ordination and resides 0.34 Å below the B(2)–B(5) basal plane. The Fe-B(2,3) distances are significantly shorter (1.97 Å) than the analogous distances in $[N(n\text{-}C_4H_9)_4]^+[2\text{-}Fe(CO)_3B_5H_9]^-$ (2.08 and 2.13 Å),[5] $Cu[P(C_6H_5)_3]_2B_5H_8Fe(CO)_3$ (2.075 and 2.115 Å),[5c] and $[\mu\text{-}(Fe(CO)_4B_7H_{12}]^-$ (2.22 and 2.20 Å)[15] due to the absence of Fe–H–B bonding in complex **2**. The structure of **2** represents the first crystallographically characterized neutral *nido*-ferrahexaborane cluster, although the structure of the directly related species $[N(n\text{-}C_4H_9)_4]^+[2\text{-}Fe(CO)_3B_5H_9]^-$ has been determined.[5]

The high-yield preparation of **2** by the irradiation of the σ-metalated complex **1** is in sharp contrast to the observed very low yield (1–3%) of the only product isolated from the irradiation of the related decaborane(14) cluster $[6\text{-}Fe(\eta^5\text{-}C_5H_5)(CO)_2B_{10}H_{13}]$ (**5**).[3a] The product obtained from this reaction, $6\text{-}Fe(\eta^5\text{-}C_5H_5)(CB_{10}H_{13}L)$ (where L = $O(CH_2CH_3)_2$ or THF), was found to result from the photolytic insertion of the carbonyl carbon into a borane cluster framework. No analogue of this type of carbonyl-inserted complex was observed in the photochemistry of complex **1**.

The clean, high-yield photochemical synthesis of complex **2** provides an excellent route to this complex in relatively large quantities. The photochemistry of metal borane clusters is expected to allow for the observation of new structural types and reaction pathways. Insights into these processes are critical to the understanding of the reaction chemistry of other organometallic cluster species. The further study of the organometallic reactions and photochemistry of similar classes of organometallic cluster compounds is currently in progress in our laboratory.

Acknowledgment. We wish to thank the National Science Foundation (Grant No. MSS-89-09793), the National Science Foundation Research Experiences for Undergraduates Site Award (Grant No. CHE-8900471), the General Electric Co., the Wright-Patterson Laboratory (Award No. F33615-90-C-5291), and the Industrial Affiliates Program of the Center for Molecular Electronics for support of this work. We also wish to thank Mr. Robert Ostrander for assistance with the X-ray crystallographic determination of complex **2**.

Supplementary Material Available: Tables of all atom coordinates including all hydrogen atoms, anisotropic thermal parameters, and bond distances and angles for non-hydrogen atoms for **1** (5 pages); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

---

(14) Gress, M. E.; Jacobson, R. A. *Inorg. Chem.* **1973**, *12*, 1746.

(15) Mangion, M.; Clayton, W. R.; Hollander, O.; Shore, S. G. *J. Chem. Soc. Chem. Commun.* **1976**, 604.

(16) (a) TEXSAN—Texray Structure Analysis Package, Molecular Structure Corp., 1985. (b) Motherwell, S.; Clegg, W. PLUTO. Program for plotting molecular and crystal structures. University of Cambridge, England, 1978.

(17) National Science Foundation Research Experiences for Undergraduates Participant 1990–1992.

Department of Chemistry and Center for
Molecular Electronics
Center for Science and Technology
Syracuse University
Syracuse, New York 13244-4100

Bruce H. Goodreau
Lianna R. Orlando[17]
James T. Spencer*

Received August 8, 1991

Emission Spectroscopic Properties of 1,2-Bis(dicyclohexylphosphino)ethane Complexes of Gold(I)

Electronic emission has been reported for a few gold(I) dimers in solution at room temperature.[1-4] Formulations of the electronic structures of the emissive excited states of these complexes have emphasized the importance of Au–Au interactions (by analogy to d^8–d^8 Pt_2[5-7] and d^{10}–d^{10} Pt_2[8] species). In the course of our work on the coordination chemistry of the ligand 1,2-bis(dicyclohexylphosphino)ethane (dcpe), we have prepared and characterized an intensely emissive gold(I) complex containing *isolated* AuP_3 units. Our results suggest that excited-state Au–L bonding is a key factor in Au^I photophysics.

Reaction of dcpe with ClAu(tetrahydrothiophene) in acetonitrile solution yields three principal products: a 1:1 (dcpe:Au) molar ratio gives $Au_2(dcpe)_2^{2+}$; a 1.5:1 (dcpe:Au) molar ratio produces $Au_2(dcpe)_3^{2+}$; and, with a large excess of dcpe, $Au(dcpe)_2^+$ is formed.[9,10] Crystal structures of $[Au_2(dcpe)_2](PF_6)_2$ (**1**) and $[Au_2(dcpe)_3][Au(CN)_2]_2$ (**2**) have been determined: **1** features

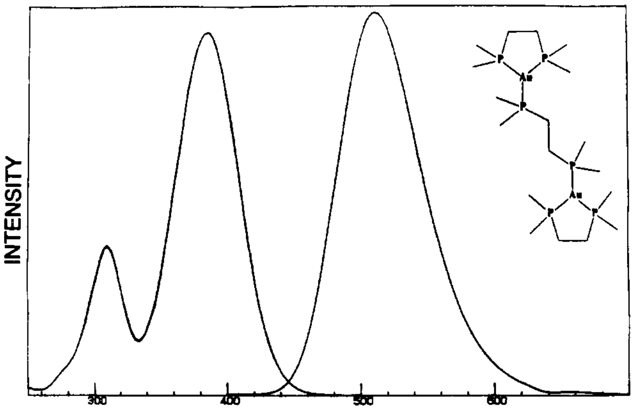

Figure 1. Excitation (left) and emission (right) spectra of $[Au_2(dcpe)_3](PF_6)_2$ (**3**) in acetonitrile at room temperature.

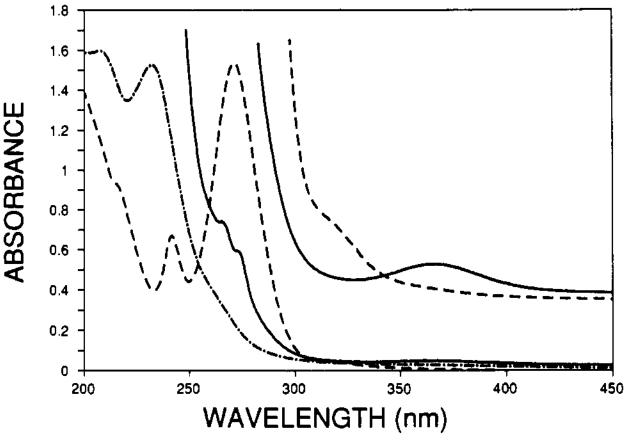

Figure 2. Absorption spectra in acetonitrile at room temperature: 5.02×10^{-4} and 5.02×10^{-5} M $[Au_2(dcpe)_3](PF_6)_2$ (—) (**3**), 7.32×10^{-4} and 7.32×10^{-5} M $[Au_2(dcpe)_2](PF_6)_2$ (--) (**1**), 4.18×10^{-5} M $[Au(dcpe)_2]PF_6$ (-··) (**4**).

---

(1) King, C.; Wang, J. C.; Khan, Md. N. I.; Fackler, J. P., Jr. *Inorg. Chem.* **1989**, *28*, 2145.

(2) (a) Che, C. M.; Wong, W. T.; Lai, T. F.; Kwong, H. L. *J. Chem. Soc., Chem. Commun.* **1989**, 243. (b) Che, C. M.; Kwong, H. L.; Yam, V. W. W.; Cho, K. C. *J. Chem. Soc., Chem. Commun.* **1989**, 885.

(3) (a) Che, C. M.; Kwong, H. L.; Poon, C. K.; Yam, V. W. W. *J. Chem. Soc., Dalton Trans.* **1990**, 3215. (b) Yam, V. W. W.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1990**, 3747.

(4) Miskowski, V. M. Unpublished results.

(5) Roundhill, D. M.; Gray, H. B.; Che, C. M. *Acc. Chem. Res.* **1989**, *22*, 55.

(6) Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4571.

(7) Fordyce, W. A.; Brummer, J. G.; Crosby, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 7061.

(8) Harvey, P. D.; Gray, H. B. *J. Am. Chem. Soc.* **1988**, *110*, 2145.

(9) ^{31}P NMR data in acetonitrile-d_3 referenced to neat H_3PO_4: $[Au_2(dcpe)_2](PF_6)_2$ (**1**), 52.4 ppm (s); $[Au_2(dcpe)_3](PF_6)_2$ (**3**), 64.20 ppm (d), 57.49 ppm (t); $[Au(dcpe)_2]PF_6$ (**4**), 29.5 ppm (s). The ^{31}P spectrum of **3** was unchanged over a period of 4 days.

(10) Only $Au_2(L\text{-}L)_2$ and $Au(L\text{-}L)_2$ products are obtained with bis(diphenylphosphino)ethane. Berners-Price, S. J.; Sadler, P. J. *Inorg. Chem.* **1986**, *25*, 3822.

0020-1669/92/1331-1733$03.00/0

binucleated, linear AuP_2 units; the ethylene groups in the dcpe bridges are twisted to give a Au–Au separation (2.936 Å) indicative of a metal–metal bonding interaction.[11] Each Au atom in **2** is bound to one chelating dcpe and one bridging dcpe, and each AuP_3 unit has a distorted trigonal planar geometry (Figure 1).[12] The **2** bridging unit is extended (Au–Au = 7.0501 Å); clearly, no Au–Au interaction is present.

The electronic absorption spectra of **1**, $[Au_2(dcpe)_3](PF_6)_2$ (**3**), and $[Au(dcpe)_2]PF_6$ (**4**) in acetonitrile solution are shown in Figure 2: **1** exhibits an intense band at 271 nm (ϵ = 10 000 M^{-1} cm^{-1}) and a weaker absorption at 320 nm (shoulder); **3** has a relatively weak absorption at 370 nm (ϵ = 300 M^{-1} cm^{-1} per AuP_3 unit); and the lowest energy absorption band in the spectrum of **4** is at 240 nm (ϵ = 35 000 M^{-1} cm^{-1}). Emission was observed for **1** as a solid at 77 K (λ_{max} = 489 nm), but not at room temperature; **3** emits both as a solid (λ_{max} = 501 nm) and in acetonitrile solution at room temperature (λ_{max} = 508 nm, τ = 21.1 (5) μs, ϕ = 0.80 (5)); **4** is nonemissive (solution or solid). The excitation spectrum of **3** confirms that absorption at 370 nm leads to emission (Figure 1).

The 370-nm absorption band in the spectrum of **3** is attributable to a $^1A_1 \rightarrow E'(^3E'')$ $[d\sigma^*(d_{xy}, d_{x^2-y^2}) \rightarrow p_z]$ transition (for D_{3h} AuP_3).[13] Spin–orbit coupling splits the $^3E''$ state into A_1', A_2', E', and E'' levels, and the $^1A_1 \rightarrow E'$ transition is allowed. In the linear AuP_2 structure of **1**, the d_{xy}, $d_{x^2-y^2}$ level is no longer destabilized by σ(AuP) interactions, and the transitions from this level to p_z are expected to occur at much higher energy. The 271- and 320-nm bands in **1**, therefore, are logically due to transitions to $d\sigma^*(d_{z^2})p\sigma(p_z)$ singlet[1] and triplet states. Owing to its approximately tetrahedral AuP_4 structure, the valence p obitals of **4** are strongly σ antibonding. Accordingly, the lowest intense absorption band in **4** appears at a relatively high energy (240 nm).

Compound **3** is the first example of a gold complex containing an isolated Au^I unit that emits in solution at room temperature. This emission appears to be a property of the sterically protected AuP_3 monomeric unit.[12] Although there are a few reports of other three-coordinate gold(I) complexes,[14,15] most of the compounds are only stable as solids. In solution, facile ligand dissociation occurs to give the more stable linear $Au_2(L-L)_2$ complexes;[16] however, the trigonal planar geometry of each AuP_3 unit in **3** retains its integrity in solution.[9]

The large Stokes shift between $^1A_1 \rightarrow E'(^3E'')$ absorption (370 nm) and $^3E''$ emission (508 nm) indicates that a severe distortion of the AuP_3 structure occurs in the excited state. Depopulation of $d\sigma^*(d_{xy}, d_{x^2-y^2})$ should strengthen the Au–P bonds, thereby leading to a substantial contraction of the AuP_3 unit. Our results clearly show that long-lived Au^I excited states can be generated efficiently by irradiation of sterically protected Au^I monomeric units in solution. The oxidation–reduction chemistry of these excited states should be a rich area for exploration.

Acknowledgment. We thank Vinny Miskowski for several helpful discussions. T.M.M. acknowledges a National Science Foundation graduate fellowship and a fellowship from the Department of Education (Graduate Assistance in Areas of National Need). This work was supported by NSF Grant CHE8922067.

---

(11) Schaefer, W. P.; Marsh, R. E.; McCleskey, T. M.; Gray, H. B. Submitted for publication.

(12) Henling, L. M.; Flanagan, K. A.; McCleskey, T. M.; Gray, H. B. Manuscript in preparation.

(13) Jaw, H. R. C.; Savas, M. S.; Mason, W. R. *Inorg. Chem.* **1989**, *28*, 4366.

(14) Jones, G. C. H.; Jones, P. G.; Maddock, A. G.; Mays, M. J.; Vergnano, P. A.; Williams, A. F. *J. Chem. Soc., Dalton Trans.* **1977**, 1440.

(15) Usón, R.; Laguna, A.; Vicente, J.; Garcia, J.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1981**, 655.

(16) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 4114.

(17) Contribution No. 8536.

Arthur Amos Noyes Laboratory[17]
California Institute of Technology
Pasadena, California 91125

T. Mark McCleskey
Harry B. Gray*

Received January 21, 1992

Articles

Contribution from the Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853-1301, and Institut für Anorganische Chemie, Universität Hannover, Callinstrasse 9, W-3000 Hannover 1, Federal Republic of Germany

Distortions in the Structure of Calcium Carbide: A Theoretical Investigation

Jeffrey R. Long,[†,‡] Roald Hoffmann,*[,‡] and H.-Jürgen Meyer[§]

Received September 20, 1991

Recent ^{13}C NMR studies claim to have uncovered a flaw in the structure of CaC_2 as previously determined by powder neutron diffraction. It has been suggested that the apparent discrepancy between the ^{13}C NMR spectra and this structure is due to statistical disorder in the orientation of the C_2 dimer. Here, alternative CaC_2 structures in which the dicarbide unit has reoriented are explored by means of tight-binding extended Hückel band calculations. These calculations show the preferred orientation to be parallel to the *c*-axis, as found in the original structural refinements. However, they also reveal an extremely low-energy barrier for distortions in which the C_2 dimer rotates into a face of its octahedral Ca environment, and a somewhat higher barrier for distortions into an edge. The orbital interactions associated with the former distortion are examined in detail. Finally, a dicarbide-pairing distortion is considered and a fluxional model for the structure proposed.

Introduction

The CaC_2 structure adopted by most alkaline-earth carbides has long been cited in inorganic texts as the simplest example of a saltlike dicarbide.[1] The structure (Figure 1) consists of Ca^{2+} and C_2^{2-} ions arranged in a tetragonally distorted derivative of the NaCl structure, the distortion being due to the alignment of the C_2 dimers along the *c*-axis. This structure was determined from a powder neutron diffraction study, revealing that CaC_2 crystallizes at room temperature in the body-centered tetragonal system with space group *I*4/*mmm* ($D_{4h}{}^{17}$) and unit cell parameters

---

[†] Present address: Department of Chemistry, Harvard University, Cambridge, MA 02138.

[‡] Cornell University.

[§] Universität Hannover.

(1) (a) Cotton, F. A. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980; pp 361–363. (b) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984; pp 318–322. (c) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1984; pp 947–953.