

semiquinone (i.e., that at the methylene end) interacts strongly with the metal ion and that this interaction causes the observed coupling of redox and complexation reactions.

The present experiments show that physical proximity of suitably situated redox-active and ion-binding groups results in coupling of redox and complexation reactions. For redox-active crown ethers reduction/oxidation of the electroactive group affords a means to "turn on" and "turn off" ion binding and offers the possibility of driving ion transport against a chemical concentration gradient by coupling the formation of a chemical concentration gradient with the discharge of an electrochemical potential gradient. In principle this coupling could be used to convert electrochemical energy into chemical concentration gradients, just as, e.g., nerve cells do. Moreover, in a biological context it suggests a means by which electrochemical and chemical energy can be interconverted in an efficient fashion—the essence of the chemiosmotic hypothesis.<sup>6</sup>

**Acknowledgment.** We are grateful to Professor E. J. Corey of this department for his advice and encouragement and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(6) Mitchell, P. *Nature (London)* **1961**, *191*, 144–8.

(7) Several reports of conceptually related compounds have appeared recently: Kaifer, A.; Echegoyen, L.; Gustowski, D. A.; Goli, D. M.; Gokel, G. W. *J. Am. Chem. Soc.* **1983**, *105*, 7168–9. Gustowski, D. A.; Echegoyen, L.; Goli, D. M.; Kaifer, A.; Schultz, R. A.; Gokel, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 1633–5. Bock, H.; Hierholzer, B.; Vögtle, F.; Hollman, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 57–8.

(8) **Note Added in Proof:** A prior report on this class of compounds has come to our attention: Sugihara, K.; Kamiya, H.; Yamaguchi, M.; Kaneda, T.; Misumi, S. *Tetrahedron Lett.* **1981**, *22*, 1619–22.

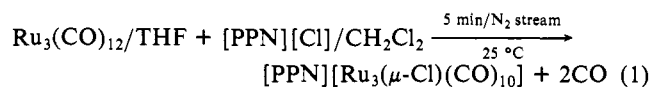
## Effects of Highly Dissociated Salts in Stoichiometric and Catalytic Reactions on Ruthenium Cluster Complexes

Guy Lavigne and Herbert D. Kaesz\*

Department of Chemistry and Biochemistry  
University of California  
Los Angeles, California, 90024

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In attempts to trace the stepwise transformation of  $\text{Ru}_3(\text{CO})_{12}$  into hydridohalogen derivatives,<sup>1</sup> we observed the stoichiometric transformation shown in eq 1.<sup>2</sup> This parallels the known reactions



of  $\text{Ru}_3(\text{CO})_{12}$  with  $[\text{PPN}][\text{NO}_2]^3$  or  $[\text{PPN}][\text{acetate}]$ ,<sup>4a</sup> yielding

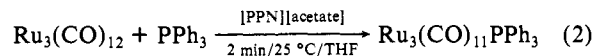
(1) Kampe, C. E.; Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 1390–1397.

(2) (a)  $[\text{PPN}^+] = \text{bis}(\text{triphenylphosphine})\text{iminium}$ . (b) For the stoichiometric reaction,  $\text{Ru}_3(\text{CO})_{12}$  (192 mg, 0.300 mmol) is dissolved in 100 mL of freshly distilled THF. A stoichiometric amount of  $[\text{PPN}][\text{Cl}]$  (172 mg) (or a slight excess) dissolved in 1–3 mL of  $\text{CH}_2\text{Cl}_2$  is added by syringe. Under bubbling  $\text{N}_2$ , the reaction is complete within 5 min (IR) proceeding with a change in color from light to dark orange. Spectroscopic yield of the anion  $[\text{Ru}_3(\mu\text{-Cl})(\text{CO})_{10}]^-$  is 100%; IR in THF (carbonyl region) ( $\text{cm}^{-1}$ ) 2069 w, 2038 w, 2025 s, 1993 vs, 1981 sh, 1971 sh, 1952 s, 1906 w, 1800 m, 1772 sh. If the  $[\text{PPN}][\text{Cl}]$  is added as a powder, the reaction requires 25 min. By contrast,  $\text{LiCl}$  shows no effect. Titration of the solution with  $\text{HBF}_4/\text{Et}_2\text{O}$  (Aldrich) gives  $\text{Ru}_3(\mu\text{-H}, \mu\text{-Cl})(\text{CO})_{10}$  in about 70–75% yield, better than what is obtained in the route using  $\text{Me}_3\text{NO}$ .<sup>1</sup> Acidification is also accompanied by formation of traces of starting material. (c) By contrast, reaction 1 in refluxing THF gives  $[\text{PPN}][\text{Ru}_4(\mu\text{-Cl})(\text{CO})_{13}]$ : Steinmetz, G. R.; Harley, A. D.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 2985–2990.

(3) Stevens, R. E.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 2034–2042.

the  $[\text{PPN}^+]$  salts of anions of general formula  $[\text{Ru}_3(\mu\text{-Nu})(\text{CO})_{10}]^-$ . The mild conditions for these transformations<sup>4b</sup> suggest stabilization of CO in some intermediate such as  $[\text{Ru}_3(\eta^1\text{-C}(\text{O})\text{-Nu})(\text{CO})_{11}]^-$ <sup>5a,b</sup> which we have not been able to detect by IR at 25 °C for  $\text{Nu}^- = \text{Cl}^-$ . By contrast, such an intermediate with  $\text{Nu}^- = \text{CH}_3\text{O}^-$ , has recently been isolated under a CO atmosphere and shown to undergo rapid substitution by phosphites.<sup>5c,d</sup>

In attempting to intercept intermediate(s), we examined reaction 1 with a variety of  $[\text{PPN}^+]$  salts and in the presence of various ligands. We report first that  $[\text{PPN}][\text{acetate}]$  is an excellent catalyst for the monosubstitution of triphenylphosphine on  $\text{Ru}_3(\text{CO})_{12}$ , eq 2. The yields and the rates match those observed



with radical ion initiators.<sup>6</sup> Typically<sup>7a</sup> a solution of  $\text{Ru}_3(\text{CO})_{12}$  in tetrahydrofuran (THF) containing a stoichiometric amount of  $\text{PPh}_3$  is treated with a catalytic amount of  $[\text{PPN}][\text{CH}_3\text{CO}_2]$ .<sup>7b</sup> Upon addition of the catalyst, the color changes instantaneously from pale to dark orange. IR spectra show 100%<sup>8a</sup> conversion of starting material to  $\text{Ru}_3(\text{CO})_{11}\text{PPh}_3$  within 2 min.<sup>8b</sup> With excess triphenylphosphine, the higher substituted derivatives  $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$  and  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$  are obtained at 25 °C.<sup>9</sup> Starting with the mono- or disubstituted derivatives, we were able to show that the rates of these subsequent reactions<sup>10</sup> are not accelerated by catalytic amounts<sup>7a</sup> of  $[\text{PPN}][\text{acetate}]$ .

By contrast,  $[\text{PPN}][\text{CN}]$  promotes instantaneous disubstitution of  $\text{Ru}_3(\text{CO})_{12}$  in the presence of excess  $\text{PPh}_3$  to give  $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$ .<sup>7a,c</sup> Substitution of  $\text{Ru}_3(\text{CO})_{12}$  by ligands of lower nucleophilicity, such as  $\text{AsPh}_3$  and trialkyl or triaryl phosphites, is also promoted by catalytic amounts of  $[\text{PPN}][\text{CN}]$  or by  $[\text{PPN}][\text{acetate}]$  in larger quantities (in both cases giving disubstitution products).<sup>7c,11</sup>

(4) (a) Darensbourg, D. J.; Pala, M.; Waller, J. *Organometallics* **1983**, *2*, 1285–1291. (b) The reported reaction of  $[\text{PPN}][\text{acetate}]$  with  $\text{Ru}_3(\text{CO})_{12}$  was carried out in refluxing THF for 90 min. We find the reaction is complete within 5 min at 25 °C, under the conditions described in ref 2b. A reaction of  $[\text{PPN}][\text{formate}]$  with  $\text{Ru}_3(\text{CO})_{12}$  was earlier found to proceed at room temperature.<sup>4a</sup>

(5) (a) Mayr, A.; Lin, Y. C.; Boag, N. M.; Kaesz, H. D. *Inorg. Chem.* **1982**, *21*, 1704–1706. (b) A triosmium analogue  $\text{Nu}^- = \text{CH}_3^-$  has recently been characterized through <sup>13</sup>C NMR: Jensen, C.; Knobler, C. M.; Kaesz, H. D. *J. Am. Chem. Soc.*, submitted for publication. (c) Anstock, M.; Taube, D.; Ford, P. C., personal communication. (d) Working under an atmosphere of CO, intermediate species for  $\text{Nu}^- = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{CH}_3\text{CO}_2^-$  are observed by IR; their characterization by <sup>13</sup>C NMR is in progress (C. E. Kampe and authors).

(6) (a) Bruce, M. I.; Matisons, J. G.; Nicholson, B. K. *J. Organomet. Chem.* **1983**, *247*, 321–343. (b) Arewogoda, M.; Robinson, B. H.; Simpson, J. *J. Am. Chem. Soc.* **1983**, *105*, 1893–1903.

(7) (a) Experimental conditions for the substitution reactions using an equivalent or excess amount of phosphine are as follows:  $\text{Ru}_3(\text{CO})_{12}$  (192 mg, 0.3 mmol) and the desired amount of phosphine are dissolved in 100 mL of freshly distilled THF. The reaction is started by the addition of  $[\text{PPN}^+]$  salt (0.015 mmol) as a powder. This serves to saturate the solution, most of the solid remaining as a suspension. Half-life is determined by the disappearance of the 2060- $\text{cm}^{-1}$  absorption of  $\text{Ru}_3(\text{CO})_{12}$ , plotting in absorbance. IR spectra also indicate the degree of substitution. (b) For the preparation of  $[\text{PPN}]$  salts, see: Martinsen, A.; Songstad, J. *Acta Chem. Scand. Ser. A* **1977**, *A31*, 645–650. (c) With active salts such as  $[\text{PPN}][\text{acetate}]$  or  $[\text{PPN}][\text{CN}]$ , catalytic amounts may be added as  $\text{CH}_2\text{Cl}_2$  or acetone solutions (1 mL containing 0.015 mmol of salt).

(8) (a) Standard solutions containing 3 mmol of substituted complexes per L of THF are used to determine spectroscopic yields from absorbance data obtained on the FT IR. (b) Experimental details are given in a supplement to this ref (supplementary material).

(9) Details for the syntheses of  $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$  and  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$  are given in a supplement to this ref (supplementary material).

(10) (a) Kinetics for substitution of  $\text{PPh}_3$  on  $\text{Ru}_3(\text{CO})_{12-n}(\text{PPh}_3)_n$ ,  $n = 1$  and 2, in decalin in the range 26–50 °C have been reported: Malik, S. K.; Poë, A. *Inorg. Chem.* **1978**, *17*, 1484–1488. (b) Our observations in THF solution are given here for comparison. Substitution of  $\text{Ru}_3(\text{CO})_{11}\text{PPh}_3$  (262 mg, 0.300 mmol) by additional  $\text{PPh}_3$  (79 mg, 0.300 mmol) in 100 mL of THF at 25 °C under argon is monitored by disappearance of the 2045- $\text{cm}^{-1}$  absorption:  $t_{1/2} = 35$ –40 min. Substitution of  $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_3)_2$  (332 mg, 0.300 mmol) by additional  $\text{PPh}_3$  (79 mg) is followed by disappearance of the 2018- $\text{cm}^{-1}$  band:  $t_{1/2} = 90$  min. Disappearance of  $\text{Ru}_3(\text{CO})_{11}\text{PPh}_3$  after its rapid formation in the presence of 2 mol equiv of  $\text{PPh}_3$  and  $[\text{PPN}][\text{acetate}]$  (as catalyst) is identical with disappearance of  $\text{Ru}_3(\text{CO})_{11}\text{PPh}_3$  in its noncatalyzed reaction with  $\text{PPh}_3$ , supplementary material, Figure 1.

Substitutions with chelating ligands are also enhanced; 100% yields of  $\text{Ru}_3(\text{CO})_{10}(\text{L}_2)$ ,  $\text{L}_2 = \text{dppm}$ , bis(diphenylphosphino)methane, or  $\text{dppe}$ , bis(diphenylphosphino)ethane, are obtained within 3 min.<sup>12</sup>

Salts of the anions  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , or  $\text{NO}_2^-$  are milder catalysts promoting substitutions over a broad range of rates.<sup>13,14</sup> These may be expressed in terms of the half-life for disappearance of  $\text{Ru}_3(\text{CO})_{12}$  under standard reaction conditions<sup>7a</sup> using a ratio  $\text{PPH}_3:\text{Ru}_3(\text{CO})_{12} = 4:1$ . The following are found for the  $[\text{PPN}^+]$  salts,  $t_{1/2}$  (min):  $[\text{CN}^-]$  or  $[\text{CH}_3\text{CO}_2^-]$ , <1;  $[\text{F}^-]$ , <2;  $[\text{Cl}^-]$ , 7;  $[\text{Br}^-]$ , 10;  $[\text{I}^-]$ , 17;  $[\text{NO}_2^-]$ , 45. With  $[\text{PPN}][\text{Cl}]$  as catalyst, integrated rate data show zero-order dependence on  $\text{Ru}_3(\text{CO})_{12}$ .<sup>13b</sup> The mildest catalysts do not give pure monosubstituted product even when only a stoichiometric amount of ligand is present: their enhancement of the first (rate determining) step is not fast enough to exclude formation of subsequent substitution products.

Greater amounts of the  $[\text{PPN}^+]$  salts of the nucleophiles may be introduced through their acetone or  $\text{CH}_2\text{Cl}_2$  solutions.<sup>7c,11</sup> The action of the halide anions, however, is attenuated in  $\text{CH}_2\text{Cl}_2$ . Catalysis is prevented in the presence of strongly hydrogen-bonding solvent (i.e.,  $\text{CH}_3\text{OH}$ ) or if the nucleophile is irreversibly consumed by chemical reaction such as conversion shown in reaction 1 which occurs in competition with coordination by weakly nucleophilic ligands.

In attempts to extend the catalysis of substitution reactions to  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$ , we found instead a rapid deprotonation. Treatment of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  with a stoichiometric amount of  $[\text{PPN}][\text{Cl}]$  in THF gives  $[\text{PPN}][\text{Ru}_4(\mu\text{-H})_3(\text{CO})_{12}]$  in 100% yield in 15 min,<sup>15</sup> paralleling the deprotonation of  $[\text{HMo}(\text{CO})_2(\text{dppe})_2]^+$ ,<sup>16</sup> or  $\text{Os}_4\text{H}_3(\text{CO})_{12}\text{X}$ ,  $\text{X} = \text{Cl}$  or  $\text{I}$ .<sup>17</sup>

Our present observations reveal a novel aspect of the chemistry of ruthenium cluster complexes in the presence of highly dissociated salts. This greatly extends the range of reactions that can be investigated at ambient temperatures.

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**Supplementary Material Available:** Supplements to ref 8, 9, and 15, and two figures of the concentration of  $\text{Ru}_3(\text{CO})_{11}\text{PPH}_3$  as a function of time and rate data for disappearance of  $\text{Ru}_3(\text{CO})_{12}$  (4 pages). Ordering information is given on any current masthead page.

(11) Acceleration of the substitutions with  $\text{AsPh}_3$  and trialkyl or triaryl phosphites observed for  $[\text{PPN}][\text{CN}^-]$  may be achieved with  $[\text{PPN}][\text{acetate}]$  by using considerably larger amounts (0.075 mmol) added in  $\text{CH}_2\text{Cl}_2$  solution;<sup>7c</sup> under these conditions, disubstituted products are obtained.

(12) (a) Synthesis of  $\text{Ru}_3(\text{CO})_{10}(\text{dppm})$ . Under experimental conditions in ref 7, a molar ratio of 1:1 of  $\text{Ru}_3(\text{CO})_{12}/\text{dppm}$  is used. Yield after chromatographic purification and recrystallization, orange crystals, 90%; IR, carbonyl region in cyclohexane ( $\text{cm}^{-1}$ ) 2082 m, 2022 m, 2011 vs, 2001 s, 1983 w, 1958 m, 1942 w, cf. ref 6 and 12b,c. Bridge closing was found to be slow in  $\text{Ru}_3(\text{CO})_{11}(\text{dppe})$ ; the dissociated salts also accelerate the bridge closing reaction. (b) Cotton, F. A.; Hanson, B. E. *Inorg. Chem.* 1977, 16, 3369-3371. (c) Coleman, A. W.; Jones, D. F.; Dixneuf, P. H.; Brisson, C.; Bonnet, J.-J.; Lavigne, G. *Ibid.* 1984, 23, 952-956.

(13) (a) Results using solid  $[\text{PPN}][\text{Cl}]$ <sup>7a</sup> were found to be erratic. Under rigorous exclusion of moisture no catalysis of substitution is observed; the catalytic amounts of  $[\text{Cl}^-]$  are irreversibly consumed according to reaction 1. Catalysis of the substitution reaction by  $[\text{PPN}][\text{Cl}]$  requires a trace of moisture. (b) Integrated rate data for disappearance of  $\text{Ru}_3(\text{CO})_{12}$  using  $[\text{PPN}][\text{Cl}]$  as the catalyst is given as supplementary material, Figure 2.

(14) For earlier observations of catalysis of substitution reactions by bases, see: (a) Morris, D. E.; Basolo, F. J. *Am. Chem. Soc.* 1968, 90, 2536-2544. (b) Hui, K.-Y.; Shaw, B. L. *J. Organomet. Chem.* 1977, 124, 262-264. (c) Darenbourg, D. J.; Baldwin, B. J.; Foelich, J. A. *J. Am. Chem. Soc.* 1980, 102, 4688-4694. (d) Kirtley, S. W.; Andrews, M. A.; Bau, R.; Grynkeiwich, G. W.; Marks, T. J.; Tipton, D. L.; Whittlesey, B. R. *Ibid.* 1977, 99, 7154-7162. (e) Butts, S. B.; Shriver, D. F. *J. Organomet. Chem.* 1979, 169, 191-197.

(15) Experimental details are given in a supplement to this ref (supplementary material).

(16) Hanckel, J. M.; Darenbourg, J. *Am. Chem. Soc.* 1983, 105, 6979-6980.

(17) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Puga, J.; Raithby, P. R.; Whitmore, K. H. *J. Chem. Soc., Dalton Trans.* 1983, 1339-1344.

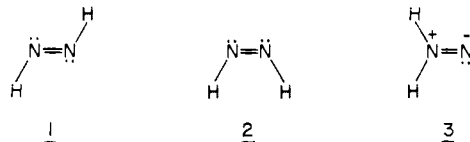
## Low-Temperature Matrix Isolation of $\text{H}_2\text{NN}$ . Electronic and Infrared Characterization

Alan P. Sylwester and Peter B. Dervan\*

Contribution No. 7008  
Division of Chemistry and Chemical Engineering  
California Institute of Technology  
Pasadena, California 91125

Received April 13, 1984

Much of our understanding of the structures of the isomers of  $\text{H}_2\text{N}_2$  (1-3) comes from theory<sup>1</sup> due to the limited experimental characterization of these reactive species.<sup>2,3</sup> Firm spectroscopic evidence exists only for the trans 1,2-isomer 1.<sup>2</sup> In 1976, it was



reported that vacuum pyrolysis of cesium tosylhydrazide affords a colorless  $\text{H}_2\text{N}_2$  product ( $\lambda_{\text{max}}$  260 nm) on a cooled surface ( $-196^\circ\text{C}$ ) that differs in physical and chemical properties from the yellow trans 1,2-isomer, 1 ( $\lambda_{\text{max}}$  386 nm).<sup>2j</sup> This "isomeric diazene" was assigned to the 1,1-diazeno 3. However, subsequent theoretical work indicates that 3 is a colored species due to relatively low lying  $n, \pi^*$  electronically excited states ( $T_1$ , 0.6 eV;  $S_1$ , 2.2 eV).<sup>1n</sup> Recent experimental evidence from the study of persistent 1,1-diazene, such as *N*-(2,2,6,6-tetramethylpiperidyl)nitrene and *N*-(2,2,5,5-tetramethylpyrrolidyl)nitrene, reveal that they are indeed violet species ( $\lambda_{\text{max}}$  543-497 nm,  $n, \pi^*$ ) and have considerable NN double bond character ( $1638\text{-}1595\text{ cm}^{-1}$ ,  $\text{N}=\text{N}$  stretch).<sup>4</sup>

(1) (a) Baird, N. C.; Swenson, J. R. *Can. J. Chem.* 1973, 51, 3097. (b) Baird, N. C.; Barr, R. F. *Ibid.* 1973, 51, 3303. (c) Merenyi, G.; Wettermark, G. *Chem. Phys.* 1973, 1, 340. (d) Wagniere, G. *Theor. Chim. Acta* 1973, 31, 269. (e) Lathan, W. A.; Curtiss, L. A.; Hehre, W. J.; Lisle, J. B.; Pople, J. A. *Prog. Phys. Org. Chem.* 1974, 11, 1975. (f) Winter, N. W.; Pitzer, R. M. *J. Chem. Phys.* 1975, 62, 1269. (g) Vasudevan, K.; Peyerimhoff, S. D.; Buenker, R. J.; Kammer, W. E. *Chem. Phys.* 1975, 7, 187. (h) Ahlrichs, R.; Staemmler, V. *Chem. Phys. Lett.* 1976, 37, 77. (i) Howell, J. M.; Kirschenbaum, L. J. *J. Am. Chem. Soc.* 1976, 98, 877. (j) Baird, N. C.; Werne, D. A. *Can. J. Chem.* 1977, 55, 350. (k) Skancke, P. N. *Chem. Phys. Lett.* 1977, 47, 259. (l) Baird, N. C.; Kathpal, H. B. *Can. J. Chem.* 1977, 55, 863. (m) Cimiriaglia, R.; Riera, J. M.; Tomasi, J. *Theor. Chim. Acta* 1977, 46, 223. (n) Davis, J. H.; Goddard, W. A. *J. Am. Chem. Soc.* 1977, 99, 7111. (o) Bigot, B.; Sevin, A.; Devaquet, A. *Ibid.* 1978, 100, 2639. (p) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* 1978, 14, 545. (q) Parsons, C. A.; Dykstra, C. E. *J. Chem. Phys.* 1979, 71, 3025. (r) Pasto, D. J.; Chipman, D. M. *J. Am. Chem. Soc.* 1979, 101, 2290. (s) Pasto, D. J. *Ibid.* 1979, 101, 6852. (t) Casewit, C.; Goddard, W. A., III. *Ibid.* 1980, 102, 4057. (u) Kemper, M. J. H.; Buck, H. M. *Can. J. Chem.* 1981, 59, 3044.

(2) (a) Foner, S. N.; Hudson, R. L. *J. Chem. Phys.* 1958, 28, 719. (b) Corey, E. J.; Mock, W. L. *J. Am. Chem. Soc.* 1962, 84, 685. (c) Rosengren, K.; Pimentel, G. L. *J. Chem. Phys.* 1965, 43, 507. (d) Wiberg, N.; Bachhuber, H.; Fischer, G. *Angew. Chem., Int. Ed. Engl.* 1972, 11, 829. (e) Willis, C.; Back, R. A. *Can. J. Chem.* 1973, 51, 3605. (f) Bondybey, V. E.; Nibler, J. W. *J. Chem. Phys.* 1973, 58, 2125. (g) Wiberg, N.; Fischer, G.; Bachhuber, H. *Chem. Ber.* 1974, 107, 1456. (h) Back, R. A.; Willis, C.; Ramsay, D. A. *Can. J. Chem.* 1974, 52, 1006. (i) Carloti, M.; Johns, J. W. C.; Trombetti, A. *Can. J. Phys.* 1974, 52, 340. (j) Wiberg, N.; Fischer, G.; Bachhuber, H. *Angew. Chem., Int. Ed. Engl.* 1976, 15, 385. (k) Frost, D. C.; Lee, S. T.; McDowell, C. A.; Westwood, N. P. C. *J. Chem. Phys.* 1976, 64, 4719. (l) Wiberg, N.; Fischer, G.; Bachhuber, H. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 780. (m) Foner, S. N.; Hudson, R. L. *J. Chem. Phys.* 1978, 68, 3162. (n) Wiberg, N.; Fischer, G.; Bachhuber, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1979, 34B, 1385. (o) Neudorfl, P. S.; Back, R. A.; Douglas, A. E. *Can. J. Chem.* 1981, 59, 506.

(3) For review, see: (a) Hunig, S.; Muller, H. R.; Thier, W. *Angew. Chem., Int. Ed. Engl.* 1965, 4, 271. (b) Lemal, D. M. In "Nitrenes"; Lowowski, W., Ed.; Interscience: New York, 1970; Chapter 10. (c) Ioffe, B. V.; Kuznetsov, M. H. *Russ. Chem. Rev. (Engl. Transl.)* 1972, 41, 131. (d) Lowowski, W. In "Reactive Intermediates"; Jones, M., Moss, R., Eds.; Wiley: New York, 1978; Chapter 6.