Table I. Exponents and Parameters Used in the Calculations

	χ_μ	ζ_μ	$H_{\mu\mu}$, eV
Sb	5s	2.323[20]	-18.8[21]
	5p	1.999	-11.7
C	2s	1.625	-21.4
	2p	1.625	-11.4
H	1s	1.3	-13.6

tivity[1] and resemble thereby the "organic metal" D-A complexes and D_2X salts.

Should the stacks of stibaphenalenyl remain one-dimensional, they would most likely be subject to CDW instabilities and undergo a metal-to-semiconductor transition at low temperatures. It is likely, however, that owing to the existence of several fractionally filled bands—some of which with a lone-pair character, **23**—the stacks will tend to interact with each other via Sb- - -Sb contacts and provide the solid with two-dimensionality, which would suppress the CDW instabilities.

There is a promise in such compounds that draws on the unique odd alternant network[2] and the presence of Sb atoms. The gradually expanding arsenal of Sb compounds and their understanding[5-8] offer some substantial benefits to the field of organometallic conductors. Thus, the incorporation of Sb (Bi) atoms into the network of conjugated organic molecules can generate compounds with low HOMO-LUMO gaps that may possess thereby (a) an inherent tendency to stack and existence of partially filled bands like the stibaphenalenyls and (b) a small tendency toward intramolecular structural localization[3c] (or small polaron binding energy[2]). In addition such molecules should be easy to both reduce and oxidize, which will lead thereby to conducting salts with two charge types.

Acknowledgment. We thank the CIRCE (Orsay) for computing facilities and M.-H. Whangbo and the Organic Metals Group at BGU for useful discussions.

Appendix

The calculations are of the extended Hückel type for both molecular[17] and extended[18] systems. The modified Wolfsberg-Helmholz formula[19] was used. Exponents and parameters employed in the calculations are those of Table I. The Sb-C and C-C bond distances were taken to be 2.05[5a] and 1.40 Å, respectively.

Registry No. **2**, 110433-48-2.

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Contribution from the Departments of Chemistry, Purdue University,
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Two-Photon Photochemistry of $[Cu(dmp)_2]^+$

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Solutions of $[Cu(dmp)_2]^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline) in methylene chloride were observed to bleach upon exposure to high-intensity 354.7-nm pulsed-laser irradiation. The intensity dependence of the observed bleaching indicates a biphotonic process in which the second photon is absorbed by a relatively long-lived charge transfer to ligand excited state. $[Cu(dmp)_2]^{2+}$ and Cl^- appear to be formed with 1:1 stoichiometry as a result of an outer-sphere electron-transfer reaction between a high-lying excited state of the complex and a methylene chloride molecule that is presumably located in the secondary solvation shell. Bleaching, albeit less efficient, is also observed in acetonitrile, but the complex appears to be photoinert in methanol, even at very high laser intensities.

Introduction

Complexes of the type $[Cu(NN)_2]^+$, where NN denotes a heteroaromatic ligand such as 1,10-phenanthroline, are members of a class of systems that exhibit low-lying charge-transfer (CT) excited states that participate in a variety of electron-transfer processes.[1-3] In the case of the copper(I) complexes, the excitation is from (largely) metal-based orbitals to (largely) ligand-based orbitals, and the formally reduced ligand centers that result have been found to function as potent reducing agents. Net photoinduced reduction of Co(III)[4,5] and the transient reduction of Cr(III)[6] centers have been observed in solution. These systems have also been used to sensitize photocurrents at semiconductor electrodes[7,8] and, in the presence of appropriate catalysts, the formation of H_2 from H^+.[9] In addition, they have been found to undergo a novel type of exciplex quenching in the presence of Lewis bases.[10-12] For this reason most emission work has been carried out in weakly basic solvents such as CH_2Cl_2.

In an attempt to characterize the molecular and electronic structures of the $[Cu(NN)_2]^+$ systems further, we have sought to measure the time-resolved resonance Raman spectrum of photoexcited $[Cu(dmp)_2]^+$ where dmp denotes 2,9-dimethyl-1,10-phenanthroline. However, in the course of this work we have discovered that two-photon photochemistry can be induced by high-intensity laser excitation. This chemistry, which involves reductive cleavage of methylene chloride, is the subject of this report.

Experimental Section

Materials. $[Cu(dmp)_2]BF_4$, $[Cu(dmp)_2]NO_3 \cdot 2.5H_2O$, and $[Cu(phen)_2]BF_4$ (phen = 1,10-phenanthroline) were prepared by a previously reported procedure.[4a] Methylene chloride and methanol were obtained from Burdick and Jackson; the acetonitrile was from Mallinckrodt. N_2O was obtained from Matheson.

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Instrumentation. Laser irradiations were carried out by using a Nd:YAG laser (Quanta Ray DCR-1) equipped with a Quanta-Ray HG-1 harmonic generator. The 354.7-nm radiation was obtained directly from the harmonic generator, while 416.0- and 502.9-nm photons were obtained as the first and second Stokes-shifted lines of the 354.7-nm beam passed through a high-pressure cell containing H_2. Laser pulse energies were monitored periodically during photolyses with a Scientech Model 362 power/energy meter. The emission intensity from $[Cu(dmp)_2]^+$ was monitored by a fast photodiode whose output was fed into the signal channel of a Quanta-Ray DGA-1 dual-gated amplifier. In the stoichiometry and N_2O studies, a Lambda Physik Excimer (EMG 202) pumped dye laser (FL 3002) was used. The use of stilbene 420 provided 425-nm photons. Arc lamp irradiations were carried out by using apparatus previously described,[4b] but modified by substitution of an Oriel 66020 lamp housing and Oriel 68730 power supply.

Ion chromatography experiments were carried out on a Wescan Ion Chromatography System I consisting of a Versa-Pump II HPLC pump, an ion-guard precolumn, a standard anion column and a Model 213A high-sensitivity conductivity detector. UV–vis measurements were made by using either a Cary 17D or a GCA-McPherson EU-700 series spectrophotometer.

Methods. Photolyte concentrations were typically in the 10^{-4} M range. Solutions were deoxygenated either by bubbling with N_2 for 15–20 min (for bulk solutions) or by repetitive freeze/pump/thaw cycles. A flow system consisting of a syringe pump, a 50-mL syringe, Teflon tubing and a 7-cm length of 3-mm-i.d. quartz tubing was assembled for laser photolyses and intensity dependence studies. The emission studies were also carried out by using the flow system. In all cases the laser beam was focused such that the beam diameter was 3 mm at the front face of the quartz tube and was diverging. Flow rates were maintained at 2.0 mL min^{-1} with a linear flow rate of less than 0.5 cm s^{-1}. With a 10-Hz repetition rate, all volume elements of the flowing solution were uniformly irradiated. Irradiated samples were collected directly in a 1-cm spectrophotometer cell for absorbance measurements.

In the excitation wavelength dependence studies, absorbance-matched samples were deoxygenated by three freeze/pump/thaw cycles and equal volumes were irradiated with stirring. Laser intensities at the three wavelengths were adjusted to maintain a constant photon flux. Changes in the absorbance of $[Cu(dmp)_2]^+$ at 454 nm (ΔA_{454}) were monitored on the Cary 17D instrument, and the apparent photochemical action at a particular wavelength for a constant photon flux was calculated as ΔA_{454} divided by the elapsed time (Δt) that the sample was in the sample holder of the laser system, divided by the concentration of complex. In like fashion the (apparent) rate of bleaching was calculated as $\Delta A_{454}/\Delta t$.

Studies of the $Cl^-/[Cu(dmp)_2]^{2+}$ stoichiometry were carried out in methylene chloride with 1×10^{-4} M solutions of $[Cu(dmp)_2]BF_4$, which were previously deoxygenated by repetitive freeze/pump/thaw cycles. A series of solutions were photolyzed for varying time periods, and the change in concentration of $[Cu(dmp)_2]^+$ was determined by the change in absorbance (corrected for the absorbance of $[Cu(dmp)_2]^{2+}$) at 454 nm. The solutions were then evaporated to dryness. The residue was then extracted with water, and the concentration of aqueous chloride was determined by ion chromatography.

In order to observe the absorption spectrum of the copper-containing photolysis product(s) of $[Cu(dmp)_2]BF_4$ and $[Cu(dmp)_2]NO_3 \cdot 2.5H_2O$, the solvent was removed after exhaustive photolysis. The residue was washed with methylene chloride and cold methanol to remove any remaining $[Cu(dmp)_2]^+$ and the residue was then taken up in an aqueous solution for the absorption measurements.

To regenerate $[Cu(dmp)_2]^+$ in photolyzed solutions, we added hydroquinone. Complete recovery required a period of days if an exhaustively photolyzed sample was used. Two attempts to detect the solvated electron were made. One involved a 1×10^{-4} M solution of $[Cu(dmp)_2]BF_4$ in methanol while the other was a 5×10^{-5} M solution of the same salt in 50% by volume aqueous methanol. The solutions were saturated with N_2O by bubbling for 30 min before photolysis.

Results

In the absence of O_2, CH_2Cl_2 solutions of the nitrate or the tetrafluoroborate salts of $[Cu(dmp)_2]^+$ are indefinitely stable both in the dark and in light.[4c] In this study we found the same solutions, in air or under nitrogen, are unaffected by exposure to 355-nm radiation from an arc lamp (ca. 10^{-8} einstein s^{-1}) for several hours. On the other hand, when deaerated CH_2Cl_2 solutions are exposed to 354.7-nm pulsed-laser irradiation at 10 Hz (ca. 1.3×10^{-8} einstein/pulse with a 7-ns fwhm), measurable bleaching occurs within seconds and complete bleaching of the CT absorption band occurs within several minutes (see Figure 1).

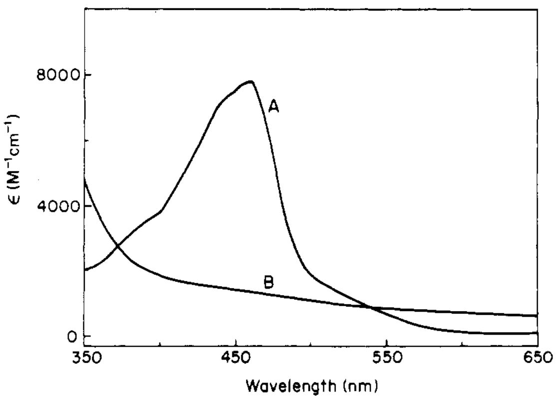

Figure 1. Electronic absorption spectrum of $[Cu(dmp)_2]^+$ in CH_2Cl_2 at 20 °C before (A) and after (B) 5 min of exposure to 354.7-nm pulsed irradiation (ca. 4.5 mJ/pulse; 10 Hz) in a spinning sample tube.

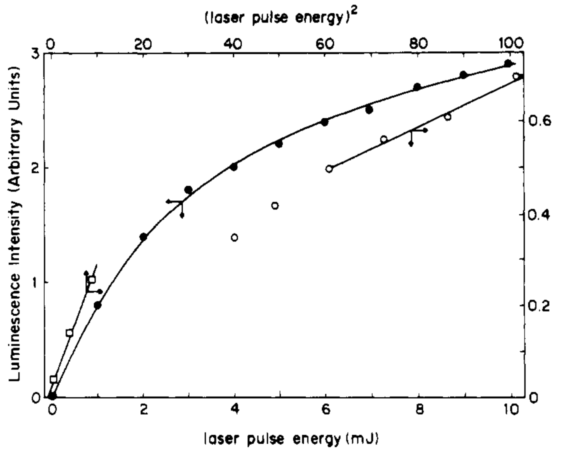

Figure 2. Relative luminescence intensity from $[Cu(dmp)_2]^+$ in CH_2Cl_2 at 20 °C versus laser output at 354.7 nm (●). Also plotted is the rate of change of the absorbance at 454 nm as different functions (□ and ○) of the energy of the laser pulse. The absorbance measurements were made on samples collected with the flow system with the flow rate held constant.

One of the photoproducts was $[Cu(dmp)_2]^{2+}$ as indicated by the absorbance that grows in at 740 nm[13] as well as the fact that the addition of excess hydroquinone led to the regeneration of $[Cu(dmp)_2]^+$. Ion chromatography established that Cl^- was another photoproduct. Analysis of a series of runs indicated that 1.2 ± 0.3 mol of chloride were formed per 1 mol of $[Cu(dmp)_2]^+$ consumed.

The reaction efficiency was found to be solvent-dependent. In mixed solvents containing 4% methanol or 50% acetonitrile in CH_2Cl_2 (both v/v), the bleaching occurred at almost the same rate as it did in neat CH_2Cl_2. However, in neat acetonitrile the bleaching rate was about 10 times slower, and in neat methanol no bleaching could be detected even with intensities of 20 mJ $pulse^{-1}$. The rate of bleaching was also examined as a function of laser pulse energy. As can be seen from Figure 2, for a fixed irradiation period the rate of change in absorbance initially varied as the second power of the laser output (□), but at high pulse energies the dependence was linear (○). More specifically, when $[Cu(dmp)_2]^+$ was irradiated with pulse energies <3 mJ, a plot of ln ΔA versus ln P, where P is the pulse energy, was linear with a slope of 1.7. For solutions containing $[Cu(phen)_2]^+$ the corresponding plot had a slope of 2.0.

The luminescence intensity from a solution of $[Cu(dmp)_2]^+$ also exhibited a complex dependence on the laser pulse energy (Figure 2). At relatively low pulse energies the emission intensity (●) increased with increasing pulse energy. However, at higher pulse

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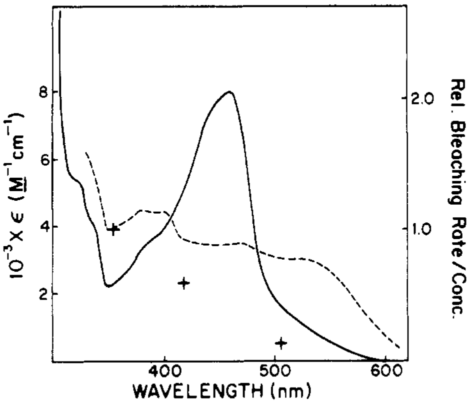

Figure 3. Ground-state (—) and excited-state[23] (- - -) absorption spectra of $[Cu(dmp)_2]^+$ in CH_2Cl_2 at 20 °C. A partial action spectrum (+), expressed as the bleaching rate per unit copper concentration relative to that at 354.7 nm, is also plotted. The scale is arbitrarily chosen so that the action spectrum meets the excited-state absorption spectrum at 354.7 nm. The experimental error for each point of the action spectrum is ±15% based on the instability of the laser pulse energy.

energies the luminescence intensity leveled off due to saturation of the CT excited state.

Finally, the rate of bleaching was also found to be dependent upon the exciting wavelength. To investigate this effect, a series of three deaerated solutions of $[Cu(dmp)_2]^+$ in CH_2Cl_2 were prepared and irradiated at different wavelengths. The concentration of complex was adjusted so that the absorbances were initially the same at the respective photolysis wavelengths—354.7, 416.0, or 502.9 nm. When a constant laser flux (ca. 8×10^{15} photons/pulse) was used to irradiate a fixed volume of solution, the bleaching rate increased as the exciting wavelength decreased (Figure 3).

Discussion

Reactant States and Products. Various observations suggest that the following photoreaction occurs in CH_2Cl_2:

$$[Cu(NN)_2]^+ + 2h\nu + CH_2Cl_2 \rightarrow [Cu(NN)_2]^{2+} + Cl^- + \text{prod.} \quad (1)$$

where prod. denotes unidentified product(s) derived from the $ClCH_2$ radical. Solvent is implicated because it is the only feasible source of chloride ion. Net oxidation of $[Cu(NN)_2]^+$ is confirmed because the product exhibited the visible absorption spectrum of $[Cu(dmp)_2]^{2+}$ and because addition of a reducing agent after photolysis restores the absorbance of $[Cu(NN)_2]^+$. Consistent with the proposed products, the reductive cleavage of carbon–halogen bonds is known to lead to the release of halide ions.[14-16] Within the experimental error, the analytical data establish that $[Cu(dmp)_2]^{2+}$ and Cl^- form with 1:1 stoichiometry.[17]

The fact that very high photon fluxes are required for reaction suggests that a two-photon process may be involved, and the dependence of ln ΔA on ln P supports this interpretation. Ordinarily, if a multiphoton process is involved, the rate of reaction is expected to vary as I^n, where I is the beam intensity and n denotes the number of photons involved.[18] In fact, the slope of a ln ΔA vs ln P plot is 2.0 for solutions of $[Cu(phen)_2]BF_4$. On the other hand, for $[Cu(dmp)_2]BF_4$ the corresponding plot has a slope of 1.7 for low laser powers, and the slope approaches 1.0 at high laser powers. This type of behavior can occur when two photons are absorbed sequentially, and the intervening resonant state is subject to saturation.[19] The power dependence of the luminescence intensity (Figure 2) provides independent evidence that the CT state becomes saturated at the higher powers. The difference in behavior of the two complexes can be understood in terms of the excited state lifetimes. The CT excited state of $[Cu(dmp)_2]^+$ is relatively long-lived in CH_2Cl_2 ($\tau \simeq 90$ ns); hence, saturation can occur. The lifetime of $[Cu(phen)_2]^+$ is unknown, but it is likely to be at least 10 times shorter because it gives no measurable luminescence in solution, consistent with the greater degree of exposure of the metal center.[12] Thus, saturation should be much more difficult to achieve. Observation of the saturation effect in the case of $[Cu(dmp)_2]^+$ is important because it establishes that the photoreaction stems from an excited state involving the copper complex. In principle, two-photon absorption by the solvent is also feasible, but no saturation effect could occur as there is no resonant state of the solvent above 230 nm.

Mechanism of Reaction. A charge transfer to solvent excited state could conceivably be involved, and it would explain the solvent dependence of the reaction. Thus, polychlorinated alkanes react much more rapidly with the solvated electron ($k > 10^{10}$ M^{-1} s^{-1}) than does CH_3CN ($k = 3 \times 10^7$ M^{-1} s^{-1}) or CH_3OH ($k < 10^4$ M^{-1} s^{-1}).[20] In fact these rates parallel the reaction efficiencies as a function of solvent:

$$CH_2Cl_2 > CH_3CN \gg CH_3OH \quad (2)$$

With this model the lack of reaction in methanol can be explained if the solvated electron recombines with $[Cu(dmp)_2]^{2+}$ in preference to reacting with solvent. However, no net reaction occurs when N_2O is added as a scavenger for the solvated electron either, even though the concentration of N_2O must be much larger than that of $[Cu(dmp)_2]^{2+}$.

In the absence of any indication of the formation of solvated electrons, we assume instead that two-photon absorption populates a high-lying, reactive excited state of the complex. A common idea is that the reduction of alkyl halides by transition-metal complexes involves coordination of the halogen at the metal center followed by reductive cleavage of the carbon-halogen bond.[14-16] Such an "inner-sphere" mechanism could apply here since the CT excited states of $[Cu(NN)_2]^+$ complexes are prone to the association of a fifth donor atom.[11,21] However, the results obtained in the mixed-solvent systems suggest that inner-sphere complex formation is not a crucial step in the photoreaction. This follows because methanol and acetonitrile are known to bind efficiently with the CT excited state of $[Cu(dmp)_2]^+$,[10-12] yet the reaction yield decreases by only a few percent even in 50:50 CH_3CN/CH_2Cl_2 solution.

These findings suggest that an outer-sphere electron transfer is involved. The following series of reactions represents a minimal kinetic scheme:

$$[Cu(dmp)_2]^+|S \xrightarrow{I} {}^*[Cu(dmp)_2]^+|S \quad (3)$$

$${}^*[Cu(dmp)_2]^+|S \xrightarrow{k_d} [Cu(dmp)_2]^+|S + \text{energy} \quad (4)$$

$${}^*[Cu(dmp)_2]^+|S \xrightarrow{I'} {}^{**}[Cu(dmp)_2]^+|S \quad (5)$$

$${}^{**}[Cu(dmp)_2]^+|S \xrightarrow{k_d'} {}^*[Cu(dmp)_2]^+|S + \text{energy}' \quad (6)$$

$${}^{**}[Cu(dmp)_2]^+|S \xrightarrow{k_r} [Cu(dmp)_2]^{2+} + \text{products} \quad (7)$$

In this scheme $[Cu(dmp)_2]^+|S$ denotes the ground-state complex and one of the solvent molecules in the secondary solvation shell. The species with asterisks denote excited states. I and I' denote pumping rates, k_d and k_d' are relaxation rates, and k_r is an electron-transfer rate. High laser intensities are required because eq 5 cannot compete with eq 4 unless a high photon flux is used. The solvent dependence reflects the competition between eq 6 and

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7 and/or eq 4 and 5. In principle, the magnitudes of both k_d' and k_r may be solvent-dependent, but it is clear that the k_r step must be quite rapid if it is to compete with relaxation of a higher energy excited state. This is feasible since the k_r represents the rate constant of an outer-sphere electron-transfer reaction involving a very potent reducing agent.

Although only three data points have been measured, the partial action spectrum depicted in Figure 3 suggests that a more complex reaction scheme may actually be required. Since the data were collected under conditions in which the CT state is nearly saturated, the points might be expected to track the excited-state absorption spectrum;[22] however, the data do not follow the published excited-state absorption spectrum (Figure 3).[23] This may indicate that there is more than one reactive excited state or that the efficiency with which the reactive state is populated depends upon the exciting wavelength. Clearly more work will be needed before the dynamics can be understood in detail.

In conclusion, we may note that multiphoton photochemistry may be a common complication associated with photophysical studies using high power lasers. Possibly related biphotonic reactions have previously been reported for $[Ru(bpy)_3]^{2+}$,[24] $[Pt_2(POP)_4]^{4-}$,[25] and $[Cr(bpy)_3]^{3+}$.[26] Since the completion of this work an excited state resonance Raman spectrum of $[Cu(dpp)_2]^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline) in methanol has been described.[27]

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Registry No. $[Cu(dmp)_2]^+$, 21710-12-3; $[Cu(dmp)_2]^{2+}$, 14875-91-3; Cl^-, 16887-00-6; CH_2Cl_2, 75-09-2; CH_3CN, 75-05-8; CH_3OH, 67-56-1.

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Interaction between Iron(0) and Heterocumulenes: "Ab Initio" Calculations on the Model Compounds $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCX)$ and $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCX)$, with X = O, S, NH, CH_2

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"Ab initio" calculations have been performed on the model systems $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCX)$ and $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCX)$, with X = O, S, NH, CH_2, to investigate the nature and the energetics of the interaction between iron and heterocumulenes. The results indicate that the main bonding interaction between the fragment $Fe(CO)_2(PH_3)_2$ and the unsaturated molecule is the π back-donation from the transition metal to the π-acceptor ligand and the strength of this coordination bond is found to increase on going from OCX to SCX. In carbonyl sulfide compounds, the stronger back-donative interaction arising in η^2-C,S coordination favors this binding mode over η^2-C,O coordination, and this has been confirmed by partial geometry optimization gradient calculations. Both the weaker π back-donation and the higher deformation energy of CO_2 upon coordination are found to be equally important factors in explaining the low tendency of carbon dioxide, compared to that of CS_2, to bind to transition-metal substrates. The delocalization of electron density on the heterogroup X increases on going from X = CH_2 to X = S in the two studied series of compounds. This trend is found to be strictly related to the different reactivities of the coordinated heterocumulene ligands.

Introduction

The activation of heterocumulenes promoted by transition-metal complexes is a problem of particular interest in organometallic chemistry since heterocumulenes imitate CO_2 in many respects and, therefore, their activation should provide useful information on the problem of CO_2 fixation, which despite intense research activity is not yet completely understood.[1-5] In this context, many interesting studies, which present the synthesis of several transition-metal complexes with heterocumulenes, such as phenyl isothiocyanate and diphenylketene, have recently been reported.[6-16]

Theoretical investigations are limited, at present, to some studies of the interaction between a transition metal and carbon dioxide, carbonyl sulfide, and carbon disulfide.[17-20] These works have clarified that the type of interaction between the transition metal and the unsaturated molecule lies at the very extreme of the Chatt-Dewar-Duncanson model,[21] being dominated by the back-donation from the metal to the heterocumulene. The π back-donation represents the main contribution to the binding energy, and the distortion of the unsaturated ligand upon coordination enhances the stabilization by increasing this interaction.

In this paper we present a theoretical study of the interaction of a transition metal with CO_2 and a series of molecules struc-

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