Figure 2. Ratio of rate of 1-pentene formation (neat) to rate in the presence of piperylene vs. concentration of piperylene.

95 and 60% triplet reaction for 2-pentanone and 2-hexanone photolyses, respectively.

The initial slope in Figure 2 can be equated to k_q/k_r (k_q = rate constant for quenching, k_r = sum of rate constants for reactions quenched) as pointed out by Wagner and Hammond. Our value of $\sim$34 is greater than that expected based on Wagner and Hammond's values of 5 and 40 for 2-hexanone and 2-pentanone, respectively which have been correlated by those authors with the relative ease of abstraction of secondary vs. primary hydrogen by alkoxy radicals. It appears that other factors also may be operative.

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Six-Coordinate Trigonal-Prismatic Complexes[1]

Sir:

The octahedral six-coordinate transition metal ion was one of the great stereochemical triumphs of the nineteenth century.[2] It is often emphasized in basic textbooks that for six-coordinate metal complexes,

(1) This research was supported by the National Science Foundation.
(2) A. Werner, Z. anorg. Chem., 3, 267 (1893).

the trigonal-prismatic or hexagonal-planar structure "...cannot be correct."[3] Thus, it is of considerable interest that the six-coordinate complex $Re(S_2C_2Ph_2)_3{}^{4-6}$ (I) has recently been shown to have a near perfect

I
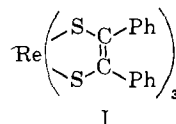
trigonal-prismatic array of donor atoms in a crystalline sample.[7] The maxim "six-coordination equals octahedral complex" has seemingly been violated for the first time. Since the requirements of crystal packing may be responsible for the unusual structure of I, it is urgent to determine whether the trigonal-prismatic structure will remain faithful in liquid solutions. Furthermore, we must ask if this exceptional geometry is limited to rhenium[8] or to this particular ligand (or to both), for it is to be noted that I is a member of a large class of six-coordinate transition metal complexes containing structurally similar sulfur-donor ligands.[9,10] This class of complexes includes at least nine different central metals and at least five different bidentate sulfur ligands.[5,6,10-14]

In this communication, we report some of the important physical properties of I, in solution and in the solid, and compare these properties with those of other members of the class. We also report some new six-coordinate complexes which almost certainly have trigonal-prismatic structures.

An analytically pure sample of compound I was prepared by treating an ethanol solution of $ReCl_5$ with P_4S_{10}–benzoin reaction product in xylene solution.[4] Green crystals of I are soluble in most organic solvents and can be recovered unchanged. The solid sample has a magnetic moment of 1.79 B.M. and in $CHCl_3$ and THF gives a single broad e.s.r. line (width, 75 gauss) at $g = 2.015 \pm 0.003$ (in good agreement with the observed magnetic moment). Furthermore, a polycrystalline sample shows but one broad line (width, 60 gauss), also at $g = 2.015 \pm 0.003$. This line appears to be symmetrical, indicating little if any anisotropy in the g tensor. A frozen glass e.s.r. spectrum of I at 77°K. in DMF–$CHCl_3$ shows a complex hyperfine pattern but little anisotropy in the g

(3) F. Basolo and R. C. Johnson, "Coordination Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p. 12.
(4) G. N. Schrauzer, V. Mayweg, H. W. Finck, U. Müller-Westerhoff, and W. Heinrich, Angew. Chem., 76, 345 (1964).
(5) G. N. Schrauzer, H. W. Finck, and V. Mayweg, ibid., 76, 715 (1964).
(6) J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer, and H. W. Finck, J. Am. Chem. Soc., 86, 4198 (1964).
(7) R. Eisenberg and J. A. Ibers, ibid., 87, 3776 (1965).
(8) Rhenium forms complexes with unusual structures, e.g., $ReH_9{}^{2-}$ (S. C. Abrahams, A. P. Ginsberg, and K. Knox, Inorg. Chem., 3, 558 (1964)), and $Re_2Cl_8{}^{2-}$ (F. A. Cotton and C. B. Harris, ibid., 4, 330 (1965)).
(9) The possibility of a trigonal-prismatic structure was first suggested for Co complexes containing bidentate sulfur-donor ligands, based on the dissimilarity of their electronic spectra with those of typical octahedral Co(III) systems.[10]
(10) C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, J. Am. Chem. Soc., 86, 2958 (1964).
(11) R. B. King, Inorg. Chem., 2, 641 (1963).
(12) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, J. Am. Chem. Soc., 86, 2799 (1964).
(13) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, Inorg. Chem., 4, 55 (1965).
(14) The metals included to date are Co, Fe, Ru, Os, Re, Cr, Mo, W, and V. The ligands are $[S_2C_2Ph_2]$, $[S_2C_2(CF_3)_2]$, tdt (toluene-3,4-dithiolate), bdt (benzene-1,2-dithiolate), and mnt (maleonitriledithiolate).

tensor.[15] The lowest band maxima in the solution absorption spectrum of I in $CHCl_3$ occur at 8230 cm.$^{-1}$ (ϵ 1090), 14,050 (24,000), and 23,450 (12,300). In a solid sample the lowest maxima are at 8000, 13,500, and 23,000 cm.$^{-1}$ (± 200 cm.$^{-1}$). The e.s.r. and electronic spectra clearly show that I retains its trigonal-prismatic structure in solution.

The polarographic behavior of I is very interesting. The complex exhibits three reversible reduction waves and one reversible oxidation wave in DMF solution, indicating the existence of the five different complexes $Re(S_2C_2Ph_2)_3{}^n$ with $n = -3, -2, -1, 0$, and $+1$. The half-wave potentials are $+0.163$ ($+1 \rightarrow 0$), -0.340 ($0 \rightarrow -1$), -1.812 ($-1 \rightarrow -2$), and -2.591 v. ($-2 \rightarrow -3$).[16] The existence of several states simply related by one-electron transfer reactions is a characteristic of the $M(S_2C_2R_2)_3{}^n$ systems.[6,12]

To facilitate the investigation of the occurrence of trigonal-prismatic coordination, we have prepared a series of $M(tdt)_3{}^n$ complexes with M = Cr, Mo, W, Re and $n = 0, -1$. Direct comparison with I is obtained with $Re(tdt)_3$ (II). Complex II, prepared by

II
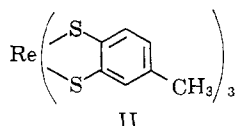
the reaction of $ReCl_5$ and toluene-3,4-dithiol in CCl_4, is green and shows a single broad e.s.r. line (width, 100 gauss) at $g = 2.010 \pm 0.003$ in $CHCl_3$ or THF and a similar single line in a polycrystalline solid at $g = 2.010 \pm 0.003$ (width, 70 gauss). The polarographic behavior of II is quite similar to that of I, with half-wave potentials at $+0.387$ ($+1 \rightarrow 0$), -0.065 ($0 \rightarrow -1$), -1.577 ($-1 \rightarrow -2$), and -2.375 v. ($-2 \rightarrow -3$),[16] indicating the existence of the corresponding five species of the type $Re(tdt)_3{}^n$. The lowest band maxima in the electronic spectrum of II in $CHCl_3$ are at 7920 cm.$^{-1}$ (ϵ 300), 9220 (500), 14,450 (16,000), and 24,930 (11,000). In addition, II shows precisely the pattern of I in its e.s.r. spectrum at 77°K. in a DMF–$CHCl_3$ glass (although the hyperfine splittings are slightly larger).[15] We conclude that complex II has a trigonal-prismatic array of donor atoms and that the ReS_6 fragment plays a dominant role in determining the electronic structure of both I and II.

We can now compare the results for I and II with the electronically similar complexes $ML_3{}^-$ [M = Cr, Mo, W; L = tdt, $S_2C_2Ph_2$,[6] $S_2C_2(CF_3)_2$[12]] and $VL_3{}^{2-}$[13] (L = tdt, bdt, $S_2C_2Ph_2$, and mnt). These complexes all have $S = \frac{1}{2}$ and their e.s.r. spectra yield g values in a narrow range near 2.00. The relatively small (or absence of) anisotropy in the g tensor in the complexes measured to date cannot be adequately accommodated assuming merely a distorted octahedral structure.[12,13] Comparing nonisoelectronic complexes, X-ray powder patterns show that $Re(S_2C_2Ph_2)_3$ and $W(S_2C_2Ph_2)_3$ are isomorphous and thus most probably isostructural.[17] Furthermore, the infrared spectra of the $M(tdt)_3$

(M = Mo, W, Re) complexes are essentially identical. From the above results we conclude that many, if not all, of these six-coordinate complexes possess the unusual trigonal-prismatic geometry.[18]

The bidentate sulfur-donor ligands which form trigonal-prismatic complexes previously have been found to stabilize the square-planar configuration over a large number of central metal atoms and unusual electronic structures.[19] It is likely that these same sulfur-donor ligands, in six-coordination, stabilize the trigonal-prismatic structure over an equally large series of metals and unusual electronic structures.

(18) It remains to be seen if the trigonal–prismatic geometry extends to such complexes as $Cr(mnt)_3{}^{3-}$. This is formally a Cr(III), d^3 case, usually considered to be an excellent octahedral situation.

(19) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, J. Am. Chem. Soc., 86, 4594 (1964), and references therein.

(20) National Science Foundation Predoctoral Fellow, 1965–1966.

(21) Alfred P. Sloan Research Fellow, 1964–1966.

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The Addition of Fluorenylidene to Olefins in the Presence of Hexafluorobenzene[1,2]

Sir:

The majority of carbenes add to olefins to give cyclopropanes in which the stereochemical relationship of the groups attached to the double bond is maintained.[3,4] Such additions are termed stereospecific. The reports[5,6] that diphenylcarbene was not stereospecific in its reactions with olefins were accompanied by the explanation of Skell[5] that triplet carbenes, typified by diphenylcarbene, would add to olefins in a nonstereospecific fashion. It has been wisely warned[7,8] that all nonstereospecific additions need not be due to triplets and that all triplets need not add in a nonstereospecific manner. Nonetheless, the use of the stereochemical outcome of the additions of carbenes to olefins as a diagnostic for spin states has been persistent and widespread.[3,4,9]

While reports of triplets are rare, the few examples available bear out Skell's explanation. Triplet methylene has been made by collisional deactivation of the

(1) Grateful acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research (P.R.F. No. 265G).

(2) Portions of this work are taken from the thesis of K. R. Rettig submitted in partial fulfillment of the requirements for the A.B. degree at Princeton University.

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(4) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964.

(5) R. M. Etter, H. S. Skovronek, and P. S. Skell, J. Am. Chem. Soc., 81, 1008 (1959).

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(15) Full details of the e.s.r. and other results, and a more complete interpretation, will be presented in a subsequent paper.

(16) Potentials in volts measured in DMF using a d.m.e. with Ag–$AgClO_4$ reference electrode. Oscillopolarography was used to establish that all waves are reversible. We thank R. Williams for assistance.

(17) We thank R. Eisenberg for assistance.