The second possibility can be eliminated since the hydrido cluster can only be extracted by ion exchange. In addition, great care was taken to remove and keep water away from the system. The third possibility can be eliminated since the level of impurities in the silica is well below the metal loadings used. In addition, the presence of impurities cannot account for the essential role of light in this process. Therefore, the first proposed reaction scheme, namely reaction with a silica hydroxy group, is the only likely alternative.

Though this scheme requires the formation of a relatively unusual Si^+ moiety, the driving force for such a reaction can be the photochemical generation of an unstable cluster intermediate. The Si^+ site is then generated in a process similar to that on alumina and stabilized by complexation to the anionic iron carbonyl cluster. The photochemical generation of a Lewis acid site on silica appears to be a new phenomenon. Experiments aimed at better understanding the details of this unique reaction are under way. In addition the ramifications on the catalysis of this system, where the iron carbonyl cluster is grafted to the surface of silica, are being investigated.

Registry No. $Fe_3(CO)_{12}$, 17685-52-8; SiO_2, 7631-86-9.

Supplementary Material Available: Figure 1S (carbonyl region from the infrared spectrum of the silica surface bound anionic triiron cluster) and Figure 2S (carbonyl region from the infrared spectrum of the extracted anionic triiron cluster) (2 pages). Ordering information is given on any current masthead page.

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Received February 22, 1989

Dihydrobis(pyrazolyl)borate Complexes of Gallium. X-ray Crystal Structure of $[H_2B(pz)_2]_2GaCl$ (pz = Pyrazolyl Ring)

The chemistry of gallium and indium is of interest for reasons ranging from their use in the diagnosis of disease[1] to uses in the preparation of new semiconductors.[2] We have shown that polypyrazolylborate ligands are very useful for the preparation of stable complexes of group 3 metals[3] and of lanthanide metals where the most common oxidation state is also +3.[4] We report here that gallium(III) complexes of the dihydrobis(pyrazolyl)borate ligand, $[H_2B(pz)_2]_2GaCl$ (**1**) and $[H_2B(pz)_2]_3Ga$ (**2**) (pz = pyrazolyl ring), form readily and are very stable. These complexes are, to our knowledge, the first complexes of gallium using the dihydrobis(pyrazolyl)borate ligand.[5] The solid-state structure of $[H_2B(pz)_2]_2GaCl$ has been determined crystallographically. This structure is a relatively rare example of neutral five-coordinate gallium(III), especially with ligands containing nitrogen donor atoms.[6]

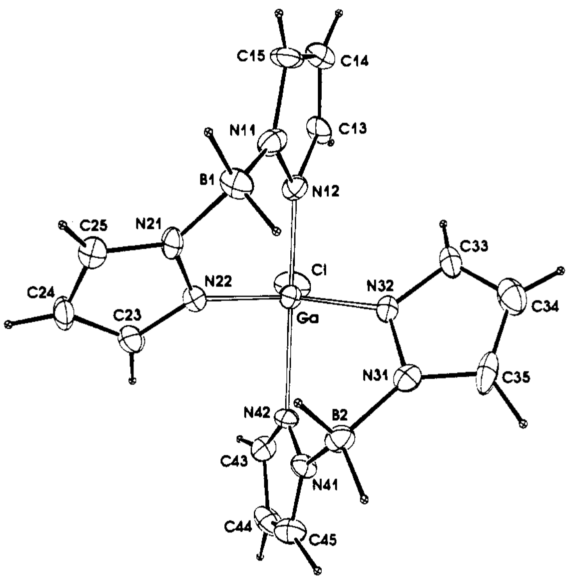

Figure 1. ORTEP diagram of $[H_2B(pz)_2]_2GaCl$ (**1**). Selected interatomic distances (Å) and angles (deg) are as follows: Ga–Cl = 2.195 (1), Ga–N12 = 2.180 (8), Ga–N22 = 1.994 (8), Ga–N32 = 1.923 (9), Ga–N42 = 1.94 (1); Cl–Ga–N12 = 90.8 (2), Cl–Ga–N22 = 121.5 (3), Cl–Ga–N32 = 121.0 (3), Cl–Ga–N42 = 91.5 (2), N12–Ga–N22 = 88.5 (3), N12–Ga–N32 = 89.8 (4), N12–Ga–N42 = 177.6 (2), N22–Ga–N32 = 117.6 (1), N22–Ga–N42 = 89.9 (3), N32–Ga–N42 = 89.6 (4).

Complex **1** is prepared from freshly sublimed $GaCl_3$ as shown in eq 1.[7] This complex is stable as a solid in air but slowly decomposes in solution. **1** is thermally stable at its melting point of 160 °C.

$$2K[H_2B(pz)_2] + GaCl_3 \rightarrow \underset{\mathbf{1}}{[H_2B(pz)_2]_2GaCl} + 2KCl \quad (1)$$

An ORTEP drawing of **1** is shown in Figure 1 along with selected interatomic distances and angles.[8] The structure is a nearly perfect trigonal bipyramid. Each $[H_2B(pz)_2]$ ligand occupies one axial and one equatorial position with the chlorine atom in the remaining equatorial site. The angles formed from the axial and equatorial sites range from 88.5 (3) to 91.5 (2)°, and within the equatorial plane the Cl–Ga–N angles are 121.5 (3) and 121.0 (3)°, and the N–Ga–N angle is 117.6 (1)°.

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(7) $K[H_2B(pz)_2]$ (1.06 g, 5.7 mmol) in THF (20 mL, −75 °C) was added to $GaCl_3$ (0.50 g, 2.8 mmol) in THF (10 mL, −75 °C). The solution was allowed to warm to room temperature and was stirred over a 5-h period. The solvent was evaporated under vacuum, the residue extracted with CH_2Cl_2 (50 mL), and the solution filtered to remove any insolubles. CH_2Cl_2 was removed under vacuum to yield **1** as a white solid (0.95 g, 2.4 mmol, 86%). The analytical sample was recrystallized from a CH_2Cl_2/hexane mixture; mp 159–160 °C. ^1H NMR (δ, $CDCl_3$): 7.74, 7.61 (4, 4; d, d; J = 2.0, 1.8 Hz; 3-H, 5-H (pz)); 6.26 (4; t; J = 2.2 Hz; 4-H (pz)); 3.4 (broad, BH_2). IR spectrum (benzene, cm^{-1}): 2458 (sh), 2434, 2422 (BH). The mass spectrum shows $M^+ - Cl + pz$ and $M^+ - H_2Bpz$ clusters at m/e 429 and 317. Anal. Calcd for $C_{12}H_{16}B_2ClGaN_8$: C, 36.11; H, 4.05. Found: C, 36.13; H, 3.98.

(8) Prismatic, colorless crystals of **1** were grown at −28 °C from $C_2H_2Cl_2$/hexane. They belong to the monoclinic crystal system: space group Cc, a = 9.542 (1) Å, b = 12.022 (2) Å, c = 15.317 (2) Å, β = 98.67 (2)°, V = 1737 Å^3, Z = 4. The structure was solved by the heavy-atom method and refined with use of SDP (Enraf-Nonius Structure Determination Package by B. A. Frenz, 1983) by full-matrix least-squares methods based on 1987 reflections that had $I > 3\sigma(I)$ to the final residuals R = 0.025 and R_w = 0.028. Hydrogen atoms were placed in calculated positions, and all non-hydrogen atoms were refined anisotropically. Data were collected at ambient temperature on a CAD-4 diffractometer using Mo Kα radiation. The strucutre can also be described in the centrosymmetric space group $C2/c$. Attempts to refine the structure in this space group led to unreasonably low temperature factors for the dihydrodipyrazolylborate ligands (nonpositive definite in the anisotropic approximation) and high temperature factors for the gallium and especially chlorine atoms.

0020-1669/89/1328-3092$01.50/0

A feature of particular interest is the arrangement of the six-membered GaN_4B rings. As is found typically[9] in dihydrobis(pyrazolyl)borate complexes, these rings are in a shallow-boat configuration with Ga–B distances of 3.22 (1) and 3.30 (1) Å. In a number of formally electron-deficient transition-metal complexes of this ligand, a strong agostic B–H···M interaction is observed that can be identified by ^{11}B NMR[10] and IR spectroscopy,[10,11] as well as short M–B distances in the solid-state structures.[10,12] In $[H_2B(pz)_2]_3Y$,[3a] we observed a much weaker agostic interaction, raising the possibility of a similar weak interaction in a main-group complex. Given the long Ga–B distances, no agostic interaction is present in **1**.

Complex **2** is prepared as shown in eq 2.[13] This complex is

$$3K[H_2B(pz)_2] + GaCl_3 \rightarrow \underset{\mathbf{2}}{[H_2B(pz)_2]_3Ga} + 3KCl \tag{2}$$

stable in air even in solution and does not react with water. From the equivalence of the pyrazolyl rings in the solution NMR spectrum, this molecule appears to be six-coordinate. We are studying the derivative chemistry of this group of complexes.

Acknowledgment is made to the NIH Biomedical Research Support Grant Award (Grant SO7 RR07160) for support of this research. The NSF (Grant CHE-8411172) and NIH (Grant RR-02425) have supplied funds to support NMR equipment, and the NIH (Grant RR-02849) has supplied funds to support mass spectrometry equipment.

Supplementary Material Available: A table of crystallographic data and full tables of bond distances and angles, positional parameters, and thermal parameters (10 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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(13) $K[H_2B(pz)_2]$ (1.58 g, 8.5 mmol) in THF (20 mL, −75 °C) was added to $GaCl_3$ (0.50 g, 2.8 mmol) in THF (10 mL, −75 °C). The solution was allowed to warm to room temperature and was stirred over a 5-h period. The solvent was evaporated under vacuum, the residue extracted with CH_2Cl_2 (50 mL), and the solution filtered to remove any insolubles. CH_2Cl_2 was removed under vacuum to yield **2** as a white solid (1.41 g, 2.7 mmol, 96%). This was recrystallized from a CH_2Cl_2/hexane mixture; mp 155–157 °C. ^1H NMR (δ, $CDCl_3$): 7.65, 6.75 (6, 6; dd, dd; J = 2.1, 0.7; 2.3, 0.7 Hz; 3-H, 5-H (pz)); 6.10 (6; t; J = 2.3 Hz, 4-H (pz)); 3.5 (broad, BH_2). IR spectrum (benzene, cm^{-1}): 2450 (sh), 2424, 2360 (BH). The high-resolution mass spectrum shows a cluster for $M^+ - H$: calcd for $C_{18}H_{23}N_{12}{}^{11}B_3{}^{69}Ga$, *m/e* 509.1704; found, *m/e* 509.1704. Anal. Calcd for $C_{18}H_{23}N_{12}B_3Ga$: C, 42.34; H, 4.76. Found: C, 42.24; H, 5.18.

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Received February 8, 1989

Reversible CO Binding to Iron(III) Isobacteriochlorins

We[2] and others[3-5] have been studying the structural, spectroscopic, magnetic, and chemical properties of iron(II,III) complexes of chlorin and isobacteriochlorin (iBC) macrocycles as models for the heme prosthetic groups in green heme and siroheme proteins and enzymes.[2a,6] The most dramatic *chemical* differences between iron porphyrins and hydroporphyrins reported to date are electrochemical: reduction potentials for iBC π-oxidation are 250–300 mV less positive than for chlorin π-oxidation and 500–600 mV less positive than for porphyrin π-oxidation.[2b,3,4e,5e,f,7]

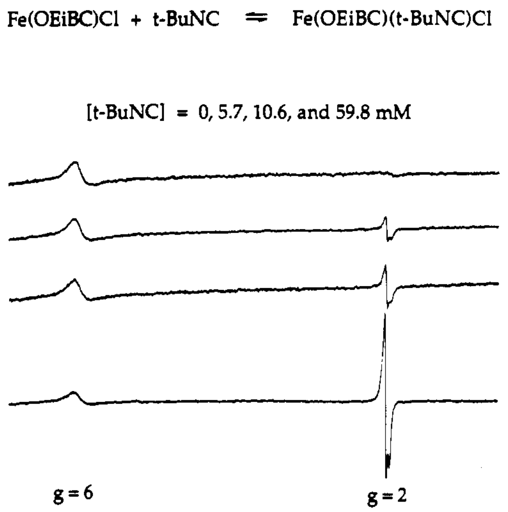

Figure 1. X-Band EPR spectra of 90 K toluene glasses of Fe(OEiBC)Cl (0.1 mM) containing varying amounts of *t*-BuNC. Experimental parameters were as follows: microwave power, 20 mW; modulation frequency, 100 kHz; modulation amplitude, 19.9 G. The parameters are a compromise between the optimal settings for high-spin iron(III) and those for a $S = {}^1/_2$ organic radical, and therefore some saturation and distortion of the g = 2.00 signal has occurred.

Herein we report that five-coordinate *iron(III)* Fe(OEiBC)X complexes exhibit a measurable affinity for CO, *t*-BuNC, and PF_3 (X^- = Cl^-, Br^-, NCS^-, PhS^-).[8] As far as coordination equilibria

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