base **2i**, however, could be formed cleanly without contamination by cyclic material (cf. the preparation of **2f**).

Finally, in the parent system 13-*cis*-**2d**, presumably possessing a predominant 12-*s-trans* conformation **2'd**,[3j–l,6] the electrocyclization process is also operating, albeit to a smaller extent. The product obtained upon treatment of 13-*cis*-retinal (**2a**) with *n*-butylamine contains, besides 8% of *all-trans*-retinal Schiff base **1d**, 7% of the corresponding DHP **3d**.[7,11] Upon heating this mixture at 78 °C in C_6D_6 for 30 min, the composition of the mixture changed to a 2:5:3 ratio of 13-*cis*-**2d**, *all-trans*-**1d**, and DHP-**3d**. Further heating led to deterioration. No DHP was observed with *tert*-butylamine, only Δ^{13} isomerization of the Schiff base **2g** (initially accompanied by 7% **1g**) being observed (a mixture containing 13-*cis*-**2g** and *all-trans*-**1g** in a ratio of 3:1 was obtained after heating in C_6D_6 at 78 °C for 30 min).

Thus, in view of the extensive use of Schiff base models in studies of bacteriorhodopsin and related pigments, it is evident then that some caution must be exercised in interpreting electronic and vibrational data of 13-*cis*-retinal Schiff base systems because of possible DHP contamination. The significance if any of the formation of 1,2-dihydropyridines (DHP) or the occurrence of other pericyclic processes to the photocycle of bacteriorhodopsin or other retinal containing pigments[12] is an intriguing question.

Acknowledgment. This study was supported by NIH Grant DK-16595. We also acknowledge NATO for a Postdoctoral Fellowship to A. R. de Lera and Badische-Anilin und Soda Fabrik, Ludwigshafen, for providing starting materials utilized in this study.

Supplementary Material Available: Tables of NMR spectral data and sample preparation (4 pages). Ordering information is given on any current masthead page.

---

(11) In numerous attempts to react the parent 13-*cis*-retinal (**2a**) with the lysine surrogate *n*-butylamine, we have invariably detected DHP **3d** formation.

(12) Findlay, J. B. C.; Pappin, D. J. C. *Biochem. J.* **1986**, *238*, 625.

Photophysics of Metal Complexes of Spheroidal Carbon Shells[†]

F. D. Weiss,[‡] J. L. Elkind, S. C. O'Brien,[§] R. F. Curl, and R. E. Smalley*

Rice Quantum Institute and
Department of Chemistry, Rice University
Houston, Texas 77251

Received January 27, 1988

In the fall of 1985 initial evidence was presented for the formation of a new class of organometallic ions consisting of a single metal atom surrounded by a spheroidal cage network of pure carbon.[1] The new species were made by laser vaporization of a $LaCl_3$ impregnated graphite disc in a pulsed nozzle followed by intense laser ionization of the neutral clusters in a supersonic beam. The most prominent of these species was $C_{60}La^+$. Its exceptionally high photophysical stability led to the suggestion that the La atom had been trapped inside the closed shell of the (putatively) icosahedral carbon cage,[2] C_{60}.

To test this rather controversial[3–5] hypothesis, we have performed extensive photophysical and chemical measurements in the magnetic trap of an FT-ICR mass spectrometer. Initial results are presented here with more extensive experiments and discussion to follow.[6] The details of this cluster beam/FT-ICR apparatus have been presented previously[7] as well as several of its early applications to metal[8,9] and semiconductor[10] cluster surface chemistry. Carbon–metal cluster ions were prepared in the supersonic beam by laser-vaporization of a graphite disk impregnated with a salt of the desired metal (La, K, Cs). After injection into the ICR trap and subsequent thermalization with neon gas,[10] the only clusters observed in the 300–1500 amu mass range were the even-numbered bare carbon clusters, C_n^+, and the same clusters with a single metal atom attached, C_nM^+. Ample evidence has been found for the presence of other, more weakly bound metal–carbon clusters in these beams,[1,6] including some containing more than one metal atom (e.g., $C_nK_2^+$).[4,5] However, these weakly

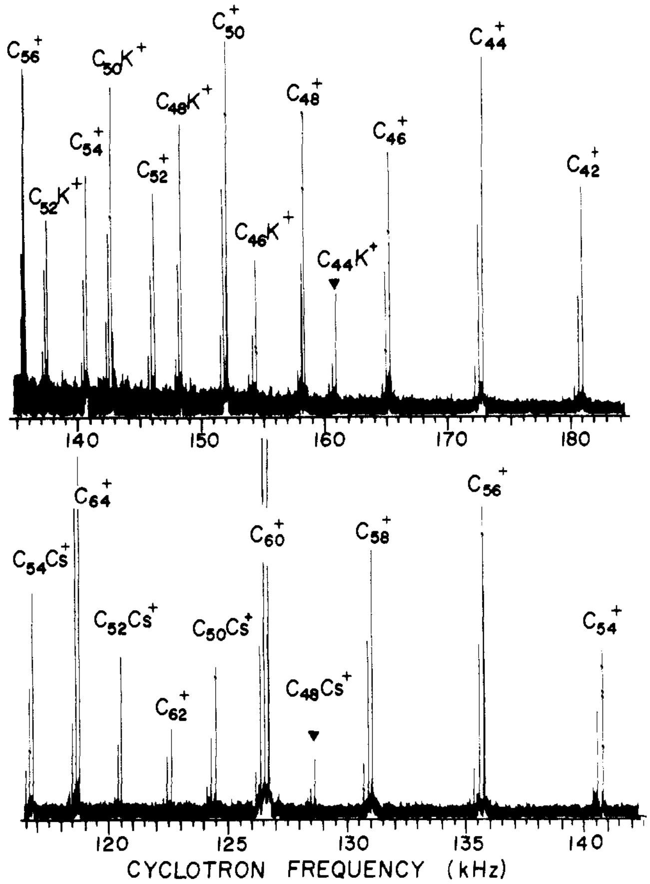

Figure 1. High-order photofragmentation pattern of $C_{60}K^+$ (top) and $C_{60}Cs^+$ (bottom) detected by FT-ICR mass spectrometry. Note the C_nK^+ fragment series breaks off at 44, while the C_nCs^+ series terminates at 48. The bare C_n^+ clusters seen in the top panel are fragments from C_{64}^+ injected into the ICR trap along with $C_{60}K^+$ providing an internal calibration, while in the bottom panel these C_n^+ fragments result from C_{72}^+ parent ions. Conditions (top panel): 200 shots at 10 Hz of ArF excimer laser radiation (193 nm) at 6 mJ cm^{-2} shot^{-1}; (bottom panel): 1600 shots ArF at 3 mJ cm^{-2} shot^{-1}. During laser excitation the pressure in the ICR trap was less than 1×10^{-8} Torr. A few noise spikes have been removed to simplify the figure.

[†] Research supported by the National Science Foundation and the Robert A. Welch Foundation.

[‡] Department of Physics, Rice University.

[§] Nettie S. Autrey Graduate Fellowship.

(1) Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Tittel, F. K.; Smalley, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 7779.

(2) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature (London)* **1985**, *318*, 162.

(3) Cox, D. M.; Trevor, D. J.; Reichmann, K. C.; Kaldor, A. *J. Am. Chem. Soc.* **1986**, *108*, 2457.

(4) Kaldor, A.; Cox, D. M.; Trevor, D. J.; Zakin, M. R. *Z. Physik D.* **1986**, *3*, 195.

(5) Cox, D. M.; Reichmann, K. C.; Kaldor, A. *J. Chem. Phys.* **1988**, *88*, 1588.

(6) O'Brien, S. C.; Weiss, F. D.; Alford, M. A.; Elkind, J. L.; Curl, R. F.; Smalley, R. E. *J. Am. Chem. Soc.*, to be submitted.

(7) Alford, J. M.; Williams, P. E.; Trevor, D. J.; Smalley, R. E. *Int. J. Mass Spectrom. Ion Processes* **1986**, *72*, 33.

(8) Alford, J. M.; Weiss, F. D.; Laaksonnen, R. T.; Smalley, R. E. *J. Phys. Chem.* **1986**, *90*, 4480.

(9) Elkind, J. L.; Weiss, F. D.; Alford, J. M.; Laaksonnen, R. T.; Smalley, R. E. *J. Chem. Phys.* **1988**, *88*, 5215.

(10) Elkind, J. L.; Alford, J. M.; Laaksonnen, R. T.; Weiss, F. D.; Smalley, R. E. *J. Chem. Phys.* **1987**, *87*, 2397.

0002-7863/88/1510-4464$01.50/0

bound species fragmented during the multiple injection/thermalization cycles used to fill the ICR cell,[9] leaving primarily just M^+ atoms as the charged fragment.

In agreement with earlier ICR measurements[11] on $C_{60}{}^+$ and the other large even-numbered clusters of carbon, we found no reaction of the bare carbon cluster ions with such species as H_2, O_2, NO, and NH_3. Similar lack of reactivity was found with the $C_{60}La^+$ complex. In agreement with previous photofragmentation studies in a tandem time-of-flight (TTOF) apparatus,[12] ArF excimer laser (6.4 eV) irradiation of these bare clusters in the ICR trap produced fragmentation only as a result of high order multiphoton processes. As expected, the $C_{60}M^+$ clusters were nearly as photoresistant as $C_{60}{}^+$ itself.

Extreme photostability of $C_{60}{}^+$ and $C_{60}M^+$ was evident from the fact that no measurable dissociation occurred for any of these trapped clusters with less than 0.5 mJ cm^{-2} $pulse^{-1}$ even after over 30-s irradiation with the ArF excimer laser at 50 Hz. Estimates of the absorption cross section of C_{60} at this wavelength[13] indicate that the average such cluster absorbs roughly 300 ArF excimer photons during this period. Cooling by infrared emission between laser shots must therefore be very facile for such clusters.

However, at sufficiently high ArF excimer laser fluence per pulse both $C_{60}{}^+$ and the $C_{60}M^+$ complexes did begin to photodissociate. The fluence dependence of this process was roughly the same for the metal-containing complexes as measured previously in the TTOF experiments for the bare clusters.[12] For both, the primary photoprocess was observed to be C_2 loss to form the next smaller even-numbered cluster. Increasing either the laser pulse energy or the length of time the clusters were irradiated in the ICR trap resulted in extensive further dissociation, producing successively smaller even-numbered clusters.

As argued in the earlier TTOF study,[12] loss of C_2 from a carbon cluster is hard to understand *unless* that cluster is a closed, edgeless carbon cage. Otherwise it should lose the much more stable C_3. The linear chain and monocyclic ring clusters in the 2–30 carbon atom range[14] are known[12,15] to lose C_3, and graphitic sheets should also lose C_3. But for closed cages a concerted C_2 loss mechanism is likely to be the lowest energy process since only then can the next smaller even product form a closed cage.[12] The observation of C_2 rather than M^+ loss from $C_{60}M^+$ suggests that the metal ion is sterically bound, since a bond between K^+ or Cs^+ and carbon should be much weaker than a carbon–carbon bond. These results are then strong evidence that $C_{60}M^+$ clusters are composed of closed carbon cages with the metal ion trapped inside.

The endpoint of the C_2 loss process for bare clusters such as $C_{60}{}^+$ is known[12] to be $C_{32}{}^+$; it appears to be the smallest viable fragment cage. In this regard the corresponding behavior for the $C_{60}M^+$ complexes presented in Figure 1 is particularly interesting. For potassium–carbon clusters the smallest stable member in the even product ions is clearly seen in Figure 1 to be $C_{44}K^+$. For cesium the smallest fragment cluster is $C_{48}Cs^+$. These results are intriguing since breaks near these cluster sizes are predicted from a simple model which places an M^+ ion in the center of a closed carbon cage, allowing for the known ionic radius of M^+, a 1.65 Å van der Waals radius for each carbon atom, and C–C bond lengths in the range of 1.4–1.5 Å. Similar experiments with $C_{60}La^+$ photodissociation show breakoff to occur at $C_{44}La^+$ (or possibly $C_{42}La^+$), again nicely in accord with expectations for a central La^+ ion completely enclosed in an inert carbon cage.

Registry No. C, 7440-44-0; K, 7440-09-7; Cs, 7440-46-2; La, 7439-91-0.

---

(11) McElvany, W. N.; Baronovski, A. P.; Watson, C. H.; Eyler, J. R. *Chem. Phys. Lett.* **1987**, *134*, 214.

(12) O'Brien, S. C.; Heath, J. R.; Curl, R. F.; Smalley, R. E. *J. Chem. Phys.* **1988**, *88*, 220.

(13) Heath, J. R.; Curl, R. F.; Smalley, R. E. *J. Chem. Phys.* **1987**, *87*, 4236.

(14) Yang, S.; Taylor, K. J.; Craycraft, M. J.; Conceicao, J.; Pettiette, C. L.; Cheshnovsky, O.; Smalley, R. E. *Chem. Phys. Lett.*, submitted for publication.

(15) Geusic, M. E.; Jarrold, M. E.; McIlrath, T. J.; Freeman, R. R.; Brown, W. L. *J. Chem. Phys.* **1986**, *86*, 1986.

Probing Metal Cluster Formation in NaY Zeolite by ^{129}Xe NMR[†]

B. F. Chmelka, R. Ryoo,[‡] S.-B. Liu,[§] L. C. de Menorval,[⊥]
C. J. Radke,[*] E. E. Petersen, and A. Pines

Department of Chemistry and Chemical Engineering
University of California
Berkeley, California 94720
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

Received February 16, 1988

The performance of zeolite-supported metal catalysts is known to depend upon preparatory treatments.[1] Homogeneous and reproducible metal dispersion can be achieved only through careful control of calcination and reduction conditions, since migration and agglomeration of cluster precursors can occur with subsequent loss of catalytic activity.[2,3] In spite of considerable research,[4-9] the transformations undergone by metal guest species during calcination and reduction have not been established, primarily due to difficulties in characterizing chemical intermediates which exist as cluster precursors. By using the ^{129}Xe NMR spectroscopy technique pioneered by Fraissard and co-workers[10-13] and applied to recent advantage by us and others,[14-16] we gain insight into the detailed chemistry of metal–zeolite catalyst preparation. We report for the first time changes in the chemical environment of NaY-supported platinum guest species by monitoring shifts in the ^{129}Xe resonance signal induced by different chemical and thermal treatments.

Pt–NaY samples containing 15 wt % platinum were prepared by introducing the tetraammine salt, $Pt(NH_3)_4{}^{2+}$, into the zeolite lattice via the ion-exchange procedure of Gallezot et al.[2] The ion-exchanged Pt–NaY samples were dried in a vacuum oven overnight at 22 °C and then calcined in purified flowing oxygen at a heating rate of 11 °C/h to maximum temperatures ranging from 200 to 400 °C. Upon reaching the upper temperature limit, the furnace was turned off, allowing the insulated reactor to cool to 40 °C over a period of many hours. After evacuation for 10 h at 22 °C, xenon gas was introduced to various equilibrium pressures, guided by separate adsorption isotherm experiments.

---

[*] To whom correspondence should be addressed.

[†] Presented, in part, at the American Institute of Chemical Engineers national meeting in New York City, November 1987.

[‡] Present address: Department of Chemistry, Korea Institute of Technology, 400 Kusong-dong, Chung-gu, Taejon-shi, Chung Chong nam-do, Korea.

[§] Present address: Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei, Taiwan, R.O.C.

[⊥] Present address: Laboratoire de Chimie Organique Physique et Cinetique Chimique Appliquées. VA 418 C.N.R.S., ENSCM, 8 rue Ecole Normale, 34075 Montpellier Cedex, France.

(1) Jacobs, P. A. *Stud. Surf. Sci. Catal.* **1982**, *12*, 71–85.

(2) Gallezot, P.; Alarcon, A.; Dalmon, J.-A.; Renouprez, A. J.; Imelik, B. *J. Catal.* **1975**, *39*, 334–349.

(3) Ribeiro, F. R.; Marcilly, C. *Geterog. Katl.* **1983**, *5*, 383–387.

(4) Jaeger, N.; Ryder, P.; Schulz-Ekloff, G. *Structure and Reactivity of Modified Zeolites*; Jacobs, P. A., et al., Eds.; Elsevier Science Publishers B.V.: Amsterdam, 1984; pp 299–311.

(5) Gallezot, P. *Catal. Rev.-Sci. Eng.* **1979**, *20(1)*, 121–154.

(6) Uytterhoeven, J. B. *Acta Phys. Chem.* **1978**, 53–69.

(7) Braun, G.; Fetting, F.; Haelsig, C. P.; Gallei, E. *Acta Phys. Chem.* **1978**, 93–97.

(8) Felthouse, T. R.; Murphy, J. A. *J. Catal.* **1986**, *98*, 411–433.

(9) Tzou, M. S.; Jiang, H. J.; Sachtler, W. M. H. *React. Kinet. Catal. Lett.* **1987**, *35(1–2)*, 207–217.

(10) Ito, T.; de Menorval, L. C.; Fraissard, J. P. *J. Chim. Phys. Phys.-Chim. Biol.* **1983**, *80*, 573–578.

(11) Ito, T.; Fraissard, J. P. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83(2)*, 451–462.

(12) de Menorval, L. C.; Ito, T.; Fraissard, J. P. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 403–410.

(13) Fraissard, J.; Ito, T.; de Menorval, L. C.; Springuel-Huet, M. A. *Stud. Surf. Sci. Catal.* **1982**, *12*, 179–189.

(14) Ryoo, R.; Liu, S.-B.; de Menorval, L. C.; Takegoshi, K.; Chmelka, B.; Trecoske, M.; Pines, A. *J. Phys. Chem.* **1987**, *91*, 6575–6577.

(15) Scharpf, E. W.; Crecely, R. W.; Gates, B. C.; Dybowski, C. *J. Phys. Chem.* **1986**, *90*, 9–11.

(16) Shoemaker, R.; Apple, T. *J. Phys. Chem.* **1987**, *91*, 4024–4029.

0002-7863/88/1510-4465$01.50/0