_4$ produced 1.497 mmol of 2-SiF$_3$B$_5$H$_8$, with consumption of 3.94 mmol of SiF$_4$, some of which, of course, would have gone to form Li$_2$SiF$_6$. The question of formation of SiF$_2$(B$_5$H$_8$)$_2$ was not decided; the nonvolatile resinous product could have included its successor. The yield of 1-SiF$_3$B$_5$H$_8$ may have been close to 1%; it was completely separable from 2-SiF$_3$B$_5$H$_8$ by slow high-vacuum fractional condensation at $-40°$.

For larger samples of 1-SiF$_3$B$_5$H$_8$, catalytic isomerization of 2-SiF$_3$B$_5$H$_8$ can be accomplished by contact with resins made from pentaborane, such as the nonvolatile yellow residue from the SiF$_3$B$_5$H$_8$ synthesis, but the process is sharply limited by inactivation of the catalyst—an effect varying widely among different samples of such resins. Also, the loss of SiF$_3$B$_5$H$_8$ material often exceeds the amount converted. The conversion is accompanied by formation of small amounts of highly volatile products, including SiF$_4$ and HSiF$_3$, easily detected by their infrared spectra. On account of the uncertainty about catalyst potency, the question of reversibility of the isomerization has not been decided. Both isomers seem stable for months at 25°.

Hexamethylenetetramine has served as an effective catalyst for isomerizing halogenated pentaboranes[3] or 2-(CH$_3$)$_3$-SiB$_5$H$_8$,[4] but it had only a limited effect upon crude 2-SiF$_3$B$_5$H$_8$, and even then apparently only through resin formation. With pure samples of either 1-SiF$_3$B$_5$H$_8$ or 2-SiF$_3$B$_5$H$_8$ (12 hr at 60°) it failed to cause any detectable isomerization.

The most successful procedure for the LiB$_5$H$_8$-SiF$_4$ reaction was repeated with HSiF$_3$ and with PF$_3$, yielding neither HSiF$_2$B$_5$H$_8$ nor PF$_2$B$_5$H$_8$, but only yellow resins. If the desired compounds actually were formed at low temperatures (but perhaps base catalyzed to resins on warming), they might be isolated by some special method, such as low-temperature solution chromatography.

Physical Properties. The melting range of a nearly pure sample of 2-SiF$_3$B$_5$H$_8$ (for which the ^{19}F nmr spectrum showed 0.3% presence of 1-SiF$_3$B$_5$H$_8$) was -11.5 to $-10.8°$, whereas well-purified 1-SiF$_3$B$_5$H$_8$ (isomer not detectable) melted in the range 7.7–8.1°. The equilibrium vapor pressure of solid 1-SiF$_3$B$_5$H$_8$ at 0° is 1.04 mm, or for the liquid, 6.35 mm at 24.5°; a rough estimate of the normal boiling point would be 140°. The 99.7% pure sample of 2-SiF$_3$B$_5$H$_8$ showed vapor pressure values of 5.02 mm at 0°, 22.18 mm at 22.5°, 31.40 mm at 31.1°, 50.02 mm at 40.35°, and 78.58 mm at 50.0°, determining the equation $\log P = 6.6605 + 1.75 \log T - 0.005T - 2367/T$ (bp 113.3°; Trouton constant 21.7 eu; calculated values: 5.03, 22.13, 31.48, 50.05, 78.50 mm). The vapor-phase molecular weight measurements gave 147.5 for 1-SiF$_3$B$_5$H$_8$ and 148.8 for 2-SiF$_3$B$_5$H$_8$ (calculated for both 147.2).

Nmr Spectra. The ^{11}B spectra of 1-SiF$_3$B$_5$H$_8$ and the presumed 1-HSiF$_2$B$_5$H$_8$ are nearly identical: a broad but clean doublet at 30.4 or 30.8 ppm upfield of methyl borate ($J = 169$ cps for both) and a broad singlet at 80.1 ppm, one-fourth as intense. This B-1 singlet is considerably farther upfield than B-1 for other known B$_5$H$_9$ derivatives, possibly because the fluorine lone-pair electrons exert a π-type electronic induction across the Si 3d orbitals, toward the B-1 atom.

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