There are very likely some complexes for which the BISC pathway dominates.

Note Added in Proof. Waltz and co-workers[65] have just reported the first direct evidence for the generation of a chemically active intermediate as the product of (^2E)Cr(III) excited-state relaxation. These workers find that an aquated, apparently 7-coordinate complex with a lifetime longer than $\tau(^2E)$ is formed in the thermally activated relaxation of *cis*-(^2E)-Cr([14]aneN$_4$)(NH$_3$)$_2$$^{3+}$ under ambient conditions in water.

(65) Waltz, W. L.; Lee, S. H.; Friesen, D. A.; Lilie, J. *Inorg. Chem.* **1988**, *27*, 1133.

Kinetic and Spectroscopic Studies of Mo(CO)$_2$(PR$_3$)$_2$Br$_2$ Compounds

Richard S. Herrick,* Christopher H. Peters, and Ronald R. Duff, Jr.

Flash-photolysis and stopped-flow experiments are reported for a series of aryl-, alkyl-, and mixed aryl–alkylphosphine derivatives of Mo(CO)$_3$(PR$_3$)$_2$Br$_2$. The photochemically generated dicarbonyl transient rapidly recombines with carbon monoxide under a CO atmosphere to re-form the tricarbonyl via the rate law $R = k[Mo(CO)_2(PR_3)_2Br_2][CO]$. Bimolecular rate constants between 2.5×10^3 and 7.3×10^5 M^{-1} s^{-1} were measured in 1,2-dichloroethane. The natural logarithm of the rate constants for CO recombination fit a two-parameter free energy relationship based on the electronic and steric nature of the phosphines. Electron-donating and sterically bulky phosphines inhibit reaction. There is a pronounced solvent effect on the reactivity and the electronic spectrum of dicarbonyl compounds. Hexane as solvent accelerates the reaction while methanol essentially quenches it relative to 1,2-dichloroethane. Electronic spectral measurements show that λ_{max} for the HOMO–LUMO transition shifts from 570 nm in CH$_2$Cl$_2$ to 755 nm on Teflon (diffuse-reflectance spectrum). These observations are consistent with solvent interaction with the LUMO.
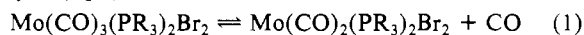
Introduction

The study of formally electron-deficient group 6 d^4 complexes has recently enjoyed renewed interest in an effort to explain their counterintuitive stability. Among the systems that have been studied are the 6-coordinate compounds with the general formula M(CO)$_n$(RC≡CR)$_{2-n}$L$_2$X$_2$ (L$_2$X$_2$ = (PR$_3$)$_2$X$_2$, n = 1, 2;[1] L$_2$X$_2$ = (S$_2$CNR$_2$)$_2$, n = 0, 1, 2;[2] L$_2$X$_2$ = (π-C$_5$H$_5$)X, n = 0, 1;[3] M = Mo, W; X = Cl, Br, I). Non-6-coordinate 16-electron d^4 compounds have also been reported and generally have π-base alkyne ligands as in Mo(S-*t*-Bu)$_2$(CN-*t*-Bu)$_2$(RC≡CR).[4] Crystallographic,[5] spectroscopic,[6] theoretical,[5b,7] and electrochemical[8] studies

have contributed greatly to an understanding of this stability now known to stem from the presence of both π-acid and π-base ligands or from severe distortion away from an ideal geometry.

Surprisingly, little mechanistic research has been reported for these compounds. A study of the reaction of alkynes with electron-deficient Mo(CO)(RC≡CR)(S$_2$CNR$_2$)$_2$ compounds[9] demonstrated that substitution for carbon monoxide proceeds by a slow dissociative process while alkyne exchange proceeds by a faster associative step. The π-base alkyne ligand controls the reactivity by either stabilizing the 14-electron intermediate after CO loss or preferentially dissociating from the 18-electron intermediate following alkyne addition due to loss of the alkyne π-donor interaction in the saturated intermediate.

Kinetic studies have not been reported for systems containing no strongly π-donating ligand. We have initiated a mechanistic study of this class of electron-deficient compounds to explore their reactivity toward Lewis base nuelcophiles. We chose to begin with a study of the addition of CO to Mo(CO)$_2$(PR$_3$)$_2$Br$_2$. This is a useful starting point because the compounds are isolable, have been amply characterized, contain simple monodentate ligands, and are in equilibrium with the corresponding 18-electron tricarbonyl[10] (eq 1).

$$Mo(CO)_3(PR_3)_2Br_2 \rightleftharpoons Mo(CO)_2(PR_3)_2Br_2 + CO \quad (1)$$

This paper gives the results of flash-photolysis studies of the tricarbonyl in the presence of excess carbon monoxide. Reaction rates of the photochemically generated dicarbonyl with carbon monoxide were determined by watching the disappearance of the d–d absorbance band of the dicarbonyl at around 600 nm.

(1) (a) Anker, M. W.; Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1966**, *20*, 9. (b) Moss, F. R.; Shaw, B. J. *J. Chem. Soc. A* **1970**, 595. (c) Winston, P. B.; Burgmayer, S. J. N.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1986**, *5*, 1707. (d) Davidson, J. L.; Vasapollo, G. *J. Chem. Soc., Dalton Trans.* **1985**, 2239.

(2) (a) Templeton, J. L.; Ward, B. C. *Inorg. Chem.* **1980**, *19*, 1753. (b) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318. (c) Herrick, R. S.; Templeton, J. L. *Organometallics* **1982**, *1*, 842.

(3) (a) Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1975**, 2531. (b) Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1977**, 287.

(4) Kamata, M.; Yoshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T.; Kido, M.; Tatsumi, K.; Hoffmann, R. *Organometallics* **1982**, *1*, 227.

(5) (a) Drew, M. G. B.; Tomkins, K. B.; Colton, R. *Aust. J. Chem.* **1970**, *23*, 2517. (b) Cotton, F. A.; Meadows, J. H. *Inorg. Chem.* **1984**, *23*, 4688.

(6) (a) McDonald, J. W.; Newton, W. E.; Creedy, C. T. C.; Corbin, J. L. *J. Organomet. Chem.* **1975**, *92*, C25. (b) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

(7) (a) Kubacek, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4320. (b) Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713.

(8) Templeton, J. L.; Herrick, R. S.; Morrow, J. R. *Organometallics* **1984**, *3*, 535.

(9) Herrick, R. S.; Leazer, D. M.; Templeton, J. L. *Organometallics* **1983**, *2*, 834.

(10) Anker, M. W.; Colton, R.; Tomkins, I. B. *Rev. Pure Appl. Chem.* **1968**, *18*, 23.

Variation of the CO concentration confirms the anticipated mixed second-order rate law. Use of different phosphine ligands permitted measurement of the effect of phosphine steric and electronic properties on reaction rate. Diffuse-reflectance electronic spectroscopy and variation of reaction solvent shed light on the interaction of solvent with the unsaturated dicarbonyl.

Experimental Section

Materials. Chemical reagents for syntheses were acquired from commercial sources and used without further purification. Teflon was obtained as Chromosorb T 40/60 mesh from Supelco, Inc. KBr and BaSO$_4$ were purchased as spectroscopic and reagent grade materials. Hexane solvent was purified for flash photolysis by consecutive treatment with H$_2$SO$_4$/H$_2$O/saturated aqueous NaHCO$_3$/H$_2$O/MgSO$_4$ before distillation from CaH$_2$. The same purification procedure was used for 1,2-dichloroethane except it was distilled from P$_2$O$_5$. Benzene was washed with H$_2$SO$_4$ and distilled. Methanol was dried over molecular sieves and distilled from CaH$_2$. Carbon monoxide (Matheson, 99.99%) was used without further purification.

Syntheses. Standard Schlenk techniques were used for all syntheses. Mo(CO)$_3$(PR$_3$)$_2$Br$_2$ (PR$_3$ = PEt$_3$, P(C$_6$H$_4$-p-OMe)$_3$, P(C$_6$H$_4$-p-Me)$_3$, PPh$_3$, P(C$_6$H$_4$-p-F)$_3$, P(C$_6$H$_4$-p-Cl)$_3$, PEt$_2$Ph, PEtPh$_2$) derivatives were prepared by a modification of a published procedure.[3a] [Mo(CO)$_4$Br$_2$]$_2$ was prepared and stored at −20 °C[11] instead of being prepared and used in situ. Typically, 0.5–1.0 g of the dimer were treated with 4 equiv of the appropriate phosphine in methylene chloride. After 15 min of stirring the solvent volume was reduced, hexane added, and the flask placed in the freezer. Following isolation, the yellow solid was recrystallized at least once from CH$_2$Cl$_2$/hexane. The PEt$_2$Ph derivative formed an oily solid, which was converted to a yellow solid by trituration with hexane.
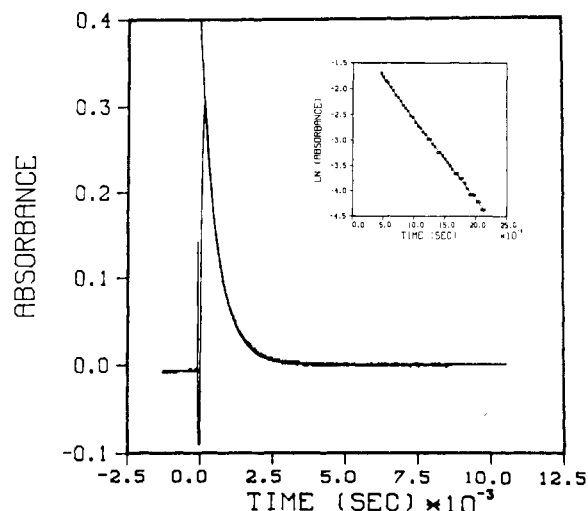
Mo(CO)$_2$(PR$_3$)$_2$Br$_2$ compounds were prepared by heating a CH$_2$Cl$_2$ solution of the recrystallized tricarbonyl under reflux for 1–2 h.[1a,b] Only the PEt$_3$ and PPh$_3$ derivatives could be stoichiometrically converted to the pure dicarbonyl and isolated as blue solids. The P(C$_6$H$_4$-p-OMe)$_3$ and P(C$_6$H$_4$-p-Me)$_3$ derivatives could be converted to a soluble mixture of the tri- and dicarbonyls for nonquantitative UV–vis work. Other triarylphosphine derivatives decomposed during the conversion attempt.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 681 spectrometer and calibrated with a polystyrene standard. The angle between the two carbonyls in the dicarbonyls was estimated from the relative intensities of the two carbonyl bands in the absorbance spectrum.[12] Electronic spectra were recorded on a Perkin-Elmer 559 or Lambda 4C spectrometer with connection to a data station. Diffuse-reflectance electronic spectra were obtained on either spectrometer by using a reflectance sphere. Spectra on KBr and BaSO$_4$ were recorded against a BaSO$_4$ reference. Spectra on Teflon were recorded against a Teflon background, since under experimental conditions Teflon was a better reflector. Spectra are plotted as the Kubelka–Munk equation[13] $(F(R_\infty) \equiv (1 - R_\infty)^2/2R_\infty = kc/s$, where $F(R_\infty)$ is the Kubelka–Munk function, R_∞ is the absolute reflectance of an infinitely thick sample, c is the molar concentration at high reflectance, s is the scattering coefficient, and k is the extinction coefficient) versus wavelength.

Flash-Photolysis Studies. Flash-photolysis studies were performed on an Applied Photophysics, Ltd., KN-100 kinetic flash-photolysis unit. The instrument is configured to charge a 200 J capacitor bank (1 μF) with up to 25 kV. Typically, light pulses of 70–100 J were generated by the two linear xenon flashlamps (fwhm < 40 μs). A Hamamatsu R936 photomultiplier tube alowed observation of transients from 400 to 1000 nm. The output of the photomultiplier following the flash was stored in a 100-MHz 8-bit digital storage oscilloscope. The data, 1024 values, were transfered to an IBM 80286 AT compatible microcomputer via an RS-232 interface. The microcomputer was interfaced to a VAX 8600 computer for data transfer and subsequent kinetic analysis. The setup was tested for accuracy by examining the reaction of Mn$_2$(CO)$_7$[P(n-Bu)$_3$]$_2$ with CO in the manner reported previously.[14] The measured rate constant agreed with the literature value.

Samples for flash photolysis were prepared by two methods.

Method A: Vacuum Degassing. Solutions were prepared by weighing out a suitable quantity of the appropriate tricarbonyl in an evacuable

(11) Hillhouse, G. L.; Haymore, B. L. *J. Am. Chem. Soc.* **1982**, *104*, 1537.
(12) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; pp 1074–1075.
(13) (a) Frei, R. W.; MacNeil, J. D. *Diffuse Reflectance Spectroscopy in Environmental Problem-Solving*; CRC: Cleveland, OH, 1973. (b) Kortium, G. *Reflectance Spectroscopy: Principles, Methods, Applications*; Springer-Verlag: New York, 1969. (c) Ditzler, M. A.; Allston, R. A.; Casey, T. J.; Spellman, N. T.; Willis, K. A. *Appl. Spectrosc.* **1983**, *37*, 269.
(14) Herrick, R. S.; Brown, T. L. *Inorg. Chem.* **1984**, *23*, 4550.

Figure 1. Change in absorbance vs time at 510 nm on flash photolysis of a CO saturated 1,2-dichloroethane solution of Mo(CO)$_3$(PEt$_3$)$_2$Br$_2$. The line through the decay curve represents the nonlinear first-order-squares fit of the data for the disappearance of the transient. Insert: Linear least-squares first-order fit of the data to a first-order rate law. Every fourth data point out to 3.9 half-lives was used. A correlation coefficient of $R = -0.9993$ was determined.

10-cm cell with a 100-mL degassing bulb and a threaded Teflon vacuum stopcock. Following flushing with CO or nitrogen, the solvent (which was carefully distilled and collected in the absence of air and water) was added via syringe. The 10^{-4}–10^{-5} M solution was transfered to a vacuum line capable of 10^{-5} mmHg. The sample was degassed by five freeze-pump–thaw cycles. After the last cycle CO was admitted as a cover gas, with a manometer being used to monitor the CO gas pressure. The solution was allowed to remain at room temperature for 15 min with constant agitation to ensure that an equilibrium of cover gas and dissolved gas had been reached.

Method B: CO Sparge. The metal reagent was weighed into a 10-cm cell with a neck and female joint. A rubber septum was wired into place, and the cell was degassed with CO. The solvent, again carefully distilled and collected in the absence of air and water, was added via syringe. The 10^{-4}–10^{-5} M solutions were degassed at least 10 min by a vigorous stream of CO dispensed by a needle through the septum. After 10 min, both the CO and exhaust needles were removed and the sample was ready to flash.

Time-dependent absorbances following flash photolysis were analyzed by least squares fits of absorbance vs time or by use of a first-order integrated rate law equation. All 1024 data points were used in the fits of absorbance vs time. Data through 2 or more half-lives were employed in fitting rate expressions. Reported rate constants are averages of several trials from at least three separate experiments usually involving both methods of degassing. All analyses gave linear least-squares correlation coefficients of less than −0.995.

Stopped-Flow Experiments. A Hi-Tech SFA-11 rapid kinetics accessory with an experimental dead time of <100 ms in a Bausch & Lomb Spectronic 70 instrument was used to perform stopped-flow experiments. The path length in the cuvette was 2 mm. The digital storage oscilloscope was used to capture decay curves. Mo(CO)$_2$(PPh$_3$)$_2$Br$_2$ solutions (ca. 5 × 10^{-4} M) were prepared by dissolving the metal reagent in 20–30 mL of purified 1,2-dichloroethane. The solutions were degassed with a vigorous train of N$_2$ through the solution for at least 15 min. A solution of CO-saturated 1,2-dichloroethane was prepared by vigorously bubbling CO through it for 15 min. The data was manipulated in the same fashion as the flash-photolysis data. Stopped-flow results were not as accurate as flash-photolysis experiments apparently because of slow CO leakage from the CO-saturated solution. The rate constant values were thus always slightly smaller than those made by flash-photolysis techniques and had larger uncertainties.
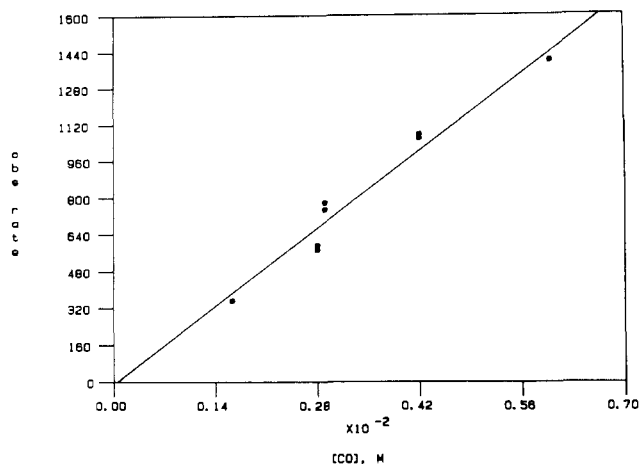
Results

Flash-Photolysis Studies. Flash photolysis of CO-saturated Mo(CO)$_3$(PEt$_3$)$_2$Br$_2$ in 1,2-dichloroethane at 22 °C produces a transient absorption in the 500–650-nm range with maximum intensity at 570 nm. The transient decays steadily back to the base line, and the process may be repeated numerous times without decomposition. The decay is first order in metal complex with a rate of 1.4 × 10^3 s^{-1}. No dependence of the rate constant on

Figure 2. Plot showing the linear dependence of observed rate constant against CO concentration for disappearance of the transient generated by flash photolysis of $Mo(CO)_3(PEt_3)_2Br_2$ in 1,2-dichloroethane at 22 °C.

Table I. Visible Absorption Parameters for $Mo(CO)_2(PR_3)_2Br_2$ Complexes[a]

compd	λ_{max},[a] nm	ϵ, M^{-1} cm^{-1}
$Mo(CO)_2[P(C_6H_4\text{-}p\text{-}OMe)_3]_2Br_2$	610[b]	
$Mo(CO)_2[P(C_6H_4\text{-}p\text{-}Me)_3]_2Br_2$	611[b]	
$Mo(CO)_2(PPh_3)_2Br_2$	610	610
$Mo(CO)_2(PEt_3)_2Br_2$	568	485

[a] Measured in CH_2Cl_2. [b] Taken as a mixture of the dicarbonyl and tricarbonyl.

Table II. Bimolecular Rate Constants for the Reaction of $Mo(CO)_2(PR_3)_2Br_2$ with CO in 1,2-Dichloroethane at 22 °C

phosphine	k,[a] M^{-1} s^{-1}	θ,[b] deg	ν,[b] cm^{-1}
PEt_2Ph	7.3×10^5	136	2063.7
$PEtPh_2$	5.8×10^5	140	2066.7
PEt_3	2.4×10^5	137[c]	2061.7
$P(C_6H_4\text{-}p\text{-}Cl)_3$	2.2×10^4	145	2072.8
$P(C_6H_4\text{-}p\text{-}F)_3$	1.5×10^4	145	2071.3
PPh_3	9.2×10^3	145	2068.9
$P(C_6H_4\text{-}p\text{-}Me)_3$	2.7×10^3	145	2066.7
$P(C_6H_4\text{-}p\text{-}OMe)_3$	2.5×10^3	145	2066.1

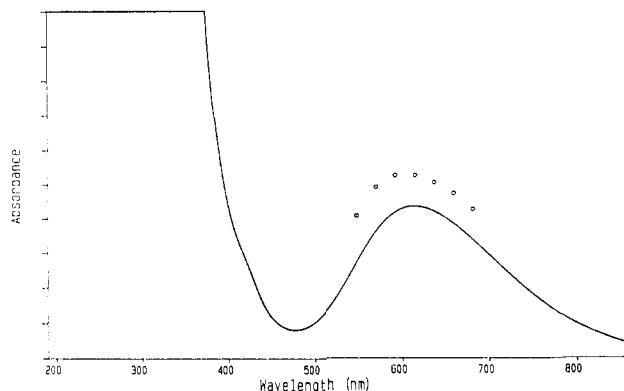[a] Rate constants are accurate to ±10%. [b] Reference 21. [c] Corrected cone angle from ref 31.

the method of sample preparation was observed. A representative decay trace with the kinetic fit superimposed is shown in Figure 1. Flash photolysis of $Mo(CO)_3(PEt_3)_2Br_2$ was also performed in 1,2-dichloroethane under various partial pressures of CO. Carbon monoxide concentrations were calculated by assuming Henry's law and using the experimentally measured concentration in 1,2-dichloroethane covered by 1 atm of CO (6.0×10^{-3} M^{15}). A plot of the observed rate constant versus the CO concentration is linear (Figure 2). Least-squares analysis indicates the y intercept is within error limits of the origin. Thus the reaction follows the mixed second-order rate law

$$R = k[M'][CO] \qquad (2)$$

where M' is the metal-containing transient. The slope of the line is 2.4×10^5 M^{-1} s^{-1}, identical within error limits with the bimolecular rate constant obtained by dividing the pseudo-first-order rate constant by the CO concentration.

Flash photolysis of aryl- or mixed aryl–alkylphosphine derivatives provided an intense transient with λ_{max} in good agreement with λ_{max} of the authentic dicarbonyl in dichloroalkane (see Table I and Figure 3). The transient decayed back to the base line via

(15) (a) *Solubilities of Inorganic and Metal-Organic Compounds*, 4th ed.; American Chemical Society: Washington, DC, 1965. (b) Skirrow, F. W. *Z. Phys. Chem.* **1902**, *41*, 144.

Figure 3. Absorbance spectrum of $Mo(CO)_2(PPh_3)Br_2$ in CH_2Cl_2. The points overlaid are absorbances plotted against the wavelength of the transient generated by flash photolysis of $Mo(CO)_3(PPh_3)_2Br_2$. The transient absorbances were multiplied by approximately a factor of 10 for purposes of comparison.

Table III. Rate of CO Recombination for $Mo(CO)_2(PEt_3)_2Br_2$ and Position of the Dicarbonyl Visible Band in Different Solvents

solvent	k,[a] M^{-1} s^{-1}	λ_{max}, nm
hexane	7.0×10^5	555 ± 10
DCE[b]	2.4×10^5	568 ± 3
benzene	2.4×10^5	
MeOH	<10	<500

[a] Rate constants accurate to ±10%. Carbon monoxide concentrations in different solvents were obtained from ref 15. [b] DCE is 1,2-dichloroethane.

pseudo-first-order kinetics. Bimolecular rate constants ranging between 2.5×10^3 and 7.3×10^5 M^{-1} s^{-1} were calculated. The results are compiled in Table II.

Stopped-flow experiments on 1,2-dichloroethane solutions of $Mo(CO)_2(PPh_3)_2Br_2$ and carbon monoxide gave exponential decay of the dicarbonyl. For a CO concentration of 3.0×10^{-3} M,[16] a bimolecular rate constant of $(5.0 \pm 2.5) \times 10^3$ M^{-1} s^{-1} was calculated. The rate constants for stopped-flow experiments were much less precise than measurements by flash photolysis (see Experimental Section).

Flash-photolysis studies of $Mo(CO)_3(PEt_3)_2Br_2$ were also performed in hexane, benzene, and methanol. Hexane and benzene solutions produced well-behaved first-order decays. The decay in methanol was too slow to measure and returned to the base line over a period of minutes. Rate constants measured in various solvents are collected in Table III.

Visible Spectral Studies. Absorbance spectroscopy in CH_2Cl_2 and reflectance spectra on solid supports was used to observe the visible absorption band of $Mo(CO)_2(PEt_3)_2Br_2$. The λ_{max} was measured as 565 nm in CH_2Cl_2, 615 nm on KBr, 620 nm on $BaSO_4$ and 755 nm on Teflon (Figure 4). The electronic spectrum of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ was recorded under identical conditions as a control. The $d\pi \rightarrow \sigma^*$ band at 520 nm showed little or no variation with the medium.
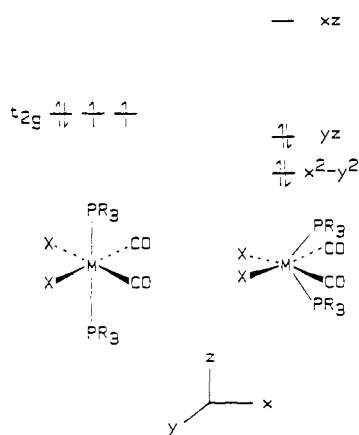
Discussion

Molecular Orbital Description of $Mo(CO)_2(PR_3)_2Br_2$. The kinetic and spectroscopic results are best understood by utilizing previously presented molecular arguments for the stability of the dicarbonyl.[5b,7a] The idealized octahedral geometry with trans phosphines and mutually cis pairs of carbonyls and halides is energetically disfavored because of the incomplete filling of the t_{2g} orbitals (Scheme I). The molecule is allowed to distort via bending of the phosphines toward the carbonyls, the halides pinching together, and the carbonyls moving away from each other. This C_{2v} symmetry, with the C_2 axis bisecting the C–M–C and X–M–X angles, approximates the experimentally determined
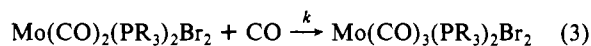
(16) The mixed solutions volumes are equal, so the carbon monoxide is 50% of the concentration under 1 atm of CO.
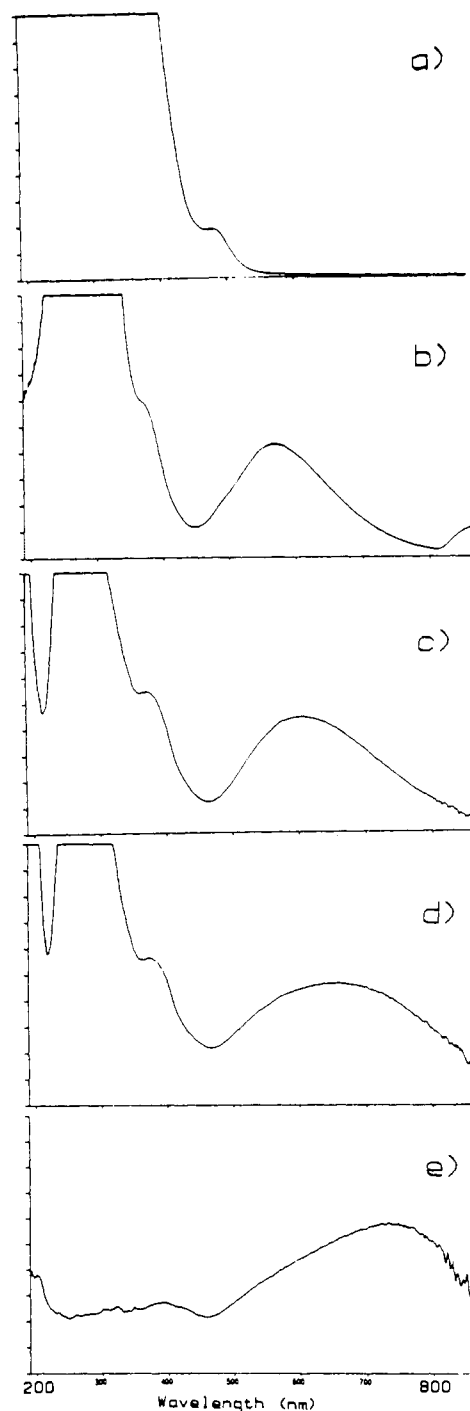
Scheme I

molecular structure.[6] Calculations have determined that this geometry, which has the lowest energy, gives the splitting of the formerly t_{2g} orbitals shown in Scheme I with an energy difference close to that of the visible absorption band at 550–650 nm.[5b] For the Cartesian axes as described by Hoffmann, the four electrons completely fill the $x^2 - y^2$ and yz orbitals while the destabilized xz orbital becomes the LUMO.

Recombination of Mo(CO)$_2$(PR$_3$)$_2$Br$_2$ with CO. The identity of the reaction following photolysis as the addition of carbon monoxide to the dicarbonyl in its ground electronic state has three main points of evidence. All flash-photolysis transients had a maximum absorbance at the same wavelength that independently synthesized dicarbonyls showed maximum absorbance. Also, stopped-flow experiments on Mo(CO)$_2$(PR$_3$)$_2$Br$_2$ gave rate constants in agreement with flash-photolysis results, indicating Mo(CO)$_2$(PR$_3$)$_2$Br$_2$ is the species that decays following flash photolysis.[17] Finally, the experimental rate law (eq 2, where M' is Mo(CO)$_2$(PR$_3$)$_2$Br$_2$) is first order in both Mo(CO)$_2$(PR$_3$)$_2$Br$_2$ and CO. The only mechanism that adequately fits the data is the single-step addition of CO to Mo(CO)$_2$(PR$_3$)$_2$Br$_2$ (eq 3).

$$Mo(CO)_2(PR_3)_2Br_2 + CO \xrightarrow{k} Mo(CO)_3(PR_3)_2Br_2 \quad (3)$$

The fact that a CO sparge can be successfully used for sample preparation is interesting given prior reports on group 6 penta-carbonyl transients.[18–20] In that work, trace amounts of water and other contaminants affected the observed rates of CO addition; the rate constants were greatly lowered when contaminants were present. Apparently H$_2$O has a moderately strong interaction with the vacant coordination site, slowing down CO addition. For Mo(CO)$_2$(PR$_3$)$_2$Br, not only does the method of preparation not affect the kinetics but also injection of distilled water (providing concentrations up to 3 × 10^{-4} M) has no effect on the kinetics. The reason for this insensitivity to water is undoubtedly related to the stability of the dicarbonyl in the absence of nucleophiles.

The electronic nature of the phosphine clearly affects the rate of reaction as demonstrated by the five triarylphosphine derivatives. As ν increases for the sterically identical phosphines, the rate constant increases with PR$_3$ = P(C$_6$H$_4$-p-OMe)$_3$ < P(C$_6$H$_4$-p-Me)$_3$ < PPh$_3$ < P(C$_6$H$_4$-p-F)$_3$ < P(C$_6$H$_4$-p-Cl)$_3$. The parameter, ν, is the infrared ν(CO) frequency for the A$_1$ stretch of Ni-(CO)$_3$PR$_3$[21] and is inversely proportional to electron donation. Thus decreased electron donation leads to a faster reaction. This

Figure 4. Electronic absorption spectra for Mo(CO)$_3$(PEt$_3$)$_2$Br$_2$ (a) and Mo(CO)$_2$(PEt$_3$)$_2$Br$_2$ (b) in CH$_2$Cl$_2$ and diffuse-reflectance spectra for Mo(CO)$_2$(PEt$_3$)$_2$Br$_2$ on KBr (c), BaSO$_4$ (d), and Teflon (e). The absence of the intense high energy band in spectrum e is symptomatic of systematic errors for a medium with a high specular reflectance and a sample with a low percent reflectance at small wavelength. See ref 13c.

is consistent with the argument that decreasing the electron density at the electron-poor dicarbonyl metal center makes the metal center more reactive.

Increases in the phosphine cone angle, θ,[21] also inhibit the reaction. Hence the PEt$_3$ derivative, with a cone angle of 137°,[21b] reacts much more rapidly than the triarylphosphine derivatives containing larger phosphines, despite the considerably higher basicity of PEt$_3$. To corroborate this effect on the rate, other phosphine derivatives were prepared. Tricarbonyls with PMe$_3$, PMe$_2$Ph, and PMePh$_2$ showed no decay trace, and calculations from the free energy relationship (vide infra) indicate their recombination would be too fast to observe by conventional flash photolysis. Alternatively these compounds may not show the same
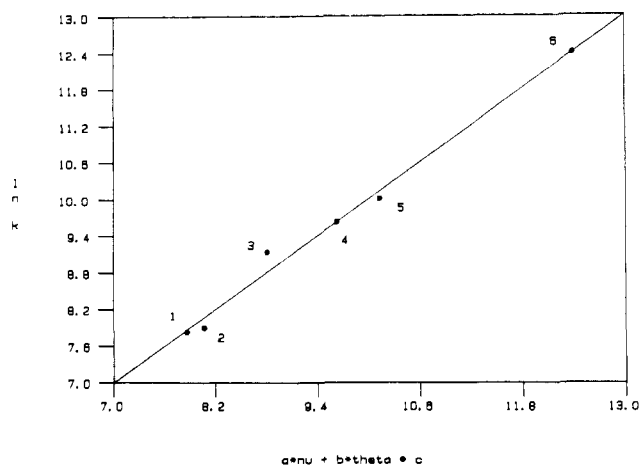
(17) Several W(CO)$_2$(PR$_3$)$_2$Br$_2$ derivatives give bimolecular rate constants in agreement with the corresponding flash photolysis results. Herrick, R. S.; George, M. S., unpublished observations.

(18) Kelly, J. M.; Bent, D. V.; Hermann, H.; Schulte-Frohlinde, D.; Koerner von Gustorf, E. *J. Organomet. Chem.* **1974**, 69, 259.

(19) Hermann, H.; Grevels, F.-W.; Henne, A.; Schaffner, K. *J. Phys. Chem.* **1982**, 86, 5151.

(20) Church, S. P.; Grevels, F.-W.; Hermann, H.; Schaffner, K. *Inorg. Chem.* **1985**, 24, 418.

(21) (a) Tolman, C. A. *Chem. Rev.* **1977**, 77, 313. (b) See ref 31 for the recently corrected cone angle value for PEt$_3$.

Figure 5. Correlation of ln k with the steric and electronic phosphine parameters for the reaction of $Mo(CO)_2(PR_3)_2Br_2$ with carbon monoxide. Points on the plot correspond to the phosphine derivatives: $1 = P\text{-}(C_6H_4\text{-}p\text{-}OMe)_3$, $2 = P(C_6H_4\text{-}p\text{-}Me)_3$, $3 = PPh_3$, $4 = P(C_6H_4\text{-}p\text{-}F)_3$, $5 = P(C_6H_4\text{-}p\text{-}Cl)_3$, $6 = PEt_3$.

chemical reactivity upon photolysis. $P(i\text{-}Pr)_3$ and $P(C_6H_{11})_3$ derivatives could not be isolated. PEt_2Ph and $PEtPh_2$ were utilized, therefore, to test the variation of cone angle on the rate. Again, smaller cone angles led to increased rates despite the higher basicity relative to triarylphosphines.

It is also necessary to consider the possibility that the steric effect is actually a disguised electronic effect. It is conceivable that the steric bulk of the phosphine could affect the molecular distortion through steric interactions. Since orbital splittings will change as the degree of deformation from an octahedron increases,[5b,7] it must be ascertained if the distortion is constant for all derivatives. Infrared measurement of the relative intensities of the two $v(CO)$ stretches[12] shows that the C–Mo–C angle in the PEt_3 ($114 \pm 2°$) and PPh_3 ($112 \pm 2°$)[22,23] congeners are the same within experimntal error. If we assume that this angle is a measure of the overall deformation of the molecule, these two derivatives (and presumably the others as well) have similar geometries. Thus the steric effect is apparently a true steric effect.

A more extensive analysis of steric and electronic effects can be attained through the two-parameter free energy relationship in eq 4. Similar relationships have been reported by using either

$$\ln k = av + b\theta + c \qquad (4)$$

the ligand pK_a[24-27] or the ^{13}C NMR chemical shift value for the carbonyl carbon in $Ni(CO)_3PR_3$[28,29] as the electronic parameter. We have used v as the electronic parameter since previous explanations of phosphine effects on reaction rates have used the $v(CO)$ stretch[14,30] and the trend in ^{13}C chemical shifts for the $P(C_6H_4\text{-}p\text{-}Me)_3$ and $P(C_6H_4\text{-}p\text{-}OMe)_3$ phosphines is opposite to the observed trend in rate constants reported in this study. Figure 5 shows the linear relationship achieved for eq 4 by multiple linear

regression using rate constants and phosphine parameters for the six derivatives with symmetrical phosphines. The corrected cone angle of 137° was used for PEt_3.[31] A correlation coefficient of 0.995 was obtained between the observed and calculated values of ln k. The values for coefficients a and b and the constant c were 0.34, −0.75, and −581, respectively. The ratio of a/b was −0.41. The coefficient signs again show that increased electron donation and a larger cone angle inhibit the reaction.

The two mixed aryl–alkylphosphines were not included in the free energy relationship, because a lowered correlation coefficient of 0.968 was obtained with the $PEtPh_2$ derivative lying well off the line. There are several conceivable explanations why the mixed phosphine derivatives do not follow the free energy relationship as closely as the trisubstituted phosphines. It may be that the cone angle of one or both of the mixed phosphines is larger than previously thought, as recently shown for PEt_3.[31a] Another potential problem is that in the ground state of the dicarbonyl the unsymmetrical phosphines would be expected to align such that the smaller ethyl groups are oriented closest to a region of steric congestion while the phenyl groups are directed away from this region. Depending on the orientation of attack, the phosphines might appear to be PEt_3 or PPh_3 ligands to the incoming CO.[32]

Solvent Effects on Dicarbonyl Recombination with CO. The isolability of these flash-photolysis transients in the absence of nucleophiles is a great advantage with respect to spectroscopic analysis. In particular, electronic spectra taken on different media were extremely useful in studying the nature of the intermediate. The electronic absorption band attributed to the d–d HOMO–LUMO transition was found to be strongly dependent on the medium. This is believed due to the utilization of the solvent as a token ligand.[33] A solvent molecule becomes weakly bound to the LUMO at a vacant coordination site. The destabilization of the LUMO by solvent interaction increases the HOMO–LUMO gap[34] with a comcomitant increase in the d–d absorption band energy. In accord with this model, the absorption maximum was observed to move to increasingly higher wavelength as less interactive media were employed with λ_{max} for $CH_2Cl_2 <$ KBr $<$ $BaSO_4 <$ Teflon. Methylene chloride and halides have previously been observed to interact with analogous electron-deficient compounds, in some cases forming stable compounds.[35-37] Sulfate is expected to be less nucleophilic than halide, explaining barium sulfate's higher λ_{max}. Teflon is expected to be the least interactive of all common solvents or solids and does display a much higher λ_{max} than other media. This characteristic spectroscopic behavior has been observed for $M(CO)_5$[38-40] (M = Cr, Mo, W) and is considered evidence for very weak or nonexistent interaction of the perfluoro solvent with the pentacarbonyl. Similarly we interpret the 190-nm shift of absorption maxima on changing from CH_2Cl_2 to Teflon media as an indication of the very weak or nonexistent interactive ability of the perfluoro polymer.

$Mo(CO)_3(PEt_3)_2Br_2$ was the only compound whose solubility permitted flash photolysis in a variety of solvents. The bimolecular rate constant decreased as the solvent nucleophilicity increased with k in hexane $>$ 1,2-dichloroethane $=$ benzene $\gg$ methanol. Solvent interaction with the LUMO in the 16-electron complex

(22) Drew et al. (ref 5a) report a C–Mo–C angle of 119.4° while Cotton says the correct value is close to 110° (ref 5b, footnote 9).

(23) The tungsten dicarbonyls also give consistent values for the C–M–C angle, but they tend to be a little higher; typically 119 ± 3°. George, M. S.; Herrick, R. S., unpublished observations.

(24) Rerek, M. E.; Basolo, F. *Organometallics* **1983**, *2*, 372.

(25) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771.

(26) Shi, Q.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 71.

(27) Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981.

(28) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951.

(29) Lee, K.-W.; Brown, T. L. *Inorg. Chem.* **1987**, *26*, 1852 and references therein.

(30) Herrick, R. S.; Herrinton, T. R.; Walker, H. W.; Brown, T. L. *Organometallics* **1985**, *4*, 42.

(31) (a) Stahl, L.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 5673. (b) The need for recalculation of θ for PEt_3 arises from the fact that all three ethyl groups are not folded back when it is bound to a metal.

(32) In fact using θ as 137° for all three ethyl-containing phosphines gives a correlation coefficient following multiple linear regression of 0.989 with a ratio of a/b of −0.38. While the mixed-phosphine kinetic experiments clearly show the effect of steric bulk on the reaction, we felt it is best to use a free energy relationship omitting these two values since the underlying behavior of the phosphines is not understood.

(33) Dobson, G. R.; Hodges, P. M.; Healy, M. A.; Poliakoff, M. Turner, J. J.; Firth, S.; Asali, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 4218.

(34) See ref 8 for a discussion of electron donation to a LUMO.

(35) Beck, W.; Schloter, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1214.

(36) Burgmayer, S. J. N.; Templeton, J. L. *Inorg. Chem.* **1985**, *24*, 2224.

(37) Herrick, R. S.; Templeton, J. L. *Inorg. Chem.* **1986**, *25*, 1270.

(38) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.

(39) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220.

(40) Kelly, J. M.; Long, C.; Bonneau, R. *J. Phys. Chem.* **1983**, *87*, 3344.

can again be invoked to explain these observations. Hexane should be a poorer solvent for interaction with a vacant coordination site, and more nucleophilic methanol should form a stronger interaction. Similar behavior has been reported for the group 6 pentacarbonyls[31,41,42] in coordinating solvents. As a comparison of relative reactivities, the recombination rate of $Mo(CO)_2(PEt_3)_2Br_2$ in hexane is only a factor of 4 smaller than that observed for $Cr(CO)_5$ (7.0×10^5 M^{-1} s^{-1} vs 3×10^6 M^{-1} s^{-1}). This is surprisingly large given the isolability of the dicarbonyl in the absence of nucleophile.

Chromium, molybdenum, and tungsten pentacarbonyls have been observed to react with CO at nearly diffusion-controlled rates in perfluoromethylcyclohexane.[38-40] In contrast, stabilization of a coordinatively unsaturated compound occurring via interaction of a bridging carbonyl in $Mn_2(CO)_9$[14,43,44] does not permit a

diffusion-controlled reaction rate. The reaction rate of $Mo(CO)_2(PEt_3)_2Br_2$ in noncoordinating perfluoroalkane solvent could not be measured because of the lack of solubility. The measured shift of the d–d absorbance band to low energy in Teflon does indicate there would be minimal solvent interaction. It is probable, though, that the rate constant in perfluoroalkane would not approach the diffusion-controlled encounter rate because the dicarbonyl is a stable isolable intermediate with a nonzero activation energy barrier.

(41) Dobson, G. R.; Awad, H. H.; Basson, S. S. *Inorg. Chem. Acta* **1986**, *118*, L5.
(42) Asali, K. J.; Basson, S. S.; Tucker, J. S.; Hester, B. C.; Cortes, J. E.; Awad, H. H.; Dobson, G. R. *J. Am. Chem. Soc.* **1987**, *109*, 5386.
(43) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5935.

(44) Church, S. P.; Hermann, H.; Grevels, F.-W.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1984**, 785.

Contribution from the Laboratoire de Chimie Théorique (CNRS, UA 506), ICMO, Université de Paris-Sud, 91405 Orsay Cedex, France

Is Delocalization a Driving Force in Chemistry? First- and Second-Row Heteroannulenes

G. Ohanessian,* P. C. Hiberty, J.-M. Lefour, J.-P. Flament,† and S. S. Shaik‡

Conjugated squares and hexagons X_n ($n = 4, 6$; X = CH, N, SiH, P) are investigated computationally in the context of the title question. These species exhibit contrasting distortive behaviors with respect to a localizing distortion to bond-alternated structures. In contrast to the case for benzene, P_6 and Si_6H_6 are found to resist only weakly such a distortion, and the square rings Si_4H_4 and P_4 are indifferent to a distortion toward a rectangular geometry, at variance with the case for C_4H_4 and N_4. These trends are rationalized on the basis of valence bond (VB) correlation diagrams, leading to the following general features: (i) the adequate unified description of all conjugated molecules is in terms of a competition between symmetrizing σ frames and distortive π; (ii) the π singlet–triplet energy gap of the corresponding localized two-electron–two-center bonds is the very parameter that correlates with the π distortion energy; (iii) all molecules possess a sizable quantum-mechanical resonance energy (QMRE), but there is a large quantitative difference between "aromatic" and "antiaromatic" compounds. It follows that the Hückel rule cannot be a safe base for predicting geometries of molecules other than hydrocarbons. On the other hand, the VB approach allows an understanding of why the rule is successful for hydrocarbons and when contradictions to it should be expected. In such cases, new structural behaviors emerge that are potentially interesting for the synthesis of molecules with new properties.

Introduction

Electron delocalization and concepts devised to describe its effects, such as aromaticity, have a vital importance in the chemistry of conjugated organic molecules, their stability, and modes of reactivity. Quantum chemistry has produced a very simple means of accounting for much of these phenomena, the $4n/4n + 2$ Hückel rule.[1] As made clear by its very name, this rule states that the stability of π systems derives from their electron count. Several theoretical refinements have been subsequently developed,[2] but electron counting remains their essential building block.

This simple picture has, however, been questioned by recent advances in other areas of chemistry, in particular the synthesis of gas-phase clusters of monovalent atoms, which are isoelectronic analogues of organic π systems. A striking example is the stability of numerous alkali-metal clusters,[3] in contrast with the instability of hydrogen clusters.[4] Halogen[5] and noble-metal[6] trimers together with the former ones have in fact provided a whole spectrum of stability, the explanation of which requires one to go beyond the Hückel rule. In addition, this rule leads one to expect a sharp

alternation of properties with cluster size, which is not observed. Thus, for example, despite their "antiaromatic" nature, planar

(1) Hückel, E. *Z. Phys.* **1932**, *76*, 628.
(2) Some leading references follow: (a) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, Ser. A* **1960**, *257*, 445. (b) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 685. (c) Dewar, M. J. S.; deLlano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789. (d) van der Hart, W. J.; Mulder, J. J. C.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1972**, *94*, 5724. (e) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305. (f) Randic, M. *J. Am. Chem. Soc.* **1977**, *99*, 44. (g) Gutman, I.; Milun, M.; Trinajstic, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692. (h) Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722. (i) Kollmar, H. *J. Am. Chem. Soc.* **1979**, *101*, 4832. (j) Malrieu, J. P.; Maynau, D. *J. Am. Chem. Soc.* **1982**, *104*, 3021. (k) Kuwajima, S. *J. Am. Chem. Soc.* **1984**, *106*, 6496. (l) Klein, D. J.; Trinajstic, N. *J. Am. Chem. Soc.* **1984**, *106*, 8050.
(3) The first prediction of the stability of the lithium trimer was in: (a) Companion, A. L.; Steible, A. J.; Starshak, J. *J. Chem. Phys.* **1968**, *49*, 3637. Numerous theoretical studies have subsequently been devoted to the structure and stability of alkali-metal oligomers. For a recent study and bibliography, see: (b) Koutecky, J.; Beckmann, H.-O.; Bonacic-Koutecky, V.; Fantucci, P.; Pacchioni, G.; Pewestorf, W. *J. Phys. B* **1986**, *19*, L451. The experimental literature is also abundant. A selection is as follows: (c) Foster, P. J.; Leckenby, R. E.; Robbins, E. J. *J. Phys. B* **1969**, *2*, 478. (d) Lindsay, D. M.; Herschbach, D. R.; Kwiram, A. L. *Mol. Phys.* **1976**, *32*, 1199. (e) Wu, C. H. *J. Chem. Phys.* **1976**, *65*, 3181. (f) Thompson, G. A.; Lindsay, D. M. *J. Chem. Phys.* **1981**, *74*, 959. (g) Howard, J. A.; Sutcliffe, R.; Mile, B. *Chem. Phys. Lett.* **1984**, *112*, 84 and references therein.

†Groupe DCMT, Ecole Polytechnique, 91128 Palaiseau, France.
‡Department of Chemistry, Ben-Gurion University, Beer-Sheva 84105, Israel.