

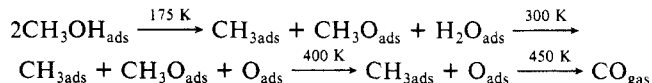
**Figure 3.** Carbon 1s XPS spectra for a 1.5 L exposure of methanol to Pd{111}: (a) 110 K; (b) heated to 225 K; (c) heated to 300 K; (d) heated to 400 K.

several ions resulting from a 2 L  $\text{CH}_3\text{OH}$  exposure are shown as the surface is heated from 110 K. This picture reveals that the intensity of the methanol-related secondary ions,  $\text{CH}_2\text{OH}^+$  and  $\text{CH}_3\text{OHH}^+$ , decrease to zero at 225 K, while the  $\text{CH}_3^+$  and the  $\text{H}_2\text{O}^+$  ions signals increase and then eventually decrease at higher temperatures. These trends, along with the corresponding XPS C 1s intensity measurements for a 2 L exposure,<sup>14</sup> suggest that as the surface is heated, approximately  $1/4$  of the  $\text{CH}_3\text{OH}$  desorbs from the surface while the remaining  $3/4$  of the  $\text{CH}_3\text{OH}$  dissociates at the C-O or O-H bond. By 300 K the only SIMS signal apparent is at  $m/e$  15. Since the  $\text{CH}_3^+$  ion yield from  $\text{CH}_3\text{O}_{\text{ads}}$  on O/Pt{111}<sup>4</sup> has been reported to be negligible, this ion almost certainly arises from a surface methyl species. We note that oxygenated species such as  $\text{O}_{\text{ads}}$  and  $\text{CH}_3\text{O}_{\text{ads}}$  are suggested by the XPS experiments but are not directly detected in the SIMS measurements. The fact that only  $\text{CH}_3^+$  ions are observed with SIMS implies that  $\text{CH}_{3\text{ads}}$  does not decompose to  $\text{CH}_{n(n=0-2)}$  during the primary ion impact and ion ejection event. By 450 K the  $\text{CH}_3^+$  SIMS signal is no longer detected in agreement with previous TPD experiments<sup>12</sup> which show a CO thermal desorption peak denoting recombination and desorption of adsorbed carbon and oxygen. At no time during the decomposition of methanol are SIMS (or XPS) signals attributable to CO formation<sup>13</sup> observed. This suggests that until 450 K, CO plays no part in the thermal decomposition mechanism of methanol adsorbed at 110 K on the Pd{111} surface.

The XPS results for this system are in agreement with the mechanism presented above with one addition. The carbon 1s region for surface temperatures above 175 K reveals the presence of a methoxide adsorbate which is approximately equal in intensity to the methyl surface species. The carbon 1s photoelectron spectra for a 1.5 L  $\text{CH}_3\text{OH}$  exposure on Pd{111} at 110 K are shown in Figure 3a. The C 1s binding energy of 286.2 eV is that of methanol on Pd{111}.<sup>14</sup> After heating the surface to 175 K the carbon 1s spectrum contains two peaks as shown in Figure 3b. The peak at 284.2 eV is consistent with a methyl species and the peak at 285.9 eV is assigned to the methoxide adsorbate. This assignment was determined by a comparison to methanol adsorbed on Pd{111} precovered with oxygen and heated to 175 K,<sup>14</sup> a procedure known to produce methoxide.<sup>8</sup> The presence of methoxide on clean Pd{111} is reasonable in our case since this species typically forms on an oxygen site, and an oxygen site is created, as  $\text{OH}_{\text{ads}}$ , every time  $\text{CH}_3\text{OH}$  dissociates at the C-O bond. It should be noted, however, that a mechanism wherein the

methoxide is first formed, and then decomposes to methyl and hydroxyl, has not yet been ruled out. At 300 K the methyl and methoxide still exist on the surface, Figure 3c, but by 400 K the methoxide species has decomposed completely to  $\text{CH}_{3\text{ads}}$  as shown in Figure 3d.

In summary, we propose the following mechanism for the thermal decomposition of methanol on the Pd{111} surface from the evidence presented herein



The SIMS and XPS evidence suggests that methyl is an unusually stable adsorbate on the Pd{111} surface. The lack of  $\text{C}^+$ ,  $\text{CH}^+$ , or  $\text{CH}_2^+$  SIMS signals at 400 K suggests that the methyl group is the only surface hydrocarbon present at this temperature. The fact that  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  are<sup>15</sup> the major hydrocarbon products from palladium catalysts is consistent with a mechanism wherein only  $\text{CH}_{3\text{ads}}$  can combine with  $\text{H}_{\text{ads}}$  or  $\text{OH}_{\text{ads}}$ .

**Acknowledgment.** We acknowledge the financial support of the National Science Foundation and the Office of Naval Research.

(15) Sudhakar, C.; Vannice, M. A. *J. Catal.* **1985**, *95*, 227.

### Stereoselective Alkylation of Chiral $\alpha$ -Nitro Keto Imine Dianions. Observations on the Role of Amide Bases

Scott E. Denmark\* and Jeffrey J. Ares

Roger Adams Laboratory, Department of Chemistry  
University of Illinois, Urbana, Illinois 61801

Received January 19, 1988

In the context of our investigations on the use of nitroalkenes as  $4\pi$  components in  $[4+2]$ -cycloadditions,<sup>1</sup> we recently developed a new, general method for the synthesis of 3-substituted 1-nitrocycloalkenes<sup>2</sup> (Scheme 1). The key step is the alkylation of an  $\alpha$ -nitro imine or  $\alpha$ -nitro hydrazone dianion. Since the reduction-elimination of the nitro imines occurs under mild conditions ( $\text{NaBH}_4/\text{CeCl}_3/\text{room temperature}$ ) to afford nitroalkenes and the amine conjugate, we felt that this process was ideally suited for auxiliary based asymmetric alkylation. We report the following in this communication: (1) the stereoselective alkylation of chiral  $\alpha$ -nitro imine dianions, (2) the influence of the amide base on stereoselectivity, and (3) the production of optically active 1-nitrocyclohexenes.

Stereoselective carbon-carbon bond formation with imines and hydrazones derived from chiral adjuvants through their metal-loenamine forms has been a fertile and rewarding area of asymmetric synthesis.<sup>3</sup> The importance of coordinating appendages in the auxiliary for high selectivity has been amply demonstrated.<sup>3b,c,d</sup> Thus, our efforts were first directed at the common amino ether auxiliaries.<sup>4</sup> To survey auxiliary structure we employed

(1) (a) Denmark, S. E.; Dappen, M. S.; Cramer, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 1306. (b) Denmark, S. E.; Cramer, C. J.; Sternberg, J. A. *Helv. Chim. Acta* **1986**, *69*, 1971. (c) Denmark, S. E.; Cramer, C. J.; Sternberg, J. A. *Tetrahedron Lett.* **1986**, *27*, 3693.

(2) Denmark, S. E.; Sternberg, J. A.; Lueoend, R. *J. Org. Chem.* **1988**, *53*, 1251.

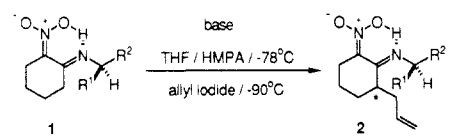
(3) (a) Enders, D. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 3, Chapter 4. (b) Bergbreiter, D. E.; Newcomb, M. *Ibid.*; Vol. 2, Chapter 9. (c) Meyers, A. I.; Williams, D. R.; Erickson, G. W.; White, S.; Druelinger, M. *J. Am. Chem. Soc.* **1981**, *103*, 3081, 3088 and references cited therein. (d) Tomioka, K.; Ando, K.; Takemasa, Y.; Koga, K. *Ibid.* **1984**, *106*, 2718. (e) Mea-Jacheet, D.; Horeau, A. *Bull. Soc. Chim. Fr.* **1968**, 4571.

(4) For reviews on the use of amino acid derived auxiliaries see: (a) Drauz, K.; Kleeman, A.; Martens, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 584. (b) Martens, J. *Top. current Chem.* **1984**, *125*, 165. (c) Mukaiyama, T.; Asami, M. *Ibid.* **1985**, *127*, 133. (d) Coppola, G. M.; Schuster, H. F. *Asymmetric Synthesis*; Wiley: New York, 1987. (e) Martens, J. *Chem. Z.* **1986**, *110*, 169.

(12) Davis, J. L.; Barteau, M. A. *Surf. Sci.* **1987**, *187*, 386.

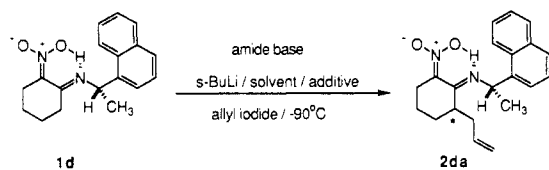
(13) Experiments determining the SIMS spectra as a function of CO exposure revealed two trends. First the  $\text{Pd}^+$  signal was enhanced several orders of magnitude with exposures of  $<0.5$  L CO. Second, a  $\text{Pd}(\text{CO})^+$  peak was always detected, even at the lowest exposures. In the methanol decomposition experiments neither phenomena was observed.

(14) Levis, R. J.; Jiang, Z.; Winograd, N., to be published.

Table I. Survey of Auxiliary Structure<sup>a</sup>


entry	compd	R <sup>1</sup>	R <sup>2</sup>	yield (1), %	base (equiv)	yield <sup>b</sup> (2), %	d.e., <sup>c</sup> %
1	<b>1a</b>	CH <sub>2</sub> OCH <sub>3</sub>	CH <sub>2</sub> Ph	59	<i>s</i> -BuLi (2)	66	30 <sup>d</sup>
2	<b>1b</b>	CH <sub>2</sub> OCH <sub>3</sub>	Ph	75	<i>s</i> -BuLi (2)	60	35
3	<b>1c</b>	CH(OCH <sub>3</sub> )Ph	CH <sub>3</sub>	54	<i>s</i> -BuLi (2)	57	30 <sup>d</sup>
4	<b>1d</b>	1-naphthyl	CH <sub>3</sub>	62	<i>s</i> -BuLi (2)	48	42
5	<b>1d</b>				LDA (1), <i>s</i> -BuLi (2)	73	87
6	<b>1b</b>				LDA (1), <i>s</i> -BuLi (2)	83	41

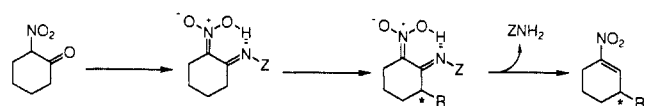
<sup>a</sup> See Supplementary Material for a general procedure. Reactions done on a 1–2 mmol scale. <sup>b</sup> Combined yield of chromatographically homogeneous diastereomers. <sup>c</sup> Determined by yields of separated, isolated products. <sup>d</sup> Determined by integration in the <sup>1</sup>H NMR spectrum of an unresolved mixture.

Table II. Optimization of Allylation of **1d** to **2da**


entry	amide base	<i>s</i> -BuLi, equiv	additive	solvent	yield <sup>a</sup> ( ), <sup>b</sup> %	d.e., <sup>c</sup> %
1	LDA	2	none	THF	34 (58)	79
2	LDA	2	HMPA	THF	73	87
3	LDA	2	DMPU	THF	74 (82)	90
4	LDA	2	DMPU	Et <sub>2</sub> O	15	48
5	LDA	2	DMPU	DME	56 (60)	81
6	LDEA	2	DMPU	THF	78 (82)	78
7	LDCA	2	DMPU	THF	59 (68)	82
8	LiTMP	2	DMPU	THF	41 (64)	83
9	LDA	1	DMPU	THF	68 (77)	83
10	LDA <sup>d</sup>	0	DMPU	THF	83	78

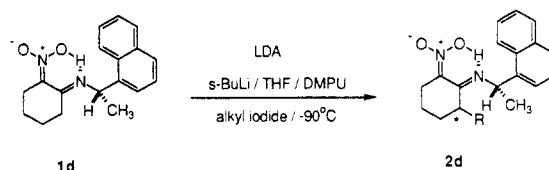
<sup>a</sup> Combined yield of chromatographically homogeneous diastereomers. <sup>b</sup> Yield based on converted starting material. <sup>c</sup> Determined by yields of separated, isolated products. <sup>d</sup> Three equivalent LDA.

Scheme I



the optimized protocol for  $\alpha$ -nitro imines developed in our earlier work:<sup>2</sup> base, *s*-BuLi; solvent, THF (5 equiv of HMPA); temperature, -78 to -90 °C; electrophile, allyl iodide. The results with various auxiliaries (Table I) were initially discouraging. Further, we were surprised to find that the highest d.e. was obtained from **1d** in which the auxiliary ((*S*)-1-(1-naphthyl)-ethylamine) bore no coordinating group! Moreover, careful examination of the procedures in nearly all published studies showed that LDA is uniformly used as base.<sup>5</sup> Thus we repeated experiments 2 and 4 (Table I) using LDA (1 equiv) and *s*-BuLi (2 equiv) (entries 5 and 6). In both cases the yield improved considerably, but *strikingly the d.e. more than doubled with 1d*.

To fully examine the influence of experimental parameters on yield and stereoselectivity in reaction of **1d** a study of additive, amide base, solvent, and stoichiometry was performed. The results are collected in Table II. The importance of coordinating additives was examined first. While it was not possible to eliminate the use of additives we were pleased to find that Seebach's DMPU<sup>6</sup> (entry 3) gave a higher yield and better d.e. than HMPA. Next, solvent was varied (entries 4 and 5) and we found no advantage in the use of Et<sub>2</sub>O or DME. To probe our model for the origin of diastereoselection in the dianion-LDA complex we next surveyed

Table III. Alkylations of **1d**


entry	R	product	yield <sup>a</sup> ( ), <sup>b</sup> %	d.e. <sup>c</sup> ( ), <sup>d</sup> %
1	CH <sub>2</sub> =CHCH <sub>2</sub>	<b>2da</b>	74 (82)	90 (80)
2	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub>	<b>2db</b>	56 (64)	85 (86)
3	CH <sub>3</sub>	<b>2dc</b>	63 (70)	59 (59)
4	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	<b>2dd</b>	59 (62)	96 (98)
5	(CH <sub>3</sub> ) <sub>2</sub> CH	<b>2de</b>	16 (34)	95 (90)

<sup>a</sup> Combined yield of chromatographically homogeneous diastereomers. <sup>b</sup> Yield based on converted starting material. <sup>c</sup> Determined by yield of separated isolated products. <sup>d</sup> Determined by HPLC analysis of purified but unresolved mixtures.

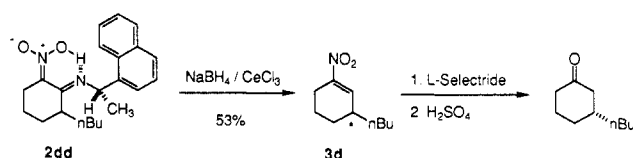
base structure (entries 6–8). While no improvement was expected for LDEA or LDCA we did anticipate a higher d.e. with LiTMP. Unfortunately, the yield dropped considerably. Using the optimum conditions but employing only 1 equiv of *s*-BuLi (entry 9), we obtained a good yield of **2da** with considerable d.e. This result is intriguing since it implies that either (1) the second pK<sub>a</sub> of **1d** is lower than *i*-Pr<sub>2</sub>NH or (2) Li<sup>+</sup> **1d**<sup>-</sup> is kinetically more acidic than *i*-Pr<sub>2</sub>NH and proton transfer is slow. In either event, *i*-Pr<sub>2</sub>NH is now serving as a ligand for the dianion. Finally, LDA alone gave high yields of **2da** but with diminished selectivity (entry 10).

The general utility of this method was explored by varying the electrophile as shown in Table III. Surprisingly neither benzyl halides nor tosylate gave good results. All of the alkylation products **2da**–**2de** were crystalline and with the exception of **2de**

(5) (a) Fraser, R. R. In *Comprehensive Carbanion Chemistry*; Buncl, E., Durst, T., Eds.; Elsevier: Amsterdam, 1984; Part B, Chapter 2. (b) Fraser, R. R.; Akiyama, F.; Banville, J. *Tetrahedron Lett.* **1979**, 3929.

(6) Mukhopadhyay, T.; Seebach, D. *Helv. Chim. Acta* **1982**, *65*, 385.

Scheme II



could be easily resolved into major and minor diastereomers. For a direct comparison of diastereoselectivities the purified, but unresolved reaction mixtures were analyzed by HPLC and the results appear in Table III.

To establish the stereochemical course of the alkylation the pure, major diastereomer of  $\alpha$ -nitro imine 2dd was reduced with  $\text{NaBH}_4/\text{CeCl}_3$  (Scheme II) to afford nitroalkene 3d ( $[\alpha]_{\text{D}}^{27} -20.7^\circ$  ( $c$  3.21,  $\text{CHCl}_3$ )) in 53% yield along with recovered (*S*)-1-(1-naphthyl)ethylamine (99.6% e.e.)<sup>7</sup> in 52% yield (distilled). The nitroalkene was converted to 3-*n*-butylcyclohexanone by the method of Kabalka<sup>8</sup> and the absolute configuration of this ketone was established to be *R* (>94% e.e.)<sup>9,10</sup> via the diastereomeric dioxolane ketals prepared from (*R,R*)-2,3-butanediol (99.4% e.e.). Thus, (*S*)-amine induced attack at the *re* face of the dianion.

It is clear that the amide base is intimately involved with the dianion and is most likely restricting the conformational possibilities of the sterogenic 1-(naphthyl)ethyl unit. The association of lithium amide bases with enolates and metaloenamines has been elegantly demonstrated by X-ray crystallography<sup>11</sup> and isotope labeling experiments.<sup>12</sup> Recent reports of enantioselective reactions of achiral lithium enolates generated by or in the presence of chiral lithium amides must also be interpreted in terms of similar aggregated structures.<sup>13,14</sup> Furthermore, Meyers has demonstrated the special role of LDA for highly selective alkylations of chiral oxazolines.<sup>15</sup> In a control experiment we repeated the alkylation of cyclohexanone using the (*S*)-phenylalaninol methyl ether imine<sup>3c</sup> with LDA and with *s*-BuLi. The enantioselectivities were identical within experimental error ( $77 \pm 0.3\%$ ), the base playing no additional role in these reactions. Thus, the  $\alpha$ -nitro imine dianions are unique in the lack of stereocontrol from a coordinating auxiliary, while being sensitive to the presence of coordinating bases.

In summary we have demonstrated the diastereoselective alkylation of chiral  $\alpha$ -nitro keto imines and their stereospecific conversion to versatile 1-nitrocyclohexenes,<sup>16</sup> in optically active form. Further investigation into the role of the amide base and use of the optically active nitroalkenes in synthesis will be the subject of future reports.

**Acknowledgment.** We gratefully acknowledge the financial support provided for this project by the National Institutes of Health (PHS RO1 GM 30938) and the Upjohn Company. This work was supported in part by the University of Illinois Mass

Spectrometry Laboratory (PHS HHS GM 27029). S.E.D. acknowledges the A. P. Sloan Foundation for a Fellowship (1985-1989).

**Supplementary Material Available:** Full characterization data for all new compounds (1a-d, 2da-2de) are provided along with a representative procedure for the alkylation of 1d (11 pages). Ordering information is given on any current masthead page.

## Doubly Charged Gas-Phase Heteronuclear Cluster Ions: Synthesis and Reaction of $\text{LaFe}^{2+}$ with Small Hydrocarbons

Yongqing Huang and Ben S. Freiser\*

Department of Chemistry, Purdue University  
West Lafayette, Indiana 47907

Received December 11, 1987

Recently there has been an intense interest in the physical and chemical properties of small transition metal containing ions in the gas phase. The species that have been studied include monatomic positive ions  $\text{M}^+$ ,<sup>1</sup> negative ions  $\text{M}^-$ ,<sup>2</sup> and homonuclear and heteronuclear cluster ions of different sizes.<sup>3</sup> Contrary to a belief that doubly charged transition metal ions might only undergo charge exchange reactions with small hydrocarbons in the gas phase, recent studies have shown that  $\text{Ti}^{2+}$  and  $\text{Nb}^{2+}$  undergo a variety of interesting reactions with these compounds.<sup>4</sup> A natural extension of this work is the study of doubly charged cluster ions. Here we report the *in situ* synthesis of  $\text{LaFe}^{2+}$  and its reactivity with a few small hydrocarbons in the gas phase. There is only one other report of a verified doubly charged metal dimer in the literature that we are aware of. Tsong recently reported observing  $\text{Mo}_2^{2+}$  using a pulsed-laser field evaporation source in conjunction with a time-of-flight mass spectrometer.<sup>5</sup> However, Jentsch and co-workers<sup>6</sup> successfully observed several doubly charged metal trimer ions and Sattler and co-workers<sup>7</sup> have observed  $\text{Pb}_n^{2+}$  for *n* above a critical number of 30.

The present experiments were performed on a prototype Nicolet FTMS-1000 instrument equipped with a 5.2 cm cubic trapping cell situated between the poles of a Varian 15 in electromagnet maintained at 0.9 T.<sup>8</sup>  $\text{La}^{2+}$  was generated by focusing the beam of a Quanta Ray Nd:YAG laser ( $1.06 \mu\text{m}$ ;  $10^8$ - $10^9 \text{ W/cm}^2$ ) onto a La target. Laser desorption forms  $\text{La}^{2+}$  in varying amounts relative to  $\text{La}^+$  depending on the focusing spot on the target, with  $\text{La}^+$  being ejected immediately after its formation to avoid any interference.<sup>9,10</sup> The isolated  $\text{La}^{2+}$  was then reacted with  $\text{Fe}(\text{CO})_5$ , which was pulsed in through a General Valve Corporation Series

(7) Pirkle, W. H.; Mahler, G.; Hyun, M. H. *J. Liquid Chromatogr.* **1986**, 9, 443.

(8) Mourad, M. S.; Varma, R. S.; Kabalka, G. W. *Synthesis* **1985**, 654.

(9) Corey, E. J.; Naef, R.; Hannon, F. J. *J. Am. Chem. Soc.* **1986**, 108, 7114. By  $^{13}\text{C}$  NMR analysis only the (*R,R,R*) ketal was visible (C(3), 43.16 ppm); none of the (*R,R,S*) epimer was detected (C(3), 44.01 ppm) with a S/N of 33.2. See also: Hiemstra, H.; Wynberg, H. *Tetrahedron Lett.* **1977**, 2183.

(10) By chiroptical methods Seebach<sup>10a</sup> has correlated 3-butyl- and 3-methylcyclohexanone (both dextrorotatory isomers are *R*), the latter of which has been chemically correlated to (*R*)-pulegone.<sup>10b</sup> (a) Langer, W.; Seebach, D. *Helv. Chim. Acta* **1979**, 62, 1710. (b) Allinger, N. L.; Reiw, C. K. *J. Org. Chem.* **1975**, 40, 1316.

(11) (a) Laube, T.; Dunitz, J. D.; Seebach, D. *Helv. Chim. Acta* **1985**, 68, 1373. (b) Williard, P. G.; Hintze, M. J. *J. Am. Chem. Soc.* **1987**, 109, 5539.

(12) Strazewski, P.; Tamm, C. *Helv. Chim. Acta* **1986**, 69, 1041.

(13) (a) Eleveld, M. B.; Hogeveen, H. *Tetrahedron Lett.* **1986**, 27, 631. (b) Hogeveen, H.; Menge, W. M. P. B. *Ibid.* **1986**, 27, 2767. (c) Regan, A. C.; Staunton, J. J. *J. Chem. Soc., Chem. Commun.* **1983**, 764. (d) Regan, A. C.; Staunton, J. *Ibid.* **1987**, 520. (e) Ando, A.; Shioiri, T. *Ibid.* **1987**, 1620.

(14) Related enantioselective enolizations have been reported. (a) Hogeveen, H.; Zwart, L. *Tetrahedron Lett.* **1982**, 23, 105. (b) Shirai, R.; Tanaka, M.; Koga, K. *J. Am. Chem. Soc.* **1986**, 108, 543. (c) Simpkins, N. S. *J. Chem. Soc., Chem. Commun.* **1986**, 88.

(15) Meyers, A. I.; Knaus, G.; Kamata, K.; Ford, M. E. *J. Am. Chem. Soc.* **1976**, 98, 567.

(16) Corey, E. J.; Estreicher, H. *J. Am. Chem. Soc.* **1978**, 100, 6294.

(1) For a recent review, see: Allison, J. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley-Interscience: New York, 1986; Vol. 34, p 628.

(2) Sallans, L.; Lane, K.; Squires, R. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, 105, 6352.

(3) Some examples are the following: Ervin, K.; Loh, S. K.; Aristov, N.; Armentrout, P. B. *J. Phys. Chem.* **1983**, 87, 3593. Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, 102, 7129. Smalley, R. E. *Laser Chem.* **1983**, 2, 167. Kaldor, A.; Rohlfing, E.; Cox, D. M. *Laser Chem.* **1983**, 2, 185. Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, 106, 4623.

(4) Tonkyn, R.; Weisshaar, J. C. *J. Am. Chem. Soc.* **1986**, 108, 7128. Buckner, S. W.; Freiser, B. S. *J. Am. Chem. Soc.* **1987**, 109, 1247.

(5) Tsong, T. T. *J. Chem. Phys.* **1986**, 85, 639.

(6) Jentsch, Th.; Drachsel, W.; Block, J. H. *Chem. Phys. Lett.* **1982**, 93, 144.

(7) Sattler, K.; Muhlbach, J.; Echt, O.; Pfau, P.; Recknagel, E. *Phys. Rev. Lett.* **1981**, 47, 160.

(8) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, 54, 96.

(9) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, 103, 4360.

(10) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, 57, 413.