transition in the pure copper complexes and for the close similarity of the transition temperatures in the ClO_4^- and BF_4^- salts is obtained from bulk susceptibility measurements in powder samples. Figure 2 illustrates a Curie–Weiss plot for the perchlorate salt and indicates that the susceptibility cannot be adequately described with a single Weiss constant. The plot for the tetrafluoroborate salt is essentially the same.

A similar well-defined phase transition has been observed in the temperature variation of the single-crystal magnetic anisotropy of $Cu(en)_3SO_4$,[15] and the transition temperature correlates very well with that observed for the dynamic to static change in the ESR spectra.

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Registry No. $Cu(C_5H_5NO)_6(ClO_4)_2$, 14245-15-9; $Zn(C_5H_5NO)_6(BF_4)_2$, 23013-69-6; $Cu(C_5H_5NO)_4(MeCN)_2^{2+}$, 68876-54-0.

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Gas-Phase Photodissociation of $(\eta^5\text{-}C_5H_5)NiNO^+$

Sir:

Ion cyclotron resonance spectroscopy[1,2] (ICR) has proven to be invaluable in the study of gas-phase ion photochemistry. In particular, by monitoring photodissociation process 1 as a

$$AB^+ + h\nu \rightarrow A^+ + B \qquad (1)$$

function of wavelength, the photoexcitation spectrum is obtained. From such studies, a wide range of spectroscopic, thermodynamic, kinetic, and dynamic information about ions can be derived.[3-8] While numerous photochemical studies utilizing ICR have been reported for organic ions, only a few studies have been reported for ions generated from transition-metal complexes. The latter studies have been limited to transition-metal carbonyl anions and have yielded mainly interesting qualitative information.[7,8]

In this paper we report application of ICR photodissociation techniques to determining the binding energy of NO to $(\eta^5\text{-}C_5H_5)Ni^+$, hereafter referred to as $CpNi^+$, and to the determination of two low-lying excited states of $CpNiNO^+$ which indicate the potential of this method for obtaining such quantitative, as well as qualitative, information about this important class of compounds.

The availability of the photoelectron spectrum of CpNiNO[9] and a precise determination of $D(NO\text{–}CpNi^+) = 45.9 \pm 1.0$ kcal/mol obtained recently from photoionization experiments[10] in conjunction with elegant ICR trapped-ion gas-phase equilibrium measurements[11] made $CpNiNO^+$ a logical candidate for initiating our photochemical studies in this exciting area.

The cyclopentadienylnickel nitrosyl parent ion, $CpNiNO^+$, was generated from the neutral compound at an electron energy of 20 eV. Trapping times were typically 1.5 s and CpNiNO pressures were $\leq 1 \times 10^{-7}$ torr. Upon irradiation, the parent ion undergoes photoreaction 2. Interference from

$$CpNiNO^+ + h\nu \rightarrow CpNi^+ + NO \qquad (2)$$

other species present[11] was not observed. The photodissociation spectrum of $CpNiNO^+$, obtained by monitoring the disappearance of $CpNiNO^+$ in reaction 2 as a function of wavelength at 10-nm resolution,[12] is compared in Figure 1 with the photoelectron spectrum of CpNiNO reported by Evans et al.[9] The photodissociation spectrum represents an average of several runs, and the energy axis of the photoelectron spectrum is adjusted such that the first adiabatic ionization potential of CpNiNO is zero on the photodissociation energy scale.

As shown in Figure 1, there is an overlap between the photoexcitation curve and the state assigned by Evans et al. as arising from ionization from a C 2pσ type orbital having e_2 symmetry. This overlap suggests (but not unequivocably) that the observed transition at 4.13 eV (300 ± 10 nm) is $^2E_1 \rightarrow {}^2E_2$ (ligand-localized transition) electric dipole allowed along the x,y axes. In contrast, the photodissociation maximum in Figure 1 at 2.35 eV (530 ± 10 nm) does not overlap precisely with the photoelectron spectrum and suggests a transition of an electron to an unfilled orbital not detailed by PES. Alternatively, this behavior can be explained by the fact that the photodissociation band is in the vicinity of the thermodynamic threshold.[6] The onset for photodissociation observed at 1.9 ± 0.1 eV (≃660 nm) yields an upper limit on the bond dissociation energy of $D(NO\text{–}CpNi^+) \leq 43 \pm 3$ kcal/mol, in good agreement with the photoionization results. The addition of collision gases was found to have no significant effect upon the threshold region.

In summary, photodissociation is a powerful method for yielding absorption information about gas-phase metal-ion complexes. This initial study also indicates the utility of

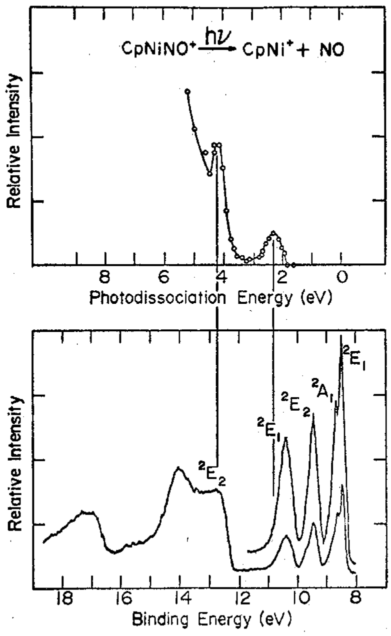

Figure 1. Comparison of the photodissociation spectrum of $CpNiNO^+$ to the photoelectron spectrum of CpNiNO. The energy axis of the photoelectron spectrum is adjusted such that the first adiabatic ionization potential of CpNiNO is zero on the photodissociation energy scale.

photodissociation for determining upper limits on metal–ligand bond energies.[13] The technique will not only aid complementary methods such as photoionization but also in some instances may be the only way to make the measurement, especially in those systems where a stable, neutral parent molecule is difficult to generate. We are currently investigating the photochemistry of $CpNi^+$ bound to a range of n- and π-donor bases to determine upper limits on bond dissociation energies and the effect of various bases on the transitions observed. In addition, experiments on methyl-substituted CpNiNO, where substitution lowers the ionization potential of electrons localized on the cyclopentadienyl moiety relative to those on the metal, will clarify the tentative transition assignments and photoelectron orbital assignments reported above.

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(12) A 3.5-kW mercury–xenon arc lamp was used in conjunction with a Schoeffel 0.25-m monochromator. Two gratings were employed in order to cover the full wavelength range. A cutoff filter was also used at long wavelengths to eliminate second-order radiation from the monochromator.
(13) Photodissociation yields only an upper limit on the metal–ligand bond energy since an absorption band may not lie at an energy in the vicinity of the thermodynamic threshold for dissociation. For $CpNiNO^+$, an absorption band does occur in the thermodynamic threshold region.

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Molecular Structure of Tetracyclohexylsilane

Sir:

In species of the type R_4M, where R is a twofold rotor, the molecular symmetry must be a subgroup of D_{2d}[1] and is usually found to be S_4. This is the case for the tetraphenyl compounds of C,[2] Si,[3] Ge,[4] Sn,[5] and Pb,[6] for tetraphenylphosphonium,[7] -bismuthonium,[8] and -arsonium[9] ions, for tetrakis(pentafluorophenyl) compounds of Si,[10a] Ge,[10b] and Sn,[10b] for tetrakis(4-methylphenyl)tin,[11] tetranitromethane,[12] tetraphenylborate,[13] and, to a close approximation, for tetramesitylvanadium.[14] This marked preference for S_4 symmetry is maintained even when the local symmetry of the ligand R is lowered from (essentially) C_{2v} to C_s; in that case, the most stable arrangement seems to be one in which the four R groups arrange themselves in an all-exo conformation,[1] leading to molecular S_4 symmetry. This is what is found by X-ray crystallography for tetrakis(3-methylphenyl)tin[15] and for the tetra-2-thienyl compounds of Si,[16a] Ge,[16b] Sn,[16b] and Pb[16b] and what is found by empirical force field calculations[1] for tetrakis(2-methylphenyl)methane and -silane.

In light of this overwhelming predilection for S_4 symmetry, a recent report[17] that tetracyclohexylsilane (**1**) assumes a C_2 conformation takes on special significance. The purpose of this communication is to demonstrate that although the exact crystallographic symmetry of **1** is C_2, the molecular conformation is in fact very near S_4 and therefore fits into the general pattern described above.

Starting from a D_{2d} conformation (Figure 1, top),[18] we can obtain a structure with D_2 symmetry by twisting all four cyclohexyl groups in the same sense and to the same extent. A structure with S_4 symmetry is obtained by twisting pairs of groups to the same extent but in opposite directions. To obtain C_2 symmetry, the pairs of groups must be twisted to different extents. In the reported[17] X-ray structure of **1**, two of the dihedral angles, C(2)–C(1)–Si–C(1^a) and C(8)–C(7)–Si–C(7^a) (cf. Figure 1, bottom), were found to have values of −56.2 and −71.0°, respectively, from which it was concluded[17] that two of the rings were "twisted by about 15° from an "idealized" S_4 conformation". However, these two dihedral angles are not related by an S_4 operation. The symmetry-related angles are C(2)–C(1)–Si–C(1^a) and C(12)–C(7)–Si–C(7^a), and C(8)–C(7)–Si–C(7^a) and C(6)–C(1)–Si–C(1^a). In each pair, the values are expected to be of equal magnitude, but oppositely signed. Values for these angles[19] are found to be −56.2, 57.7, −71.0, and 72.1°, respectively. Thus, although **1** lies in a crystallographic site of C_2 symmetry and is therefore not constrained to adopt a symmetry higher than C_2, the deviation from S_4 symmetry is in fact negligible, i.e., less than 2°.

We further note that the values of dihedral angles H(1)–C(1)–Si–C(1^a) and H(12)–C(7)–Si–C(7^a) are −171.7 and 172.8°, respectively. Thus the cyclohexyl groups are twisted by 7–8° from a D_{2d} conformation.

To determine whether S_4 symmetry is also maintained in the isolated molecule, we performed empirical force field (EFF) calculations[20] on **1**. The ground state was found to have

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