edged.

Department of Chemistry | **C. Benelli**
University of Florence | **A. Dei***
Florence, Italy | **D. Gatteschi**

Institut fur Anorganische Chemie | **H. U. Güdel**
Universitat Bern
Bern, Switzerland

Department of Chemistry | **L. Pardi**
University of Florence
Florence, Italy

Received February 28, 1989

Photochemical Grafting of Triiron Dodecacarbonyl to Silica. Formation of a Surface-Bound Anionic Trinuclear Cluster

Supported metal carbonyl clusters have attracted much attention in the preparation of catalysts containing highly dispersed metals on inorganic oxide supports.[1-4] Several transition-metal carbonyl clusters attached to oxide supports have been produced by thermally induced reactions between the cluster and surface hydroxy groups.[5-16] It has been shown that the interaction between $Fe_3(CO)_{12}$ and the hydroxy groups of silica is weak and no grafted cluster can be formed by thermal activation.[15-17] Thermal treatment between 323 and 373 K in vacuo results in complete decomposition of the physisorbed $Fe_3(CO)_{12}$.[18] Reported here is the first case of anchoring an intact triiron carbonyl cluster to the surface of silica by photochemical grafting to form the same type of anionic cluster species, $[HFe_3(CO)_{11}]^-$, resulting from a thermal reaction on alumina.[14,15]

The adsorption of $Fe_3(CO)_{12}$ onto silica was performed by dry mixing the cluster (typically 2 wt % iron metal loading) with silica (previously calcined at 450 °C under 10^{-4} Torr vacuum for 12 h) followed by thermal aging under vacuum at 313 K for 2 h.[16] Diffuse-reflectance UV-visible and FTIR analysis of the iron cluster supported on silica confirmed that the cluster is simply physisorbed.[16]

$Fe_3(CO)_{12}$ physisorbed on silica was irradiated at room temperature under an argon atmosphere with use of a Xe lamp (Ushio UXL-500D, 500 W) through a water filter (to remove infrared irradiation) and either a Toshiba O55 cutoff filter (passes light greater than 500 nm) or Toshiba L42 + C40A + B46 filter combination (passes light between 400 and 500 nm). Irradiation in this manner converted the initially dark green material to a rose color. During irradiation the UV–visible absorption spectrum was monitored. As shown in Figure 1, the absorptions at 610 and 450 nm (corresponding to $\sigma^{*\prime} \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$, respectively[19]) disappeared while an absorption at 540 nm grew in. In a similar manner the FTIR spectrum was found to change from that for the physisorbed cluster on silica to one with two strong bands at 2025 and 2002 cm^{-1}. The resulting red cluster could not be extracted from the silica surface by pure dichloromethane. However, when the rose-colored silica was stirred with a dichloromethane solution containing tetraethylammonium chloride, the silica was decolorized and the solution became red. The UV–visible absorption spectrum of the red dichloromethane solution showed an absorption maximum at 543 nm. The FTIR spectrum of the solution showed absorptions at 2002 (s), 1971 (s), and 1712 cm^{-1} (m).

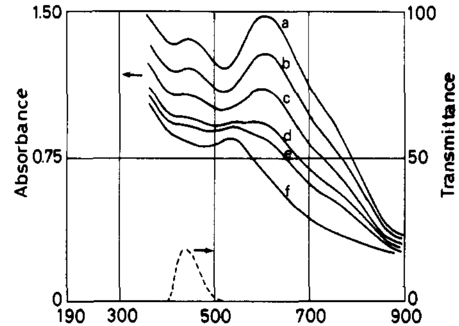

Figure 1. Light-induced UV–visible diffuse-reflectance spectral changes of $Fe_3(CO)_{12}$ physisorbed on SiO_2 versus time (hours): (a) 0; (b) 4; (c) 20; (d) 55; (e) 88; (f) 160. The transmittance curve of the filter combination used (Toshiba L42 + C40A + B46) is also shown (---).

Both the UV–visible and FTIR absorption bands for the photochemically produced cluster on silica are the same as those for $[HFe_3(CO)_{11}]^-$ bound to the surface of alumina.[15] In addition, the UV–visible and FTIR absorption bands for the extracted red cluster are the same as those for $[HFe_3(CO)_{11}]^-[Et_4N]^+$ in solution.[15] From these results, the species formed photochemically on the surface of silica can be assigned as the hydrido cluster $[HFe_3(CO)_{11}]^-$.

The efficiency for the photochemical generation of $[HFe_3(CO)_{11}]^-$ on silica can be compared to that for the thermal reaction on alumina by comparing the UV–visible absorption intensities at 540 nm (same metal loadings). These were found to be approximately the same for a variety of irradiations in which the irradiating wavelengths were greater than 350 nm. This indicates that the photochemical process on silica is as efficient as the thermal process on alumina.

Three possibilities can be envisaged for the formation of the hydrido cluster $[HFe_3(CO)_{11}]^-$ on the surface of silica. One is nucleophilic attack of a surface hydroxy group onto the iron carbonyl cluster:

$$\mathrm{Fe_3(CO)_{12} + HO{-}Si{\equiv} \rightarrow [HFe_3(CO)_{11}]^-[Si{\equiv}]^+ + CO_2} \tag{i}$$

The second is nucleophilic attack by water present on the silica surface:

$$\mathrm{Fe_3(CO)_{12} + 2H_2O \rightarrow [HFe_3(CO)_{11}]^-[H_3O]^+ + CO_2} \tag{ii}$$

The third is a reaction with impurities such as aluminum in the silica, leading to a reaction similar to that on alumina:[14,15]

$$\mathrm{Fe_3(CO)_{12} + HO{-}Al{\equiv} \rightarrow [HFe_3(CO)_{11}]^-[Al{\equiv}]^+ + CO_2} \tag{iii}$$

---

(1) Brenner, A. *J. Chem. Soc., Chem. Commun.* **1979**, 251.
(2) Ichikawa, M. *J. Chem. Soc., Chem. Commun.* **1976**, 26–27.
(3) Anderson, J. R.; Elmes, P. S.; Howe, R. F.; Mainwaring, D. E. *J. Catal.* **1977**, *50*, 508–518.
(4) Anderson, J. R.; Mainwaring, D. E. *J. Catal.* **1974**, *35*, 162–165.
(5) Besson, B.; Moraweck, B.; Smith, A. K.; Basset, J. M.; Psaro, R.; Fusi, A.; Ugo, R. *J. Chem. Soc., Chem. Commun.* **1980**, 569–571.
(6) Smith, A. K.; Besson, B.; Basset, J. M.; Psaro, R.; Fusi, A.; Ugo, R. *J. Organomet. Chem.* **1980**, *192*, C31–C34.
(7) Watson, P.; Schrader, C. L. *J. Mol. Catal.* **1980**, *9*, 129–138.
(8) Deeba, M.; Gates, B. C. *J. Catal.* **1981**, *67*, 303–307.
(9) Theolier, A.; Choplin, A.; Dornelas, L.; Basset, J. M.; Zanderighi, G.; Sourisseau, C. *Polyhedron* **1983**, *2*, 119.
(10) Dieter, T.; Gafney, H. D. *Inorg. Chem.* **1988**, *27*, 1730–1736.
(11) Scott, J. P.; Budge, J. R.; Rheingold, A. L.; Gates, B. C. *J. Am. Chem. Soc.* **1987**, *109*, 7736–7744.
(12) Choplin, A.; Huang, L.; Basset, J. M.; Mathieu, R.; Siriwardane, U.; Shore, S. G. *Organometallics* **1986**, *5*, 1547–1551.
(13) Budge, J. R.; Luecke, B. F.; Gates, B. C.; Toran, J. *J. Catal.* **1985**, *91*, 272–282.
(14) Hugues, F.; Smith, A. K.; Taarit, Y. B.; Basset, J. M.; Commereuc, D.; Chauvin, Y. *J. Chem. Soc., Chem. Commun.* **1980**, 68–71.
(15) Hugues, F.; Basset, J. M.; Taarit, Y. B.; Choplin, A.; Primet, M.; Rojas, D.; Smith, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 7020–7024.
(16) Iwasawa, Y.; Yamada, M.; Ogasawara, S.; Sato, Y.; Kuroda, H. *Chem. Lett.* **1983**, 621–924.
(17) Rojas, D.; Bussiere, P.; Dalmon, J. A.; Choplin, A.; Basset, J. M.; Olivier, D. *Surf. Sci.* **1985**, *156*, 516.
(18) Psaro, R.; Ugo, R.; Gates, B. C.; Knözinger, H. *Metal Clusters in Catalysis*; Elsevier: Amsterdam, Oxford, New York, Tokyo, 1986; pp 427–496.
(19) Tyler, D. R.; Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1978**, *100*, 7888–7893.

0020-1669/89/1328-3091$01.50/0

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.

Kuroda Solid Surface Project
Tsukuba Research Consortium
Research Development Corporation of Japan
5-9-9 Tokodai, Tsukuba 300-26, Japan

Sadaaki Yamamoto*
Robert M. Lewis
Hajime Hotta
Haruo Kuroda

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]

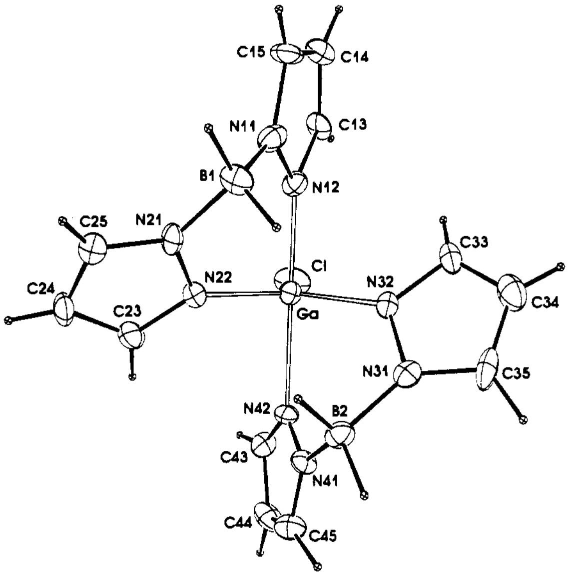

Figure 1. ORTEP diagram of $[H_2B(pz)_2]_2GaCl$ (**1**). Selected interatomic distances (Å) and angles (deg) are as follows: Ga–Cl = 2.195 (1), Ga–N12 = 2.180 (8), Ga–N22 = 1.994 (8), Ga–N32 = 1.923 (9), Ga–N42 = 1.94 (1); Cl–Ga–N12 = 90.8 (2), Cl–Ga–N22 = 121.5 (3), Cl–Ga–N32 = 121.0 (3), Cl–Ga–N42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

---

(1) (a) Moerlein, S. M.; Welch, M. J.; Raymond, K. N. *J. Nucl. Med.* **1982**, *23*, 501-506. (b) Taliaferro, C. H.; Martell, A. E. *Inorg. Chim. Acta* **1984**, *85*, 9-15. (c) Green, M. A.; Welch, M. J.; Mathias, C. J.; Fox, K. A. A.; Knabb, R. M.; Huffman, J. C. *J. Nucl. Med.* **1985**, *26*, 170-180.

(2) Keyes, R. W. *Science (Washington, D.C.)* **1985**, *230*, 138.

(3) (a) Reger, D. L.; Lindeman, J. A.; Lebioda, L. *Inorg. Chem.* **1988**, *27*, 1890. (b) Reger, D. L.; Lindeman, J. A.; Lebioda, L. *Inorg. Chem.* **1988**, *27*, 3923.

(4) Reger, D. L.; Knox, S. J.; Lindeman, J. A.; Lebioda, L. Submitted for publication in *Inorg. Chem.*

(5) Cowley and co-workers have recently reported the preparation and structure of a cationic complex, $\{[HB(3,5\text{-}Me_2pz)_3]_2Ga\}[GaCl_4]$, of the bulky methyl-substituted tris(pyrazolyl)borate ligand: Cowley, A. H.; Carrano, C. J.; Geerts, R. L.; Jones, R. A.; Nunn, C. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 277.

(6) (a) Tayler, M. T. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1987; Vol. 3, p 105. (b) McPhail, A. T.; Miller, R. W.; Gross, P. M.; Pitt, C. G.; Gupta, G.; Srivastava, S. C. *J. Chem. Soc., Dalton Trans.* **1976**, 1657. (c) Pellerito, L.; Cefalu, R.; Ruisi, G.; Lo Giudice, M. T. *Z. Anorg. Allg. Chem.* **1981**, *481*, 218.

(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, $\beta = 98.67$ (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