

nism.<sup>5</sup> In agreement with this the trans diastereomer **26/28** had negligible optical rotation  $[\alpha]_D^{25} + 2^0$  (*c* 0.6, C<sub>2</sub>H<sub>5</sub>OH) and in compounds **27/29** from deuterated carveol **21** the label was distributed equally between vinyl and methine positions.<sup>5a</sup>

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(5) Review: U. Schöllkopf, *Angew. Chem.*, **82**, 795 (1970); J. E. Baldwin, J. DeBernardis, and J. E. Patrick, *Tetrahedron Lett.*, 353 (1970), and earlier papers; V. Rautenstrauch, *J. Chem. Soc., Chem. Comm.*, 4 (1970).

(5a) NOTE ADDED IN PROOF. Condensation of CH<sub>2</sub>=C(C<sub>6</sub>H<sub>5</sub>)-CH<sub>2</sub>OH in *o*-dichlorobenzene at 175° with 2.5 equiv of dimethylformamide dineopentyl acetal during 4 hr gave CH<sub>2</sub>=C(C<sub>6</sub>H<sub>5</sub>)CH<sub>2</sub>CON(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> in 55% yield.

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### Photochemical Cleavage of the Quadruple Bond in [Re<sub>2</sub>Cl<sub>8</sub>]<sup>2-</sup>

Sir:

The thermal chemistry of [Re<sub>2</sub>Cl<sub>8</sub>]<sup>2-</sup> has been extensively investigated in recent years.<sup>1-6</sup> The quadruply bonded Re<sub>2</sub> unit has proved to be exceptionally inert, although occasionally monomeric products have been obtained.<sup>1,3,4</sup> We now report that bond cleavage has been achieved by ultraviolet irradiation of CH<sub>3</sub>CN solutions of [Re<sub>2</sub>Cl<sub>8</sub>]<sup>2-</sup>, providing a very convenient synthetic route to monomeric chloro complexes of Re(III).

The absorption spectrum of [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>2</sub>[Re<sub>2</sub>Cl<sub>8</sub>] (**1**) in CH<sub>3</sub>CN is shown in Figure 1 ("0" min). A detailed polarized single crystal electronic absorption spectral study of **1** and several closely related complexes has established that the 680-nm band is attributable to a  $\delta \rightarrow \delta^*$  transition,<sup>7,8</sup> and has further suggested that the low intensity band at 370 nm represents a  $\sigma \rightarrow \delta^*$  excitation.<sup>8</sup> Irradiation of a  $6 \times 10^{-5}$  M solution of **1** in CH<sub>3</sub>CN with a 1000-W Hg-Xe lamp equipped with a Pyrex filter results in the spectral changes shown in Figure 1.<sup>9</sup> The decrease in intensity of the 680-nm band suggests that the  $\delta$  bond, and possibly the entire Re<sub>2</sub> unit, has been cleaved. Confirmation of Re<sub>2</sub> dissociation is provided by the observation that two mono-

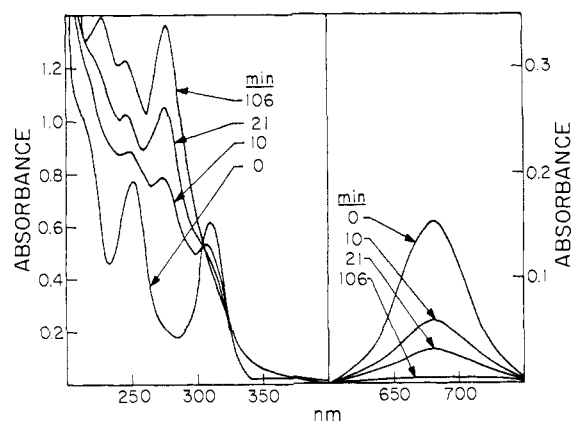


Figure 1. Pyrex-filtered irradiation of a  $6 \times 10^{-5}$  M acetonitrile solution of [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>2</sub>[Re<sub>2</sub>Cl<sub>8</sub>].

meric products are isolated from a preparative scale photolysis.<sup>10</sup> The most abundant is an orange solid, [ReCl<sub>3</sub>(CH<sub>3</sub>CN)]<sub>2</sub><sup>11</sup> (**2**). The magnetic moment of **2**, 1.60 BM, accords well with values obtained<sup>12-14</sup> for monomeric Re(III) complexes. Complex **2** should be a valuable starting material for the preparation of related [ReCl<sub>3</sub>L<sub>3</sub>] compounds. A tan compound, **3**, was isolated in very small yield. Although an insufficient amount of **3** was obtained to allow an elemental analysis, spectroscopic data suggest formulation as [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N][ReCl<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>]. The ir spectrum of **3** establishes that tetrabutylammonium is present, and the uv-visible and ir spectra attributable to the anionic component are identical with analogous features measured on a known sample of [(CH<sub>3</sub>)<sub>3</sub>NH][ReCl<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>].<sup>15</sup> The disappearance quantum yield of [Re<sub>2</sub>Cl<sub>8</sub>]<sup>2-</sup> upon 313 nm excitation, determined by monitoring the decrease in absorbance at 680 nm, was found to be  $0.017 \pm 0.005$ . Irradiation of **3** in CH<sub>3</sub>CN results in a rapid conversion to **2**, but the spectral similarity of **2** and **3** precluded a quantum-yield determination for this photolysis. However, the quantum yield appears to be at least an order of magnitude greater than that for the disappearance of **1**. Infrared and electronic absorption spectral data of **1-3** are set out in Table I.

As it is difficult to visualize the one-step conversion **1**  $\rightarrow$  **2**, we prefer the reaction pathway outlined in Scheme I. The initial photoproduct under Pyrex-

(1) F. A. Cotton, N. F. Curtis, and W. R. Robinson, *Inorg. Chem.*, **4**, 1696 (1965).

(2) F. A. Cotton, C. Oldham, and W. R. Robinson, *Inorg. Chem.*, **5**, 1798 (1966).

(3) F. A. Cotton, C. Oldham, and R. A. Walton, *Inorg. Chem.*, **6**, 214 (1967).

(4) F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *Inorg. Chem.*, **6**, 929 (1967).

(5) F. Bonati and F. A. Cotton, *Inorg. Chem.*, **6**, 1353 (1967).

(6) F. A. Cotton, *Accounts Chem. Res.*, **2**, 240 (1969).

(7) C. D. Cowman and H. B. Gray, *J. Amer. Chem. Soc.*, **95**, 8177 (1973).

(8) C. D. Cowman, Ph.D. dissertation, California Institute of Technology, 1973.

(9) [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>2</sub>[Re<sub>2</sub>Cl<sub>8</sub>] was prepared by the method of Cotton *et al.* (F. A. Cotton, N. F. Curtis, B. F. Johnson, and W. R. Robinson, *Inorg. Chem.*, **4**, 326 (1965)). Photolysis was conducted in 1-cm quartz cuvettes thermostated at 25° using MC and B spectroquality CH<sub>3</sub>CN. Spectral data were obtained using Cary 17 and Perkin-Elmer 225 spectrophotometers. Magnetic susceptibility measurements were performed on a Princeton Applied Research FM-1 vibrating sample magnetometer calibrated with HgCo(SCN)<sub>4</sub>.

(10) Pyrex-filtered light was used to photolyze a solution containing 1 g of [(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>2</sub>[Re<sub>2</sub>Cl<sub>8</sub>] in 75 ml of spectroquality CH<sub>3</sub>CN. A continuous argon purge was maintained throughout the photolysis. After the solution had turned from blue to orange (typically 24-48 hr), the irradiation was discontinued and the solution was concentrated by evaporation. The resultant solution and precipitate were chromatographed on silica gel with CH<sub>2</sub>Cl<sub>2</sub> as eluent. Evaporation of the CH<sub>2</sub>Cl<sub>2</sub> eluent solution, followed by recrystallization of the resultant solid from CH<sub>2</sub>Cl<sub>2</sub>-C<sub>4</sub>H<sub>10</sub>O, gave analytically pure **2**. Continued CH<sub>3</sub>CN-elution from the same column, followed by evaporation, gave **3**.

(11) *Anal.* Calcd for [ReCl<sub>3</sub>(CH<sub>3</sub>CN)]<sub>2</sub>: Re, 44.80; Cl, 25.59; C, 17.32; N, 10.11; H, 2.17. Found: Re, 44.50; Cl, 25.53; C, 16.99; N, 10.46; H, 2.32.

(12) G. Rouschias and G. Wilkinson, *J. Chem. Soc. A*, 489 (1968).

(13) G. Rouschias and G. Wilkinson, *J. Chem. Soc. A*, 993 (1967).

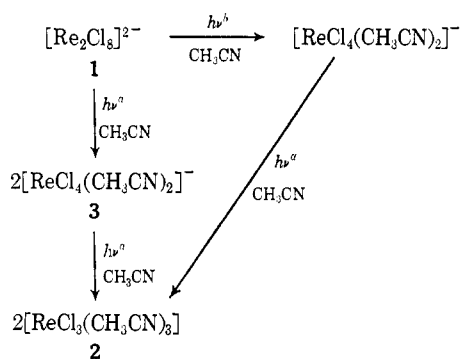
(14) B. F. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 152 (1964).

(15) Photolysis of orange [(CH<sub>3</sub>)<sub>3</sub>NH][ReCl<sub>4</sub>(CH<sub>3</sub>CN)]<sub>2</sub><sup>12</sup> (**4**) in CH<sub>3</sub>CN yields a tan compound, **5**, also analyzing for [(CH<sub>3</sub>)<sub>3</sub>NH][ReCl<sub>4</sub>(CH<sub>3</sub>CN)]<sub>2</sub>. Calcd: Re, 39.60; Cl, 30.20; N, 8.93; C, 17.86; H, 3.40. Found: Re, 40.37; Cl, 30.48; N, 8.71; C, 17.69; H, 3.51. Presumably, **4** and **5** are cis and trans isomers and ir evidence suggests that **4** is cis. The spectral properties of the anion of **3** are identical with those of the anion of **5**.

**Table I.** Infrared and Electronic Spectral Data for Compounds 1-3

Compound	$\nu_{\text{Re-Cl}}$ , $\text{cm}^{-1}$	Electronic absorption maxima, <sup>a</sup> nm
$[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$ (1)	333 <sup>b</sup>	680, 370, 353, 309, 252
$[\text{ReCl}_3(\text{CH}_3\text{CN})_3]$ (2)	<i>c</i>	310 sh, 275, 245, 230
	315 <sup>d</sup>	
	293 <sup>d</sup>	
$[(\text{CH}_3)_3\text{NH}][\text{ReCl}_4(\text{CH}_3\text{CN})_2]$ (3)	<i>c</i>	315 sh, 271, 255, 232
	301 <sup>d</sup>	

<sup>a</sup> In  $\text{CH}_3\text{CN}$  solution. <sup>b</sup> Nujol mull. <sup>c</sup> Bands at 2970, 2911, 1405, 1355, 1015, 939, and  $720\text{ cm}^{-1}$  are attributable to coordinated  $\text{CH}_3\text{CN}$ . <sup>d</sup> KBr disks.

**Scheme I**

<sup>a</sup>  $366\text{ nm} \geq \lambda > 300\text{ nm}$ . <sup>b</sup>  $\lambda 254\text{ nm}$ .

filtered excitation is **3**, but **3** is then further photolyzed to **2**.  $[\text{ReCl}_3(\text{CH}_3\text{CN})_3]$  is isolated in higher yield because of the much greater quantum yield of the second photolysis compared to the first.  $[\text{ReCl}_4(\text{CH}_3\text{CN})_2]^-$  is also the primary photoproduct under higher energy (254 nm) excitation, although in this case the spectral changes are very complex, indicating secondary and tertiary photoreactions. A chromatographic separation of a partially 254-nm photolyzed solution on silica gel produces a small amount of a tan compound whose uv-visible and ir spectra are identical with those of **3** and that when photolyzed with Pyrex-filtered light produces **2**.

$[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$  does not react with  $\text{CH}_3\text{CN}$  when stored in the dark or when kept under reflux for 12 hr, indicating that  $\text{Re}_2$  cleavage occurs in an electronic excited state. The quantum yield of disappearance of  $[\text{Re}_2\text{Cl}_8]^{2-}$  was found to be independent of the intensity of the exciting light,<sup>16</sup> suggesting that a one-photon process is responsible. Surprisingly, irradiation of **1** in  $\text{CH}_3\text{CN}$  with a He-Ne laser (632.8 nm) does not lead to reaction, which means that bond cleavage occurs from one of the excited states higher than that derived from the  $\delta \rightarrow \delta^*$  transition. Cleavage is observed when solutions are irradiated at 366 nm, which is in the region of  $\sigma \rightarrow \delta^*$  absorption.

Although we cannot present a detailed mechanism for the excited-state cleavage of  $\text{Re}_2$ , the fact that the reaction occurs at all has important implications concerning the characteristics of the quadruple bond. Previous bond-energy estimates in the range 300–400 kcal/mol<sup>6,17</sup> seem unreasonably high. If the mechanism involved simple dissociation to  $\text{ReCl}_4^-$ , photolysis at 366 nm would place an upper limit of 78 kcal/mol on the bond

(16) The intensity experiment was conducted using the 1000-W Hg-Xe lamp equipped with neutral density filters having an absorbance of 0.3, 0.6, and 1.2.

(17) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 924 (1967).

dissociation energy. However, the solvent undoubtedly plays an important role in the reaction and may lower the effective dissociation energy below that of the free ion. Such lowering could not be attributed to classical ionic solvation energy, as dissociation converts a doubly charged anion to two singly charged species. However, the monomeric ion is probably bound much more strongly than the dimer to acetonitrile molecules. If  $[\text{Re}_2\text{Cl}_8]^{2-}$  is weakly bound to two acetonitrile molecules oriented along the Re-Re axis in the ground state, these molecules may become tightly bound and aid dissociation of the excited state. We do not believe that more complex reorganization of the system can be involved since the reaction must occur during the very short lifetime of an upper excited state. It would be extraordinarily difficult to imagine interactions of this kind with the solvent which would lower the dissociation energy by more than 50 kcal/mol. Consequently, we doubt that the  $\text{Re}_2$  bond energy in the dimer can exceed 130 kcal/mol.

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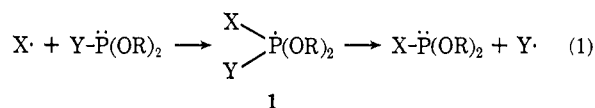
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### Stereochemistry of Free-Radical Displacements at Trivalent Phosphorus

Sir:

We wish to report the first study of the stereochemistry of a free-radical displacement at trivalent phosphorus (reaction 1). Although such displacements



do occur at various heteroatoms in organometallic and organometalloid systems, their stereochemistries are rarely determined.<sup>1</sup> Furthermore, displacements at trivalent phosphorus are of special interest because of the considerable *a priori* possibility that they may proceed with retention of configuration. Extensive amounts of chemical<sup>2</sup> and esr evidence<sup>3</sup> suggest that

(1) K. U. Ingold and B. P. Roberts, "Free-Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971. To our knowledge the only examples of truly free radical displacements whose stereochemistries are known are those on carbon in strained systems. For a recent example see J. H. Incremona and C. J. Upton, *J. Amer. Chem. Soc.*, **94**, 301 (1972).

(2) W. G. Bentrude and T. B. Min, *J. Amer. Chem. Soc.*, **94**, 1025 (1972); W. G. Bentrude and R. A. Wielesek, *ibid.*, **91**, 2406 (1969).

(3) See, e.g., P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 6033 (1972); G. B. Watts, D. Griller, and K. U. Ingold, *ibid.*, **94**, 8784 (1972); A. G. Davies, R. W. Dennis, D. Griller, and B. P. Roberts, *J. Organometal. Chem.*, **40**, C33 (1972); W. Nelson, G. Jackel, and W. Gordy, *J. Chem. Phys.*, **52**, 4572 (1970); R. W. Fessenden and R. H. Schuler, *ibid.*, **45**, 1845 (1966); G. F. Kokoska and F. E. Brinckman, *J. Amer. Chem. Soc.*, **92**, 1199 (1970).