Chemistry of Bis(η^6-naphthalene)chromium Ligand Exchange Reactions: Synthesis and Characterization of Poly[(μ-η^6,η^6-naphthalene)chromium]

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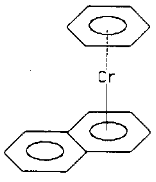
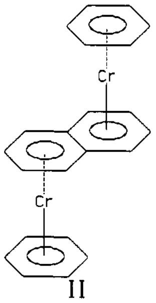
The synthesis and characterization of poly[(μ-η^6,η^6-naphthalene)chromium], an extended polymer containing repeating antarafacially bound naphthalene–chromium complex moieties, are reported. This novel polymer provides additional support for the mechanism previously proposed for ligand exchange processes of bis(η^6-naphthalene)chromium to form (μ-η^6,η^6-naphthalene)bis(η^6-arene)dichromium compounds; the structure of the polymer incorporates the structure of the proposed intermediate. The NMR spectrum of bis(η^6-naphthalene)chromium in liquid ND_3 indicated that the naphthalene moieties are constrained to the eclipsed configuration resulting in a profound change in anisotropy. Consideration of anisotropic effects suggests that poly[(μ-η^6,η^6-naphthalene)chromium] is eclipsed in configuration. The infrared spectra of bis(η^6-naphthalene)chromium, (η^6-tetralin)(η^6-naphthalene)chromium, (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium, and poly[(μ-η^6,η^6-naphthalene)chromium] are presented and utilized as a means of detecting insoluble (and thus difficult to detect) organometallic species like poly[(μ-η^6,η^6-naphthalene)chromium].

Introduction

This investigation was prompted by the observation[1] that insoluble products are formed in the arene ligand exchange reaction of bis(η^6-naphthalene)chromium that produces compounds of type I and II.

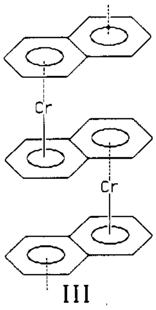


I



II

These insoluble products generally are dark colored and have been assumed to consist mainly of finely divided chromium metal. We became interested in the possibility that this insoluble product might contain poly[(μ-η^6,η^6-naphthalene)chromium] (III) since Burdett and Canadell[2] predicted that such structures might be stable and since II, which incorporates a μ-naphthalene moiety, has been synthesized and characterized in these laboratories.[1] The mechanism of formation of (μ-η^6,η^6-naphthalene)dichromium, suggested recently,[1] provides for a simple ligand exchange process of a molecule of bis(η^6-naphthalene)chromium with another molecule of the same kind which could lead to poly[(μ-η^6,η^6-naphthalene)chromium] (III) or products incorporating such structures. We present here a preliminary investigation of the insoluble product(s) formed in the exchange reactions of bis(η^6-naphthalene)chromium under a variety of experimental conditions.



III

Experimental Section

Synthesis of Bis(η^6-naphthalene)chromium. The synthesis followed that given earlier in the literature.[1,3]

Synthesis of Poly[(μ-η^6,η^6-naphthalene)chromium]. Bis(η^6-naphthalene)chromium (200 mg) was sealed in a glass ampule containing 6.5 mL of dried THF[1] and allowed to stand at ambient temperature (ca. 21 °C) for 1 week, after which time a dark precipitate had formed. The reaction products were quantitatively transferred by standard Schlenk techniques from the ampule as a slurry with dry THF into a nitrogen-filled centrifuge tube that remained sealed with a septum during the process. The insoluble product was centrifuged to the bottom of the tube and excess THF solution decanted via cannula. The insoluble products were then washed repeatedly by agitation with THF; the mixture was centrifugated and decanted until the THF wash remained colorless (indicating the absence of soluble organometallic products). The washed product was quantitatively transferred to a Schlenk flask as a THF slurry and the THF removed by vacuum distillation. Yield: 65 mg of poly[(μ-η^6,η^6-naphthalene)chromium], 56% based on bis(η^6-naphthalene)chromium taken. Elemental analysis for chromium, of different samples by multiple methods, gave an average value of 28.73% Cr (theoretical: 28.86%). Elemental analysis[4] for C and H gave average values of 66.96% C and 5.23% H (theoretical: 66.67% C and 4.48% H, based on a repeating naphthalene–chromium moiety (IV)). Thermal decomposition of 2.6 mg of another sample of poly[(μ-η^6,η^6-naphthalene)chromium] (shown to contain 28.31% chromium[4]) under vacuum liberated naphthalene which was identified by ^1H NMR and its low-resolution mass spectrum; 1.7 mg of naphthalene was collected which represents 92% of theory; uncollected and therefore unweighed naphthalene was observed in the decomposition tube. The naphthalene isolated was essentially pure; no dimerization products (binaphthalene) and insignificant hydrogenation products (tetralin-like compounds) were present in the mass spectrum of the isolated naphthalene.

Proton NMR spectra were obtained by using potassium-dried, degassed (three freeze–pump–thaw cycles), perdeuteriated ammonia (ND_3) as the solvent, with a Nicolet NT200 spectrometer.

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[1] Bush, B. F.; Lynch, V. M.; Lagowski, J. J. *Organometallics* **1987**, *6*, 1267.

[2] Burdett, J. K.; Canadell, E. *Organometallics* **1985**, *4*, 805.

[3] (a) Elschenbroich, C.; Möckel, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 870. (b) Bard, R. A.; Lagowski, J. J. Presented at the 175th National Meeting of the American Chemical Society, Anaheim, CA, March 1978; *Bis(naphthalene)chromium: Preparation and Properties.*

[4] Schwarzkopf Microanalytical Lab, 56-19 37th Avenue, Woodside, NY 11377.

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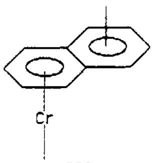

IV

The infrared spectra were obtained on a Nicolet 7000 FTIR spectrometer with a liquid-nitrogen-cooled MCT detector at a resolution of 2 cm^{-1}, using CsI pellets. The CsI pellets were formed in a screw die press, as a three-layer sandwich, two neat CsI pellets outside with a CsI/organometallic layer between them. Although these organometallic species are very air-sensitive, the combination of drying the CsI under vacuum with heat, preparing the pellets in a helium filled drybox (wherein the helium is equilibriated with Na:K (1:1) liquid alloy), transporting the pellet/die sets in tightly capped containers, and recording the spectrum under vigorous nitrogen flushing provided a reproducible technique for obtaining spectra that were stable over time.

Discussion

This investigation was undertaken to elucidate unresolved questions relating to previous observations involving compounds incorporating a μ-naphthalene moiety; our interests[1] in the (μ-η^6,η^6-naphthalene)dichromium class of polydecker sandwich compounds are also served by the work reported here. The proposed mechanism for the formation of the slipped triple-decker compounds[1] is reinforced by isolation of poly[(μ-η^6,η^6-naphthalene)chromium].

The physical properties of the substance believed to be poly[(μ-η^6,η^6-naphthalene)chromium] make it difficult to characterize. The substance is not volatile without decomposition, insoluble in organic solvents, thermally sensitive, and air-sensitive (pyrophoric). In contact with small (substoichiometric) amounts of oxygen it will disproportionate autocatalytically[1] with the evolution of free naphthalene and black chromium metal; only after longer standing with sufficient oxygen (stoichiometric) will the chromium present oxidize to the green Cr_2O_3 product. Synthesis of the compound in THF heated to 100 °C for 4 hours results in a pyrophoric mixture of poly[(μ-η^6,η^6-naphthalene)chromium] and chromium metal (50.50% chromium based on elemental analysis).[4] The X-ray powder pattern of the product did not indicate the presence of chromium metal or oxides thereof, forcing us to conclude that the excess metal implied by the elemental analysis exists in an amorphous state. Room-temperature synthesis of poly[(μ-η^6,η^6-naphthalene)chromium] does not seem to incur disproportionative decomposition and the formation of chromium metal as indicated by our metal analysis.

The proton NMR spectra of bis(η^6-naphthalene)chromium, (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium and poly[(μ-η^6,η^6-naphthalene)chromium] (Table I) in ND_3 was undertaken to provide a set of compounds for empirical comparison, in anticipation of solvent effects. On the basis of the spectrum of (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium, poly[(μ-η^6,η^6-naphthalene)]chromium would be an AA′BB′ multiplet in the area of 4–5.5 ppm downfield from TMS. That the spectrum experimentally obtained is a single, rather sharp, peak at ca. 5.13 ppm (with the central peak of the proton impurity in the ND_3 solvent being taken as 0.5 ppm) is by no means surprising, especially in view of the broadness of the peaks. The spectral peaks were generally broad and the integrals unreliable, probably due to microscopic viscosity, the presence of particulates, and correlation time, respectively.

Table I. Comparison of Proton NMR Spectra[a] between C_6D_6 and ND_3 for Selected μ-η^6,η^6-Naphthalene Compounds and Bis(η^6-naphthalene)chromium

	naphthalene		
	unbound	η^6bound	η^6benzene
bis(η^6 naphthalene) chromium: ND_3	3.42	5.06,5.74	
C_6D_6	6.92	4.37,5.29	
(μ,η^6,η^6 naphthalene) bis(η^6benzene) dichromium: ND_3		5.04,5.73	3.38
C_6D_6		3.97,5.67	3.89
poly (μ,η^6,η^6naphthalene) chromium: ND_3		5.13	
C_6D_6		INSOLUBLE	

[a] Proton signals in the perdeuteriated solvents were used as internal references, e.g., the central peak for ND_3 at 0.5 ppm and the peak at 7.15 ppm for C_6D_6.

The unusually large upfield shift of the unbound ring protons in bis(η^6-naphthalene)chromium, from 6.92 ppm in C_6D_6 to 3.42 ppm in ND_3 is astonishing. Furthermore the proton NMR spectra in ND_3 of bis(η^6-naphthalene)chromium and (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium are almost identical. The large upfield shift between the two solvents appears to be due to a change in anisotropy.

The source of the anisotropy is clearly solvent-related, and the obvious differences in the two solvents (C_6D_6 and ND_3) are their relative basicities. Ammonia is known to be a good ligand toward metal sites, and the chromium atom in bis(η^6-naphthalene)chromium is electronically less saturated than that in bis(η^6-arene)chromium species.[5] This suggestion stems from the details of the mechanism proposed[6] for the markedly easier exchange reactions observed for bis(η^6-naphthalene)chromium as compared with bis(η^6-benzene)chromium. This electronically deficient metal site in bis(η^6-naphthalene)chromium is more easily accessed by the more basic solvent (ND_3) if the complexed naphthalene rings are eclipsed rather than staggered. The eclipsed configuration places the uncomplexed portion of the naphthalene rings one above the other, an arrangement where the electronic structure in one ring affects the structure in the other ring. In this arrangement both rings are in the same overall electronic environment, and the field of the molecule is maximally anisotropic, leading to a large upfield shift. In (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium, no further anisotropic effect could be forced upon the existing structure, so that the NMR spectrum in ND_3 remains essentially identical with that found in C_6D_6 (except for peak broadness).

In poly[(μ-η^6,η^6-naphthalene)chromium], the sharpness of the single peak suggests that the proton chemical shifts of the naphthalene moieties are identical, probably because of the ring current. Poly[(μ-η^6,η^6-naphthalene)chromium] is essentially insoluble in C_6D_6, but we were fortunate to discover that it is slightly soluble in liquid ammonia. Indeed, this solubility seems to suggest (following the argument developed for the bis(η^6-naphthalene)chromium molecule) that the poly[(μ-η^6,η^6-naphthalene)chromium] units are also arranged in an eclipsed configuration. Visual observations suggest that the extinction coefficient for poly[(μ-η^6,η^6-naphthalene)chromium] (brownish green) is significantly larger than that of bis(η^6-naphthalene)chromium and (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium (both yellowish brown).

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(5) Kündig, E. P.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1980**, 991.

(6) Kündig, E. P.; Timms, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 912.

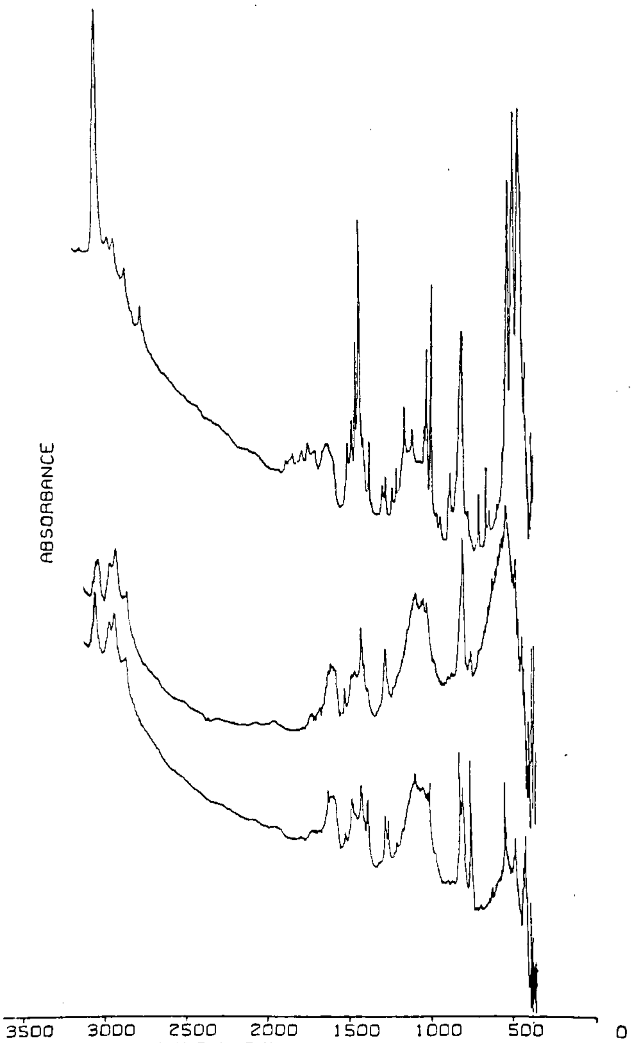


Figure 1. Infrared spectra of (top) (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium, (center) poly[(μ-η^6,η^6-naphthalene)chromium], and (bottom) bis(η^6-naphthalene)chromium, in cesium iodide pellets.

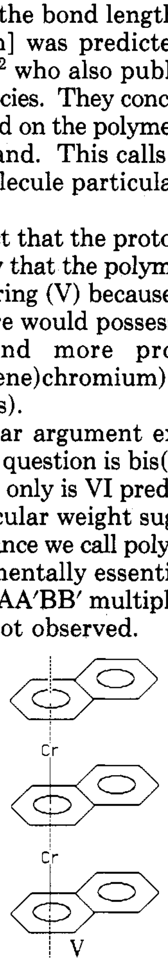
Mass spectral data were inconclusive for the characterization of poly[(μ-η^6,η^6-naphthalene)chromium] as expected. Low-resolution mass spectroscopy revealed a naphthalene–chromium fragment (180 amu) and a bis(η^6-naphthalene)chromium fragment (308 amu) at very low intensities. However, the higher fragments could not be differentiated from the noise and could not be identified by high-resolution mass spectroscopy. The presence of relatively large quantities of naphthalene in the spectrum suggest that these compounds undergo thermal decomposition easily. Importantly, no mass peak at 360 amu was observed; this mass number corresponds to the oligomer bis(μ-η^6,η^6-naphthalene)dichromium (VI), which might be expected to be volatile.

The infrared spectra of a series of related compounds were recorded to establish whether a characteristic spectrum exists for a μ-naphthalene moiety and can be used as a means of detecting such units in the insoluble residue from metal atom reactions. Aside from the general red shift and agglomeration of absorption peaks in the fingerprint region when compared to the spectrum of free naphthalene, the chromium to ligand tilt region (400–500 cm^{-1}) was found to be a strong indicator of the presence of an organochromium sandwich complex (see Figure 1). In order to study the possibility of polymer formation during the synthesis of bis(η^6-naphthalene)chromium, we isolated 1.65 g of insoluble particulates from a typical synthesis of this compound, with the scrupulous exclusion of air. This material, having been washed a number of times with 1,2-dimethoxyethane, was virtually free of soluble products. Extraction of about 100 mg of this insoluble material with liquid anhydrous ammonia produced a homogeneous solution containing some particulates; the NMR spectrum of the extract in ND_3 at −45 °C indicates the presence of a small amount of bis(η^6-naphthalene)chromium and an even smaller amount of a soluble product, poly[(μ-η^6,η^6-naphthalene)chromium]. The infrared analysis of the bulk residue (not subjected to ammonia extraction) showed it to be a mixture of bis(η^6-naphthalene)chromium (which had escaped 1,2-dimethoxyethane extraction), poly[(μ-η^6,η^6-naphthalene)chromium], and presumably chromium particulates, as estimated from the IR peak intensities. The poly[(μ-η^6,η^6-naphthalene)chromium] was probably formed through the action of 1,2-dimethoxyethane used in the workup.

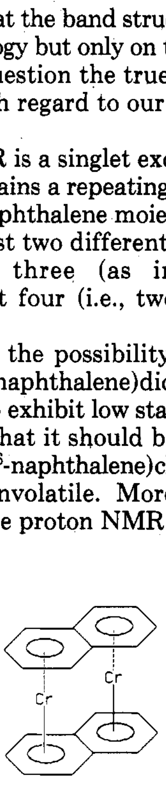
The crystal structure of (μ-η^6,η^6-naphthalene)bis(η^6-benzene)dichromium (II) indicates that the LUMO of the μ-naphthalene moiety in this compound is populated, based on the bond lengths.[1] Poly[(μ-η^6,η^6-naphthalene)chromium] was predicted to be stable by Burdett and Canadell,[2] who also published a band structure analysis of this species. They conclude that the band structure does not depend on the polymer topology but only on the nature of the ligand. This calls into question the true topology of the molecule particularly with regard to our NMR results.

The fact that the proton NMR is a singlet excludes the possibility that the polymer contains a repeating unbound aromatic ring (V) because the naphthalene moiety in such a structure would possess at least two different chemical shifts, and more probably three (as in bis(η^6-naphthalene)chromium),[7] if not four (i.e., two AA′BB′ multiplets).

A similar argument excludes the possibility that the species in question is bis(μ-η^6,η^6-naphthalene)dichromium (VI). Not only is VI predicted to exhibit low stability,[2] its low molecular weight suggests that it should be volatile; the substance we call poly[(μ-η^6,η^6-naphthalene)chromium] is experimentally essentially nonvolatile. Moreover, the expected AA′BB′ multiplet in the proton NMR spectrum of VI is not observed.



V



VI

The choice of topologies for poly[(μ-η^6,η^6-naphthalene)chromium] is thus narrowed to two, both of which contain the antarafacial (μ-η^6,η^6-naphthalene)dichromium moiety: one with the μ-naphthalene moieties staggered (VII) and the other with them eclipsed (III). According to Burdett and Canadell, V is improbable due to "π-type two-orbital, four-electron repulsions between the organic units". At first glance this argument militates against III, but consider the large upfield shift of the protons on the ring not bound to chromium in bis(η^6-

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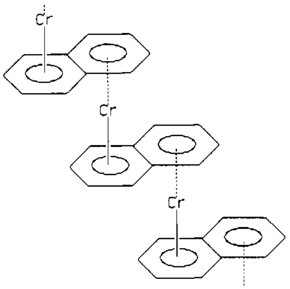
[7] Elschenbroich, C.; Möckel, R.; Massa, W.; Birkhahn, M.; Zenneck, U. *Chem. Ber.* **1982**, *115*, 334.

naphthalene)chromium when this compound is dissolved in ND_3 (3.42 ppm) as opposed to 6.96 ppm when dissolved in C_6D_6. Earlier we attributed this large upfield shift to anisotropy caused by the naphthalene moieties of bis(η^6-naphthalene)chromium being constrained to the eclipsed configuration; it is therefore reasonable to speculate that poly[(μ-η^6,η^6-naphthalene)chromium] exists in the eclipsed topology (III) while dissolved in ND_3. The argument gains strength from the recognition that the metal sites in the poly[(μ-η^6,η^6-naphthalene)chromium] structure are electron-deficient from the point of view of formal electron count. This electronic arrangement would encourage the coordination of solvent ammonia molecules to the metal sites; the eclipsed configuration (III) provides for easier access to the metal sites by solvent ammonia molecules than does the staggered configuration (VII).

It is well-known that bis(η^6-naphthalene)chromium exists as the eclipsed configuration in the crystalline solid.[7] Poly[(μ-η^6,η^6-naphthalene)chromium is not soluble in C_6D_6, while freely rotating bis(η^6-naphthalene)chromium is; eclipsed bis(η^6-naphthalene)chromium exists in ND_3 as it does in the crystalline state. Thus, it is reasonable to speculate that poly[(μ-η^6,η^6-naphthalene)chromium] is eclipsed in the solid state; however, only an X-ray crystal structure will elucidate this point. It appears that the solubility of poly[(μ-η^6,η^6-naphthalene)chromium] in liquid ammonia resides in the ability of the basic solvent to stabilize the eclipsed configuration.



VII

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Reactions of Sc^+ with Alkenes in the Gas Phase

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Fourier transform mass spectrometry (FTMS) was used to study the exothermic reactions of laser desorbed Sc^+ with various linear, branched, and cyclic olefins. Single and double dehydrogenations were observed to be the predominant processes in marked contrast to Fe^+ and Co^+ which yield predominantly C–C bond cleavage products. Structures of some of the commonly occurring product ions were probed by collision-induced dissociation and ion–molecule reactions, including H/D exchange. Evidence is presented for two stable isomers of $ScC_4H_6^+$, $ScC_4H_4^+$, and $ScC_5H_6^+$. A modification to the experimental pulse sequence was implemented which made possible the formation and isolation of various endothermic reaction products. In particular Sc^+–H was generated by an endothermic reaction of Sc^+ with ethane and was used to bracket the Sc^+–benzene bond strength at $D°(Sc^+\text{–benzene}) = 53 \pm 5$ kcal/mol.

Introduction

Over the past several years, the study of transition-metal ions in the gas phase has become the focus of a great deal of attention. These studies provide fundamental information on the kinetics, mechanisms and thermochemistry of these chemically important species in the absence of complicating effects due to solvent or ligand interferences. In addition, studies of the transition-metal ions are also important because of the promise these ions hold as selective chemical ionization reagents for mass spectral analysis.[1]

Most of the work to date has centered on the first-row groups 8–10 metals Fe^+, Co^+, and Ni^+. The reactions of these metals with alkanes, alkenes, and other organic compounds have been studied by a number of laboratories.[2] Studies involving the early first-row transition-metal ions, however, are fewer in number. A variety of V^+–ligand bond strengths have been reported,[3] in addition to studies of the reactions of this first-row group 5 metal ion with various alkanes.[4] Allison and Ridge have studied the reactions of olefins with Ti^+,[5] and Tolbert and Beauchamp have studied both alkane activation by Ti^+ [4b] and the reactions of saturated hydrocarbons with Sc^+.[6] In these cases some interesting differences in reactivity, as com-

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[1] (a) Peake, D. A.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 115. (b) Wise, M. B. Ph.D. Thesis, Purdue University, 1984. (c) Lombarski, M.; Allison, J. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *49*, 281. (d) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641.

[2] (a) Allison, J. *Prog. Inorg. Chem.* **1986**, *34*, 627. (b) Jacobson, D. B.; Byrd, G. D.; Freiser, B. S. *Inorg. Chem.* **1984**, *23*, 553. (c) Jacobson, D. B.; Freiser, B. S. *Organometallics* **1984**, *3*, 513. (d) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (e) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360. (f) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332.

[3] Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 4065.

[4] (a) Jackson, T. C.; Carlin, T. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 1120. (b) Tolbert, M. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 7509.

[5] Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 35.

[6] Tolbert, M. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 8117.