

Irradiation of pseudoortho didiazo compound **1a**⁸ in a rigid glass of 2-methyltetrahydrofuran at 11 K in an ESR cavity (Varian E112/V7800, X-band spectrometer) with Pyrex-filtered UV light gave intense quintet signals as shown in Figure 1. The zero-field splitting parameters were evaluated to be $|D| = 0.0624$ and $|E| = 0.0190 \text{ cm}^{-1}$ on the basis of a third-order perturbational calculation.⁹ The intensity of the quintet signals was found to obey the Curie law in the temperature range 11–50 K, indicating that the quintet is the ground state. A signal at 104.0 mT was detected at temperatures above 20 K. The signal intensity increased at elevated temperatures, suggesting that this species was a thermally populated triplet (T_T), although the rest of its signals were weak and not resolved well.

In sharp contrast with **1b**, signals due to the quintet species were not detected in the ESR spectrum obtained after irradiation of **2a** (Figure 2). A new set of triplet signals (T_T ; $|D| = 0.1973$, $|E| = 0.0038 \text{ cm}^{-1}$) started to appear when the temperature was raised to 20 K. The signal intensities increased as the temperature was raised but did not change with time at each temperature. The signal intensity of T_T started to decrease with time at about 70 K. The intensity behavior is unambiguously of the thermally populated triplet. Since 1, *n*-biradicals cannot have such large D value as observed in T_T , the signals should be due to the triplet state of **2b**. The absence of quintet signals together with the presence of thermally populated triplet ones lead us to conclude that the singlet is the ground state for pseudometa dicarbene **2b**.

A preliminary measurement was performed on pseudopara didiazo compound **3a** and the intense quintet signals were detected.¹⁰ The result suggests the quintet ground state for pseudopara dicarbene **3b**.

These considerable differences in spin multiplicity of dicarbenes **1b–3b** observed here are the first experimental demonstration¹¹ that the spin distribution of the π -electron in the layered benzenoid moieties can determine the ferro- or antiferromagnetic interaction between the carbene species. The results also suggest that the mode of stacking of the benzene units can be crucial in increasing the dimension and determining the intermolecular interaction which should control the bulk magnetic properties of the high-spin aromatic molecules.

(8) Three isomeric dibromo[2.2]paracyclophanes were prepared and separated according to the literature method. See: Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3527. Each isomer was dilithiated by *n*-butyllithium in ether and treated with benzaldehyde to give the corresponding diol, which was then oxidized by pyridinium chlorochromate in dichloromethane to give the dibenzoyl[2.2]paracyclophane. It was converted to the didiazo compound through the bis(hydrazone) by oxidizing with yellow HgO in benzene at room temperature. The crude product was purified by alumina column chromatography by rapid elution with benzene: pseudortho, mp 107–109 °C dec; pseudometa, mp 136–138 °C dec; pseudopara, mp 147–148 °C dec. All the new compounds gave satisfactory elemental analyses and ¹H NMR data.

(9) (a) Takui, T.; Itoh, K. *Chem. Phys. Lett.* **1973**, *19*, 120. (b) Itoh, K., private communication.

(10) The dicarbene was found to be unstable and to be converted to the biradical ($|D| = 0.0108$, $|E| = 0.0005 \text{ cm}^{-1}$) thermally. The thermal instability of the dicarbene **3b** prevented us from drawing the Curie plot in a wide temperature range.

(11) The ESR spectra of pseudoortho, pseudometa, and pseudopara [2.2]paracyclophanylenebis(*tert*-butyl nitroxide) in a glass of *o*-terphenyl are reported. See: Forrester, A. R.; Ramasseul, R. J. *Chem. Soc., Perkin Trans. I* **1971**, 1645. The triplet signals are obtained in all cases including pseudometa one. The electron spins of these nitroxides are localized in the nitroxide groups rather than delocalized to the benzene rings because of the twisting of *tert*-butylnitroxyl groups. Therefore the exchange interaction of the electron spins between the benzenoid moieties in these cases is unfortunately too small to test McConnell's theory.

Observation of a Novel Low-Lying Excited State in Zinc(II) Complexes

K. A. Truesdell and G. A. Crosby*

Chemical Physics Program
Washington State University
Pullman, Washington 99164-4620

Received May 10, 1984

Photoluminescence spectra of closed-shell zinc(II) complexes containing both *N*-heterocyclic and aromatic thiol ligands reveal the presence of a previously uncharacterized excited state. Modifications of the complexes by changing the π -donating strength of the substituents on the thiol moiety produce substances ranging from those in which the presence of the low-lying state is barely detectable to compounds whose emission spectra are dominated by the new transition. The experimental observations on a typical set of analytically pure compounds are reproduced in Figure 1.

When the $\text{ZnCl}_2(\text{phen})$ complex, a white solid, is illuminated by ca. 330-nm UV light in an organic glass at 77 K, strong fluorescence and phosphorescence characteristic of the phen ligand are observed.¹ Replacement of the chlorides by two pentafluorothiophenol anions (F_5PhS) produces a slightly offwhite solid that exhibits no phen fluorescence but does show a strong phen phosphorescence. Intensive studies of this latter emission reveal the presence of a new band maximizing at ca. 620 nm lying in the tail of the phen phosphorescence. The band shows up clearly in time-resolved spectra. Replacing the chlorides in $\text{ZnCl}_2(\text{phen})$ by the anions of 4-chlorothiophenol (4-ClPhS) produces a molecule in which the new band dominates the emission spectrum as is clearly seen in Figure 1. Phen phosphorescence is not entirely quenched, however. Finally, excitation of the $\text{Zn}(4\text{-MeOPhS})_2(\text{phen})$ complex (4-MeOPhS = anion of 4-methoxythiophenol) produces only the broad new band maximizing ca. 620 nm. (The presence of an aromatic thiol is necessary; aliphatic thiols do not produce compounds exhibiting the new band.) Although the observed structured fluorescence and phosphorescence clearly originate from the phen ligand, the subtle differences both of the spectra themselves and, in the case of the phosphorescence, the measured lifetimes decisively show that the phen ligand is coordinated to the zinc ion.

Detailed spectroscopic measurements, including time-resolved studies, determine that the new band arises from an excited state that (a) is only present when both *N*-heterocyclic and aromatic thiol ligands are coordinated to the $\text{Zn}(\text{II})$ ion, (b) decays on the order of microseconds at 77 K, (c) is tunable to some extent by making judicious change in either or both types of ligand, (d) profoundly affects the radiationless degradation rates and pathways in the complexes, and (e) is a general property of these types of complexes of metal ions with filled *d* shells. We have in the laboratory analogous results from $\text{Cd}(\text{II})^2$ and $\text{Sn}(\text{IV})$ systems.³

Absorption measurements of these types of complexes show the presence of a broad low-lying transition(s) that gradually shifts toward the visible (see Figure 1) as the electron-donating ability of the thiol ligand increases. This new band correlates with the presence of the novel emission band and is responsible for the progressive change in color of the complexes from white [$\text{ZnCl}_2(\text{phen})$] to yellow [$\text{Zn}(4\text{-MeOPhS})_2(\text{phen})$] in the crystalline state. The behavior of this absorption band in $\text{Zn}(\text{II})$ complexes has been noted previously by Koester (dithiol ligands),⁴ who assigned it to an interligand trans-metallic charge-transfer (ITCT) transition between the thiol donor and the *N*-heterocyclic acceptor. We tentatively assign the new emitting state(s) to an ITCT transition(s), although the new emission band is not the inverse of the absorption band. Both the ITCT orbital designation

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(2) Highland, R. G.; Crosby, G. A., manuscript in preparation.

(3) McGuire, B. R., unpublished results.

(4) Koester, V. J. *Chem. Phys. Lett.* **1975**, *32*, 575.

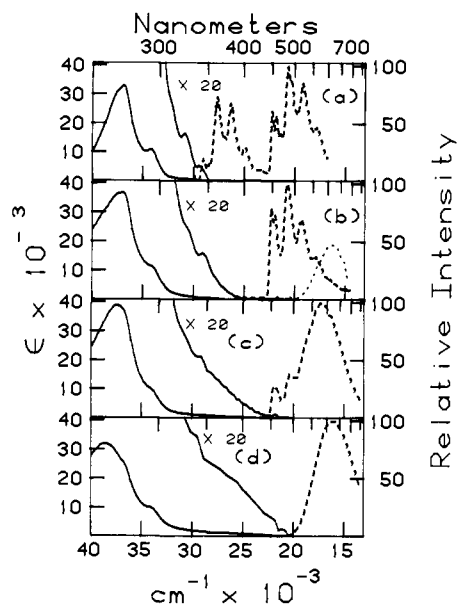


Figure 1. Absorption (—, room temperature) and corrected emission (---, 77 K) spectra of zinc(II) complexes in $\text{CHCl}_3/\text{EtOH}$ (1:19, v/v): (a) $\text{ZnCl}_2(\text{phen})$; (b) $\text{Zn}(\text{F}_3\text{PhS})_2(\text{phen})$, a time-resolved emission spectrum (···) at 77 K is included (0.5- μs delay, 0.25- μs window); (c) $\text{Zn}(4\text{-ClPhS})_2(\text{phen})$; (d) $\text{Zn}(4\text{-MeOPhS})_2(\text{phen})$.

and the spin multiplicity of the new excited state are still not definitively characterized.

Detailed spectroscopic studies between 77 and 4 K of these types of zinc(II) molecules and other (nd)¹⁰ ($n = 3, 4$) complexes containing various N-heterocyclic ligands and both mono and dihol ligands will be published elsewhere.

Acknowledgment. Research supported by AFOSR Grant 80-0038 and the Office of Naval Research.

Product Translational Energy Distributions as a Probe of Organometallic Reaction Mechanisms: Dehydrogenation of Alkanes by Groups 8-10 Transition-Metal Ions

Maureen A. Hanratty and J. L. Beauchamp*

The Arthur Amos Noyes Laboratory of Chemical Physics,¹ California Institute of Technology Pasadena, California 91125

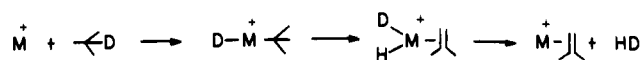
Andreas J. Illies² and M. T. Bowers*

Department of Chemistry, University of California Santa Barbara, California 93106

Received October 9, 1984

The complex mechanisms by which carbon-hydrogen and carbon-carbon bonds are cleaved by gas-phase transition-metal ions remain highly speculative.³⁻⁶ In the present work we dem-

Scheme I



onstrate the use of product translational energy distributions to characterize potential energy surfaces for organometallic reactions, using alkane dehydrogenation as an example.

Dehydrogenation of isomeric butanes by first-row group 8-10 metal ions has been investigated extensively. All three metal ions induce HD elimination from 2-methylpropane-2- d_1 to yield a metal ion-2-methylpropene complex.^{6,7} A postulated mechanism for this 1,2-dehydrogenation is shown in Scheme I where $\text{M} = \text{Fe}^+$, Co^+ , or Ni^+ .

In contrast, the products of *n*-butane dehydrogenation are metal specific. Ion cyclotron resonance^{8,9} studies indicate Ni^+ forms exclusively a bis(ethylene) complex on dehydrogenation of *n*-butane, while Fe^+ and Co^+ form both bis(ethylene) complexes and M^+ -butene complexes. High-energy collision-induced dissociation studies¹⁰ also indicate two distinct dehydrogenation products in the reaction of Fe^+ with *n*-butane. Reaction of Ni^+ in a low-energy ion beam with *n*-butane-1,1,1,4,4,4- d_6 shows exclusive loss of D_2 .⁹ These results suggest Scheme II for formation of the bis(ethylene) complex. In similar experiments with Fe^+ and Co^+ , D_2 , HD and H_2 eliminations are observed in different proportions. The latter products suggest that either a 1,2-elimination to form a metal-butene complex in analogy with Scheme I is occurring or scrambling occurs in Scheme II before hydrogen elimination, or both.¹¹ Since the two pathways can be viewed as representing fundamentally different modes of initial interaction of a metal ion with a saturated hydrocarbon, it is of interest to determine the relative importance of 1,2- vs. 1,4-elimination.¹²

To complement the ICR and low-energy ion beam results, the product translational energy distributions for the metastable loss of hydrogen from nascent metal ion-butane complexes have been studied.¹³ In Figure 1, kinetic energy release distributions associated with the metastable loss of HD from nascent (2-methylpropane-2- d_1)cobalt(+) (1,2-elimination) and loss of D_2 from (butane-1,1,1,4,4,4- d_6)nickel(+) (1,4-elimination) are compared.¹⁴ The shape and average kinetic energy release¹⁴ (0.20 eV) for HD loss from (2-methylpropane-2- d_1)cobalt(+) (Figure 1a) is quite distinct from the D_2 loss from (butane-1,1,1,4,4,4- d_6)nickel(+) (Figure 1b), which occurs with an average energy release of 0.40 eV. The maximum energy release of 1.4 eV for the 1,4-process is close to the estimated ΔH for the reaction.¹⁵

(5) (a) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360. (b) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565.

(6) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818.

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(8) (a) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197. (b) *J. Am. Chem. Soc.* **1983**, *105*, 736.

(9) Halle, L. F.; Houriet, R.; Kappes, M. M.; Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6293.

(10) (a) Larsen, B. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912. (b) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129.

(11) This assumes that no scrambling occurs with 1,2-elimination from *n*-butane. (No scrambling is observed with 1,2-elimination from isobutane.)

(12) This methodology is complementary to other techniques that provide more direct product structural information, such as the determination of the relative amounts of mono- and bis(olefin) products in the dehydrogenation of alkanes.⁸⁻¹⁰

(13) Experiments were conducted at UCSB on a reverse-geometry double-focusing mass spectrometer previously described. See: Illies, A. J.; Bowers, M. T. *Chem. Phys.* **1982**, *65*, 281. Illies, A. J.; Jarrold, M. F.; Bass, L. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 5775. Metal ions were produced by 150-eV electron impact on $\text{Co}(\text{CO})_3\text{NO}$ and $\text{Ni}(\text{CO})_4$. Metal butane adducts were formed in a high-pressure source operated typically at 10^{-4} torr of total pressure. Under these conditions metal-alkane clusters were formed and extracted from the source before undergoing subsequent collisions.

(14) For details on kinetic energy release distribution calculations, see: Jarrold, M. F.; Illies, A. J.; Kirchner, N. J.; Wagner-Redeker, W.; Bowers, M. T.; Mandich, M. L.; Beauchamp, J. L. *J. Phys. Chem.* **1983**, *87*, 2213 and references therein.

† The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

(1) Contribution 7082.

(2) Permanent address: Department of Chemistry, Auburn University, Auburn, AL 36849.

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(4) (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (b) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963.