

Finally, we list the solvents tested. In the "soluble" category were acetonitrile, methanol, 1,4-butanediol, acetone, *n*-butyl alcohol, *n*-hexyl alcohol, benzyl alcohol, methylene chloride, 1-bromohexane, 1-chloroheptane, phenyl methyl ether, and chloroform. Propionic acid was found to be soluble, even though its ($\epsilon - \epsilon_m$) is negative; we attribute this to the dimer structure of zero dipole moment which contributes nothing to ϵ but can readily dissociate to a strongly polar monomer. In the "insoluble" category with low δ and low ϵ were *n*-hexane, 1,4-dioxane, *n*-butyl ether, *n*-propyl ether, isopropyl ether, ethyl ether, and 1-bromodecane. The cohesive energy density of water is so high that it also falls in the "insoluble" category.

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XPS Data for Linear Three-Center, Four-Electron Bonding in Sulfur Species

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The addition of a nucleophile (X^-) to a main group element compound with approximately eight valence shell electrons about the central atom (e.g., the 8-S-3 sulfonium ion: SR_2X^+) often provides a stable adduct (e.g., the 10-S-4 sulfuran: SR_2X_2) in which the nucleophile is bound to the main group element.² Bonding occurs by delocalization of the lone pair of electrons of the nucleophile into an unoccupied orbital of the eight-electron species—either a d-orbital or a σ^* antibonding orbital (e.g., the S-X σ^* orbital). The early "perfect pair model" of Pauling³ suggested that d-orbital occupancy must be invoked to explain the bonding of the nucleophile to the central atom.⁴ After the discovery of xenon difluoride, theoretical calculations provided support for the alternative bonding idea—transfer of the nucleophile's electron pair into a σ^* orbital to form a trigonal bipyramidal (TBP), or pseudo-TBP (ψ -TBP), species with linear three-center, four-electron (3c-4e) bonding.⁵ Although d-orbital participation is expected, most chemists now agree that d-orbital

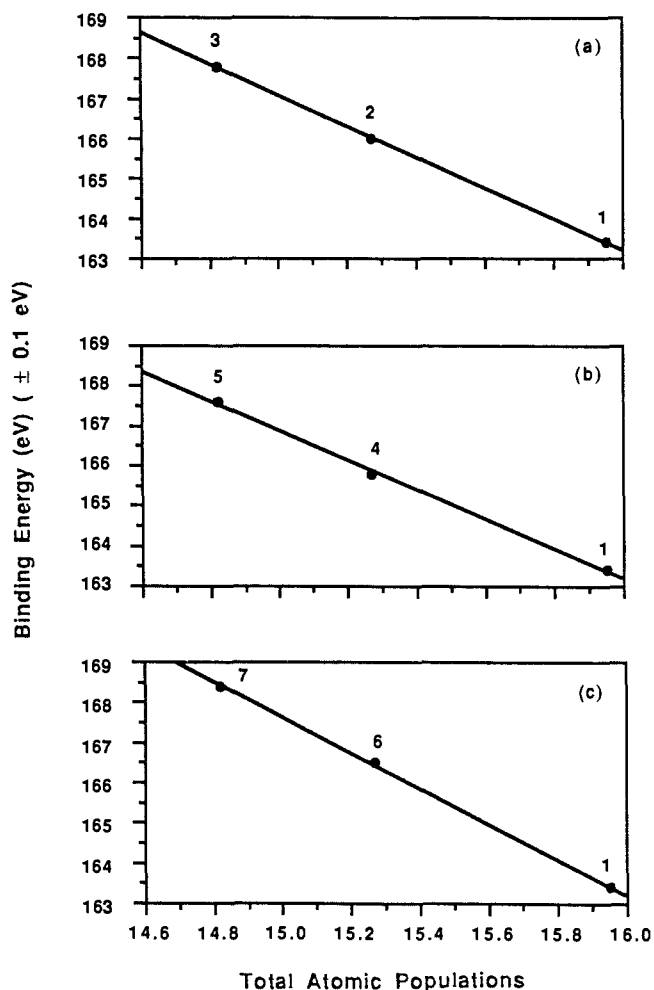


Figure 1. Plot of total atomic populations of a series of sulfur derivatives (SH_2 , SH_4 , and SH_6)⁷ vs XPS binding energies for S($2p_{3/2}$) for a range of variously oxidized sulfur species. The compounds' numbers correspond to those in Table I.

occupancy is rather small in most of these compounds, making the 3c-4e bond (partly covalent and partly ionic) an important feature in the TBP or ψ -TBP species.⁶ Ab initio calculations on sulfane (SH_2), sulfurane (SH_4), and octahedral (Oc) persulfurane (SH_6) showed⁷ very small d-orbital occupancy,⁸ with total electron populations of sulfur orbitals for SH_2 , SH_4 , and SH_6 to be 15.95, 15.27, and 14.82, respectively.⁷ The decrease in sulfur atomic population on going from SH_2 to SH_4 was 1.51 times the corresponding change between SH_4 and SH_6 . X-ray photoelectron spectroscopy (XPS) provides an accurate measure of the electron density (electronic character) at a specific element within a molecule.^{9,10} The partial ionic character of the 3c-4e bonds should

(6) (a) The term "hypervalent" to describe these species was proposed by Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54. Musher, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 1370. (b) The d-orbital occupancy was suggested to be small in these hypervalent species by Koutecky and Musher (Koutecky, V. B.; Musher, J. I. *Theor. Chim. Acta* **1974**, *33*, 227), and this suggestion was supported by the authors of ref 7.

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(8) Similar findings were reported for SF_2 , SF_4 , and SF_6 : Kiang, T.; Zare, R. N. *J. Am. Chem. Soc.* **1980**, *102*, 4024. See, also: Angyan, J. G.; Bonnelle, C.; Daudel, R.; Kucsman, A.; Csizmadia, I. G. *J. Mol. Structure (THEOCHEM)* **1988**, *165*, 273.

(9) For an introduction to XPS, see: *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*; Briggs, D., Seah, M. D., Eds.; John Wiley and Sons: New York, 1983.

(10) For recent examples from our laboratory, see: Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875. Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4224. Gassman, P. G.; Macomber, D. W.; Willging, S. M. *J. Am. Chem. Soc.* **1985**, *107*, 2380. Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470.

(1) General Electric Company Fellow, 1985-1986. American Chemical Society Division of Organic Chemistry Fellow, sponsored by the Rohm and Haas Company, 1986-1987.








(2) (a) In the $N-X-L$ system N is the number of electrons formally associated with the bonding surrounding the central atom X , with L ligands associated with atom X : Perkins, C. W.; Martin, J. C.; Arduengo, A. J. III; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753. (b) For examples of stable adducts to 8-S-3 species, see: Hayes, R. A.; Martin, J. C. In *Organic Sulphur Chemistry: Theoretical and Experimental Advances*; Csizmadia, E. G., Mangini, A., Bernardi, F., Eds.; Elsevier Scientific Publishing Company: Amsterdam, 1985; Chapter 8, pp 408-483.

(3) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. Kwart, H.; King, K. *D-Orbitals and the Chemistry of Silicon, Phosphorus, and Sulfur*; Springer-Verlag: New York, 1977.

(4) Substantial involvement of d-orbital participation in sulfuranes was suggested by the following: Angyan, J. G.; Poirer, R. A.; Kucsman, A.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1987**, *109*, 2237. Purcell, K. F.; Kotz, J. C. *Inorg. Chem.* W. B. Saunders Co.: Philadelphia, PA, 1972; p 65. See, also: Baird, N. C.; Taylor, K. F. *J. Comput. Chem.* **1981**, *2*, 225. Pietro, W. J.; Frach, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

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Table I. XPS Binding Energies of Sulfur Derivatives

compound	number	S(2p _{3/2}) binding energy (±0.1 eV)
	1 ^a	163.4
	2 ^a	166.0
	3 ^a	167.8
	4 ^b	165.8
	5 ^b	167.6
	6 ^c	166.5
	7 ^c	168.4

^aPurchased from Aldrich Chemical Company. ^bReference 11c. ^cReference 11d.

decrease electron density at the central atom. We find the XPS binding energies for stable 3c-4e bonded sulfur derivatives¹¹ (TBP and ψ -TBP geometries) give close correlations with the atomic populations calculated by Schwenger and Schaefer⁷ for analogous sulfur species. A similar correlation is observed for the diphenyl sulfane-sulfoxide-sulfone series. Table I lists the XPS binding energies for these sulfur derivatives.¹² Figure 1 shows plots of binding energies of related species vs the calculated⁷ total atomic electron populations. The correlation coefficients for Figure 1a-c were 1.000, 0.999, and 1.000, respectively.

The linear correlation of the S(II) sulfane, the S(IV) sulfoxide, and the S(VI) sulfone (1, 2, and 3) (Figure 1a) is almost identical with that of the S(II) sulfane, the S(IV) 10-S-4 sulfurane, and the S(VI) 10-S-5 sulfurane oxide (1, 4, and 5) (Figure 1b) when the apical oxygen ligands are α,α -dimethylalkoxides. Both sulfoxides and sulfones are therefore thought to have small d-orbital occupancy comparable to that calculated⁷ for the SH₄ and the SH₆ species and experimentally determined for 4 and 5 by their close correlation of XPS with the calculated⁷ electron densities for SH₄ and SH₆. Analogues 6 and 7 with the more electronegative apical oxygens of α,α -bis(trifluoromethyl)alkoxy groups are also well correlated, together with 1, to the calculated⁷ electron densities of SH₂, SH₄, and SH₆ (Figure 1c). The electron withdrawal of the four CF₃ groups provides a binding energy increase of 0.6-0.8 eV relative to the four CH₃ groups of 4 and 5.

Our results and interpretations contrast the papers of earlier investigators,¹³ who suggested that the XPS binding energies of

various sulfur derivatives, including 1, 2, and 3, correlated with the "formal" oxidation states of the sulfur atom and, as a result, suggested that these data were inconsistent with the formation of polar bonds. Correlation of the XPS data of Table I with the calculated⁷ atomic populations of SH₂, SH₄, and SH₆ suggests that d-orbital occupancy is low for all of these species.

In summary, the XPS data of Table I provides extensive insights into the nature of the bonding in sulfur species.

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A Stable η^2 -H₂ Complex of Cobalt. Role of the H-H Interaction in Hydrogen Transfer from Metal to Alkene

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Molecular hydrogen complexes of transition metals are much more widespread¹ than could be expected after the Kubas' seminal discovery of dihapto coordination of H₂ in [M(CO)₃(PR₃)₂(H₂)] [M = Mo, W; R = Cy, *i*-Pr].² In actuality, the importance of nondisruptive activation of H₂ in hydrogenation reactions must be seriously reconsidered, particularly for group VIII elements since it is these which generally give rise to the most active catalyst systems. It is with η^2 -dihydrogen and *cis*-dihydrides complexes of these metals and with their reactions with dimethyl maleate that the present communication is concerned.

The 16-electron fragments [(PP₃)Rh]⁺ and [(PP₃)Ir]⁺ [PP₃ = P(CH₂CH₂PPh₂)₃] add H₂ to give octahedral (OCT) *cis*-dihydrides of formula [(PP₃)M(H)₂]⁺ (M = Rh,³ 1; Ir,⁴ 2). However, while the iridium compound maintains the classical dihydride structure both in the solid state and in solution regardless of the temperature, the rhodium complex converts into the trigonal-bipyramidal (TBP) η^2 -H₂ isomer in solution above 173 K. The T₁(min) relaxation time of 120 ms and the JHD coupling constant of 18 Hz measured for the isotopomer [(PP₃)Rh(HD)]⁺ are strongly diagnostic for a quite long H-H bond distance.⁵ We have now synthesized the cobalt derivative [(PP₃)Co(H₂)]PF₆⁶ (3) as dark red crystals by protonation of the TBP monohydride [(PP₃)CoH]⁷ (4) in THF with HOSO₂CF₃ under argon atmo-

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(6) Compound 3 is stable for days in the solid state and in ambient temperature solutions under an argon atmosphere. $\Delta_M(\text{nitroethane}) = 86 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. The IR spectrum contains no $\nu(\text{Co-H})$. Anal. Calcd for C₄₂H₄₄CoP₃F₆: C, 57.55; H, 5.06; Co, 6.72; P, 17.67. Found: C, 57.63; H, 5.09; Co, 6.66; P, 17.45.

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