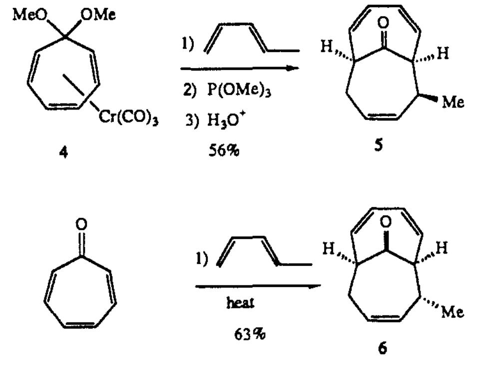
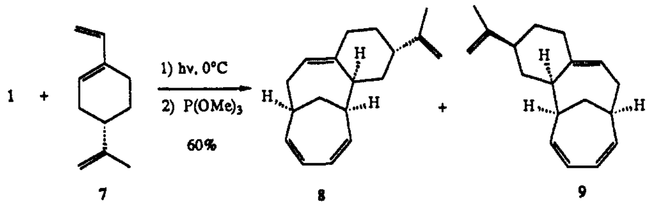
under an atmosphere of carbon monoxide. This observation may have important mechanistic implications for this class of reactions and is suggestive of a stepwise pathway.

A consistently high level of diastereoselection appears to be another characteristic of this cycloaddition process.[4a] The relative stereochemistry of the photoproducts has been established as being endo in nature by comparison with the appropriate exo tropone cycloadduct. In practice, this was accomplished by reacting the readily available 7,7-dimethoxycycloheptatriene complex **4**[6] with

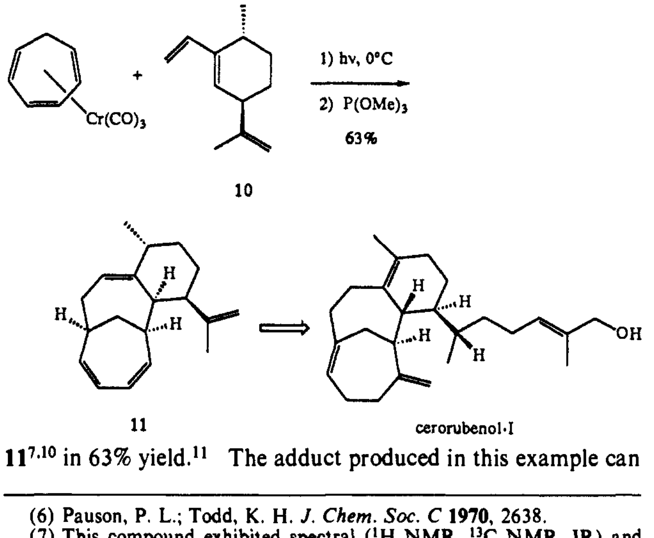


a given diene under standard conditions. This gave a single adduct which was shown not to be identical with the corresponding tropone adduct.[7] An important consequence of this feature of the metal-mediated sequence is that it provides, for the first time, a convenient method for constructing bicyclo[4.4.1]undecanone systems displaying stereogenicity complementary to that obtained in the tropone series.

The course of the photocycloaddition of more elaborate dienes has also been examined in detail. Diene **7**[7] [from (*S*)-(−)-



perillaldehyde] provided a 1:3 mixture of tricyclic adducts **8**[7] and **9**[7] in 60% overall yield.[8] A more significant level of diastereoselection was observed in the cycloaddition of optically pure diene **10**[7] [derived from *R*,*R*-(+)-dihydrocarvone],[9] which gave adduct



11[7,10] in 63% yield.[11] The adduct produced in this example can be viewed as a convenient model for the convergent synthesis of the unusual sesterterpene cerorubenol I.[12,13] A significant feature of this result is the production of an adduct displaying the natural absolute configuration at the C-ring side chain.

These last two examples point to an important fundamental distinction between the transition-metal-mediated reaction described herein and the corresponding thermal [6 + 4] process in the tropone series. It is well established that a rather limited repertoire of diene partners will successfully engage the latter in a higher order cycloaddition reaction. Indeed, neither diene **7** nor **10** provided identifiable products when exposed to tropone under standard thermal conditions, whereas we have yet to encounter a class of dienes that does not provide good yields of cycloadducts in the photochemical version of this reaction. Further work on elucidating the mechanism of this process is currently underway as is a study on general synthetic applications.

Acknowledgment. We thank the National Institutes of Health (CA-36543) and the National Science Foundation (CHE-8719185) for financial support of this research.

Supplementary Material Available: Typical experimental procedures and full characterizations (boiling points, ^{1}H and ^{13}C NMR, IR, MS, and HRMS) of all new compounds (11 pages). Ordering information is given on any current masthead page.

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[6] Pauson, P. L.; Todd, K. H. *J. Chem. Soc. C* **1970**, 2638.

[7] This compound exhibited spectral (^{1}H NMR, ^{13}C NMR, IR) and analytical (HRMS and/or combustion analysis) data consistent with the assigned structure.

[8] Available data do not permit unambiguous structural assignments to be made for the two diastereomeric products in this instance.

[9] This diene was prepared in 75% overall yield by a Pd(0)-mediated coupling of vinyltri-*n*-butylstannane with the vinyl triflate derived from the kinetic enolate of *R*,*R*-(+)-dihydrocarvone: (a) McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1983**, *24*, 979. (b) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630.

[10] Support for the structure assigned to **11** was obtained by an NOE difference experiment in which irradiation of the B-ring vinyl proton multiplet at δ 5.45 caused enhancement of the C-ring methyl group signal at δ 1.05. This result is most consistent with the assigned structure.

[11] Less than 5% of the alternative diastereomer could be detected.

[12] Tempesta, M. S.; Iwashita, T.; Miyamoto, F.; Yoshihara, K.; Naya, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 1182.

[13] For an alternative entry into a cerorubenate sesterterpene, see: Paquette, L. A.; Poupart, M.-A. *Tetrahedron Lett.* **1988**, *29*, 273.

ROH$_2^+$ Formation from Ionized *n*-Hexyl Ethers: An Unequivocal Dissociation through an Ion–Neutral Complex in the Gas Phase

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The idea that many unimolecular decompositions of ions in the gas phase occur through partially dissociated partners held together by ion–dipole and/or ion-induced dipole attractions, i.e., by a gas-phase analogue of cage effects in solution, has been widely applied.[1] Evidence for intermediate complexes consists of reactions between groups at opposite ends of rigid steroid nuclei,[2] isomerizations expected of the suspected ionic partner in the complex,[3] hydrogen exchange between the putative partners,[4] ab

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[1] (a) Morton, T. M. *Tetrahedron* **1982**, *38*, 3195–3243. (b) McAdoo, D. J. *Mass Spectrom. Rev.* **1988**, *7*, 363–393.

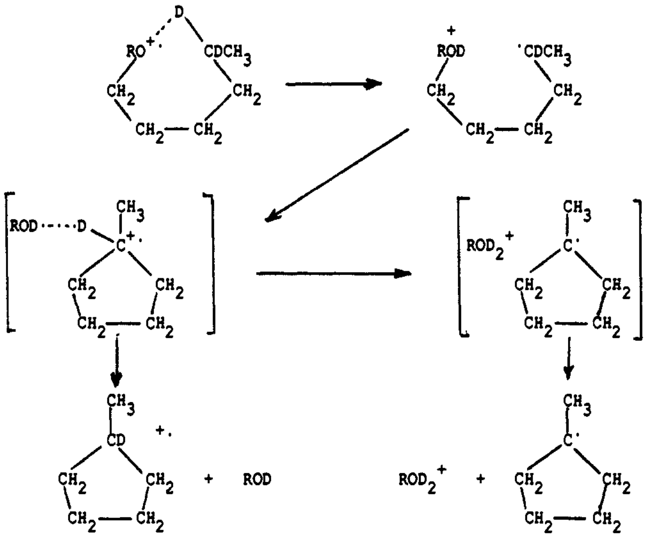
[2] Longevialle, P.; Botter, R. *J. Chem. Soc., Chem. Commun.* **1980**, 823–825.

Table I. Thermochemical Data Related to $ROC_6H_{13}^{\bullet +}$ Fragmentations[a]

	$\Delta H_f(ROC_6H_{13})$	$AE(M^{\bullet +})$	$AE(ROH_2^{\bullet +})$	$AE(C_6H_{12}^{\bullet +})$	$\Delta H_f(C_6H_{12}^{\bullet +})$
$CH_3OC_6H_{13}$	−299	≤915	929	927	854
$C_2H_5OC_6H_{13}$	−334	900	907	927	855

[a] All values are kilojoules per mole. $\Delta H_f(C_6H_{12}^{\bullet +})$ was calculated by the formula $\Delta H_f(A^+) = AE(A^+) - \Delta H_f(B) + \Delta H_f(AB) + \Delta H_{corr}$, where ΔH_{corr} is a statistical mechanical correction.[8] ΔH_{corr} was 24 kJ mol^{-1} for methyl hexyl ether and 27 kJ mol^{-1} for the ethyl hexyl ether. The heats of formation of the neutral ethers were estimated by subtracting 20.6 kJ mol^{-1} per CH_2 from ΔH_f(methyl *n*-butyl ether), −258.1 kJ mol^{-1}, and from ΔH_f(ethyl *n*-propyl ether), −272.2 kJ mol^{-1}.[10] Published[9] heats of formation are as follows: ionized methylcyclopentane 844 kJ mol^{-1}, ionized 1-hexene 869 kJ mol^{-1}, *E* isomers of ionized 2- and 3-hexene both 814 kJ mol^{-1}, CH_3OH −202 kJ mol^{-1}, and C_2H_5OH −235 kJ mol^{-1}.[9] The precision in the PIE measurements is ±1 kJ mol^{-1}, but the thresholds can have larger uncertainties due to thermal energy influences on the PIE curves.

Scheme I



initio calculations,[5] and very sharp energy dependencies of reactions thought to be complex-mediated.[6] However, controversy remains. A unimolecular decomposition involving a reaction between partners that cannot be joined by a covalent bond would unequivocally demonstrate the intermediacy of an ion-neutral complex. This could be provided by showing that ROH_2^+ formation from ionized hexyl ethers (51% $C_2H_5D_2O^+$, 40% $C_2H_6DO^+$ from ethyl hexyl-*5,5-d*$_2$ ether[7]) takes place as indicated in Scheme I.

If Scheme I is correct, methyl and ethyl hexyl-*5,5-d*$_2$ ethers should produce methylcyclopentane-*1-d*$_1$ ions, and H transfer to ethanol from C1 (C5 of the ionized ethers) of this ion would have a specificity resembling that in the second step of the unimolecular dissociation. We measured the ratio of H to D transfer by Fourier transform mass spectrometry (FTMS) to test this prediction. Hexyl-*5,5-d*$_2$ methyl ether and ethanol were admitted to the machine at an ionizing electron energy of 12.0 eV; *m/z* 17–79 were ejected from the cell to remove products of their reactions. Ejection of $C_6H_{11}D^{\bullet +}$ following the ejection of the preceding ions reduced $C_2H_5OHD^+$ by 80% relative to the signal present following ejection of only *m/z* 17–79 and the $C_2H_5OH_2^+$ and $C_2H_5OHD^+$ signals by amounts having the ratio 0.65 ± 0.04 (SD). The ratio of the decreases is the ratio of H to D transfer from $C_6H_{11}D^{\bullet +}$ to ethanol. $C_6H_{11}D^{\bullet +}$ generated from methylcyclopentane-*1-d*$_1$ was similarly reacted with ethanol, also at an ionizing electron energy of 12.0 eV. Adding ejection of $C_6H_{11}D^+$ removed 85% of $C_2H_5OHD^+$ relative to intensities following ejection of only the lower mass ions and reduced $C_2H_5OH_2^+$ and $C_2H_5OHD^+$ by amounts having the ratio 0.76 ± 0.11. This matches the $C_2H_5OHD^+/C_2H_5OD_2^+$ ratio from ionized ethyl hexyl-*5,5-d*$_2$ ether (0.78) and is similar to the ratio $C_2H_5OH_2^+/C_2H_5OHD^+$ resulting from reaction of ethanol with $C_6H_{11}D^+$ from hexyl-*5,5-d*$_2$ methyl ether.[7] Generation of ionized methylcyclopentane-*1-d*$_1$ is the only explanation we can devise for the preferential transfer of the D from the ion generated from hexyl-*5,5-d*$_2$ methyl ether. Generation of 1- or 2-hexene ions would probably be followed by suppressed or random D transfer.

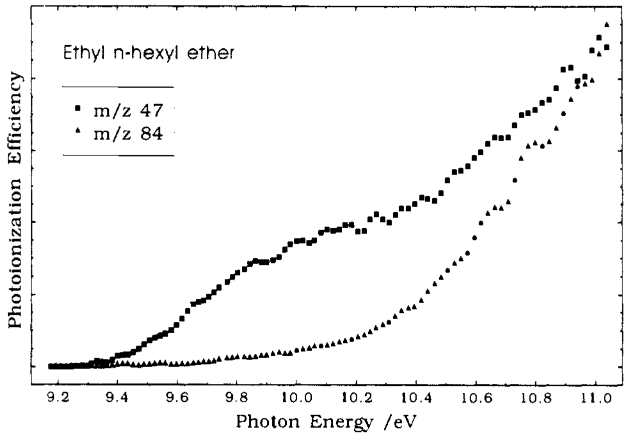


Figure 1. Photoionization ionization efficiency curves for formation of $C_2H_5OH_2^+$ and $C_6H_{12}^{\bullet +}$ from ethyl hexyl ether. Note that formation of the former ion appears to dominate that of the latter at low but not at higher energies.

$C_2H_5D_2O^+$ formed from ethyl hexyl-*5,5-d*$_2$ ether specifically lost D_2O upon collision, identifying that ion as $C_2H_5OD_2^+$, additional support for Scheme I.

Finally, we determined pertinent appearance energies by photoionization mass spectrometry[8] (Table I). $\Delta H_f(C_6H_{12}^{\bullet +})$ derived from these measurements was 855 kJ mol^{-1}, agreeing reasonably with a published value of 844 kJ mol^{-1} for the 1-methylcyclopentane cation.[9] $CH_3OH_2^+$ and $C_2H_5OH_2^+$ abundances rose continuously to the maximum energy of the measurements (Figure 1). This indicates that, in contrast to complex-mediated alkane eliminations,[8] substantial ROH_2^+ formation occurs above the onset for simple dissociation of the partners. We attribute this to enhanced stability of the complex due to the dipole moment of the alcohol.

Consistent with its lower threshold (Table I), ROH_2^+ formation dominated the metastable spectrum of ionized ethyl hexyl ether (Table I). This process was present in the normal but not in the metastable spectrum of the methyl ether, in accord with the higher threshold for forming $CH_3OH_2^+$ than for forming $C_6H_{12}^{\bullet +}$

ROH elimination from ionized hexyl ethers following H transfer from C5 produces the methylcyclopentane cation, and H transfer

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(3) (a) Bowen, R. D.; Williams, D. H. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *29*, 47–55. (b) Williams, D. H.; Stapleton, B. J.; Bowen, R. D. *Tetrahedron Lett.* **1978**, *32*, 2919–2922. (c) Morton, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 1596–1602. (d) Hall, D. G.; Morton, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 5686–5688.

(4) Hammerum, S.; Audier, H. E. *J. Chem. Soc., Chem. Commun.* **1988**, 860–862.

(5) Heinrich, N.; Louage, F.; Lifshitz, C.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 8183–8192.

(6) (a) Hudson, C. E.; McAdoo, D. J. *Int. J. Mass Spectrom. Ion Processes* **1984**, *59*, 325–332. (b) Traeger, J. C.; Hudson, C. E.; McAdoo, D. J. *J. Phys. Chem.* **1988**, *92*, 1519–1523. (c) McAdoo, D. J.; Traeger, J. C.; Hudson, C. E.; Griffin, L. L. *J. Phys. Chem.* **1988**, *92*, 1524–1530.

(7) Carpenter, W.; Duffield, A. M.; Djerassi, C. *J. Am. Chem. Soc.* **1967**, *89*, 6164–6167.

(8) (a) Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3647–3652. (b) Traeger, J. C.; McLoughlin, R. G.; Nicholson, A. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5318–5322.

(9) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Supplement).

(10) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed., Chapman and Hall: London, 1986.

from Cl of this ion produces ROH_2^+. Since the reactants in the second step cannot by joined by a covalent bond, beyond doubt ROH_2^+ formation occurs in an intermediate ion-neutral complex.

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Spatial Distribution of 3d Electrons in Sandwich Compounds Studied by Penning Ionization Electron Spectroscopy: Ferrocene and Dibenzenechromium

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Electronic properties of sandwich compounds involving transition metals such as ferrocene have attracted considerable attention for many years. The nature of the chemical bond as well as the level ordering of the d states seem to be fairly well understood at present.[1] However, information on the spatial distribution of d electrons is rather limited, although it plays an important role in the stability of the complexes, the chemical reactions with other molecules, etc. In this communication we demonstrate that such information can be obtained directly by Penning ionization electron spectroscopy, in which the kinetic energy of electrons emitted by thermal collisions of rare-gas metastable atoms with target molecules is measured. For this purpose, we have taken up ferrocene ($(C_5H_5)_2Fe$) and dibenzenechromium ($(C_6H_6)_2Cr$) as samples, because they are closed-shell (diamagnetic) molecules with formal d^6 configurations and their ionization spectra are rather simple. Our data exhibit that the 3d-type orbitals of dibenzenechromium are considerably exposed to the outside of the molecule, while the corresponding orbitals of ferrocene are shielded by the rings effectively, as pointed out in a previous paper.[2]

Figure 1 shows Penning ionization electron spectra (PIES) of ferrocene and dibenzenechromium measured by a transmission-corrected electron spectrometer.[3-5] For reference, ultraviolet photoelectron spectra (UPS) of the two compounds are also shown in the figure. The highest lying two bands in both UPS have been attributed to emissions from the metal 3d-type a_{1g} and e_{2g} orbitals, while the next two bands are assigned to the e_{1u} and e_{1g} orbitals primarily composed of the ligand π.[6] Here, we used the notation of D_{5d} symmetry (staggered conformation) for ferrocene,[7] in order to conform to the notation used in most previous works. The notation for dibenzenechromium is based on D_{6h} symmetry.[8] D_{5d} and D_{6h} symmetries give the same notations for the orbitals mentioned above. As is seen in Figure 1, the four bands observed in the UPS also appear in the PIES. The characteristics of the PIES are summarized as follows:

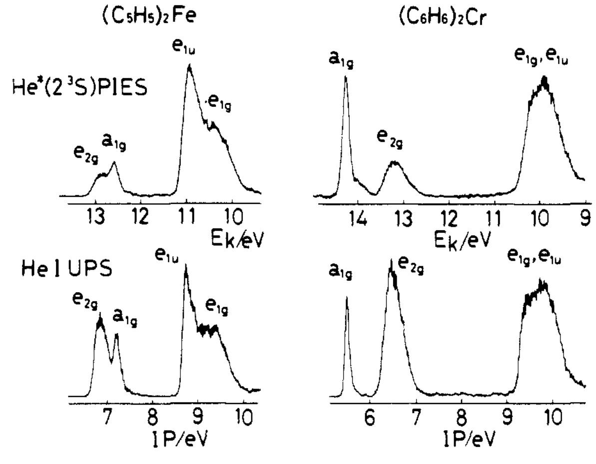

Figure 1. He*(2^3S) PIES and He I UPS for ferrocene and dibenzenechromium. The kinetic energy scale for the PIES is shifted with respect to the UPS by the difference in the excitation energies, 21.22 − 19.82 = 1.40 (eV).

Table I. Relative Band Intensity in the PIES of Ferrocene and Dibenzenechromium

	relative intensity[a]	
MO	ferrocene	dibenzenechromium
e_{2g} (d_{xy}, $d_{x^2-y^2}$)	16	42
a_{1g} (d_{z^2})	36	112
e_{1u} (π)	100	100
e_{1g} (π)		

[a] Normalized relative band intensity corresponding to one orbital.

(i) As a common feature of the two compounds, in contrast to the UPS, the metal band due to the a_{1g} orbital is much enhanced (more than twice) relative to that due to the e_{2g} orbitals, taking the orbital degeneracy into account (see Table I).

(ii) With ferrocene, the intensity of the metal bands is much suppressed compared to that of the ligand bands. Such a marked suppression is not found in the case of dibenzenechromium.

Penning ionization is regarded as an electron-exchange process, in which an electron of a target molecule (M) fills the hole of a metastable atom (A*) and the excited electron is emitted to a continuum state simultaneously.[9] Since the transition rate for the electron transfer depends largely on the spatial overlap between the relevant occupied orbital of M and the empty orbital of A*, an orbital exposed outside the repulsive surface of the molecule M is expected to give a stronger band in PIES than does an orbital localized inside the molecule.[5] On the basis of this picture, the above result i indicates that the a_{1g} (essentially d_{z^2}) orbitals are exposed further outside the molecules compared to the e_{2g} (primarily d_{xy} and $d_{x^2-y^2}$) orbitals. This feature can be understood easily from the fact that the vertical metal-to-ring distance in sandwich compounds (1.66 Å for ferrocene[7] and 1.62 Å for dibenzenechromium[8]) is rather short compared to the size of the ring (the distance between the center of ring and hydrogen is 2.34 Å for ferrocene and 2.51 Å for dibenzenechromium); the $3d_{z^2}$ orbital extending normal to the ring cannot be shielded by the orbitals of the rings so effectively as in the case of the d_{xy} and $d_{x^2-y^2}$ orbitals. Next, result ii shows that the degree of exposure of the 3d-type orbitals outside the repulsive molecular surface is significantly larger for dibenzenechromium than for ferrocene. Since the Fe in ferrocene is formally dication, the contracted 3d orbitals are screened by the rings sufficiently in comparison with the 3d orbitals of formally neutral Cr in dibenzenechromium. An incomplete shielding effect for metal orbitals has also been observed in the case of benzene adsorbed parallel to transition-metal surfaces.[10]

It is known that dibenzenechromium is chemically unstable compared to ferrocene. This is mainly because the 3d-type orbitals

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(1) See, e.g.: Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(2) Munakata, T.; Harada, Y.; Ohno, K.; Kuchitsu, K. *Chem. Phys. Lett.* **1981**, *84*, 6.

(3) Aoyama, M.; Masuda, S.; Ohno, K.; Harada, Y.; Mok, C. Y.; Huang, H. H.; Lee, S. Y. *J. Phys. Chem.* **1989**, *93*, 1800.

(4) Harada, Y.; Ohno, K.; Mutoh, H. *J. Chem. Phys.* **1983**, *79*, 3251.

(5) Ohno, K.; Mutoh, H.; Harada, Y. *J. Am. Chem. Soc.* **1983**, *105*, 4555.

(6) For ferrocene: Cauletti, C.; Green, J. C.; Kelly, M. R.; Powell, P.; Van Tilborg, J.; Robbins, J.; Smart, J. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *19*, 327, and references therein. For dibenzene chromium: Guest, M. F.; Hillier, I. H.; Higginson, B. R.; Lloyd, D. R. *Mol. Phys.* **1975**, *29*, 113.

(7) Ferrocene in the vapor phase is an eclipsed structure with D_{5h} symmetry, while in the solid phase, it is a staggered structure with D_{5d} symmetry (see: Haaland, A. *Acc. Chem. Res.* **1979**, *12*, 415).

(8) Haaland, A. *Acta Chem. Scand.* **1965**, *19*, 41.

(9) Hotop, H.; Niehaus, A. *Z. Phys.* **1969**, *228*, 68.

(10) Masuda, S.; Aoyama, M.; Harada, Y., to be published.

0002-7863/90/1512-6445$02.50/0