

Reactions of Dichalcogenide and Substituted Dichalcogenide  
Ligands of Molecular and Nonmolecular Compounds

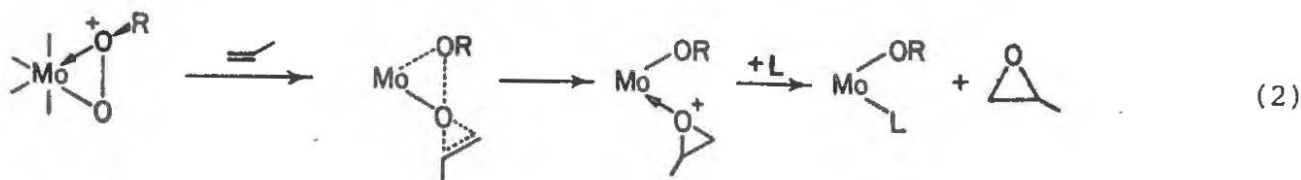
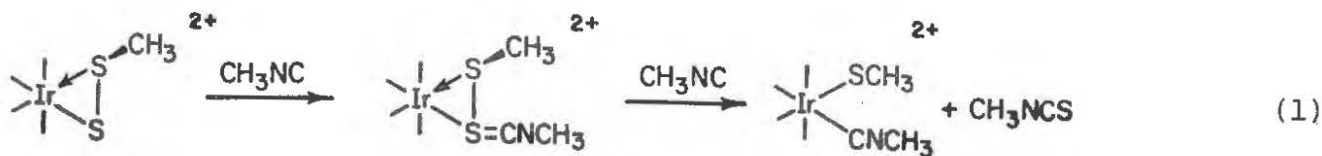
John E. Hoots

Final Seminar

October 20, 1983

Recently interest in side-bonding or  $\eta^2$ -ligands which contain chalcogens (O, S, Se) is accelerating with a wide variety of organic and inorganic systems being studied [1-3]. Three recent examples of significant work with the  $\eta^2$ -ligands have involved formation of an  $\eta^2$ -acetyl ligand by reversible CO insertion into a Zr-CH<sub>3</sub> bond [4], step-wise reduction of a thiocarbonyl ligand to CH<sub>3</sub>SH via an  $\eta^2$ -thioformyl intermediate [5], and X $\alpha$ -calculations probing the nature of bonding in  $\eta^2$ -E<sub>2</sub> complexes (E = O, S, Se) [6].

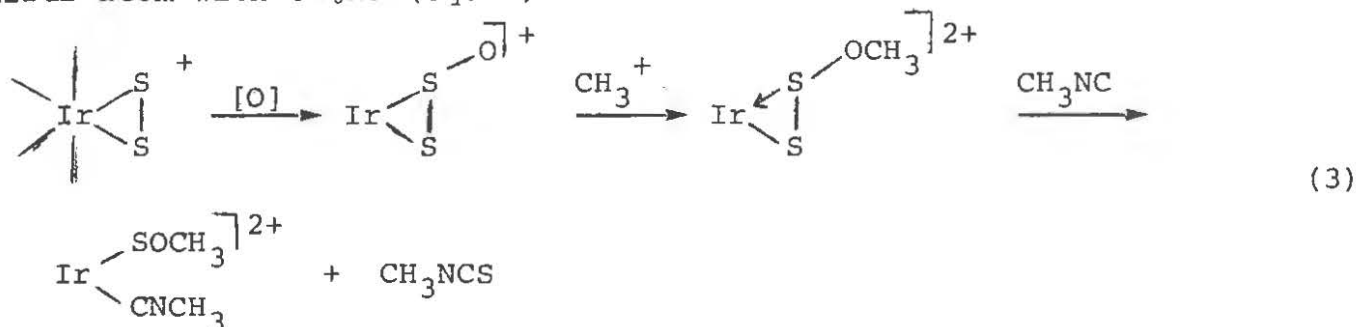
The formation of octahedral [Ir( $\eta^2$ -E<sub>2</sub>)(dppe)<sub>2</sub>]<sup>+</sup> (E = S, Se and dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) complexes is generally accomplished by "oxidative-addition" of pure chalcogens (S<sub>8</sub> or Se<sub>8</sub>) to [Ir(dppe)<sub>2</sub>]<sup>+</sup> [7]. Chalcogen transfer from (MeCp)<sub>2</sub>TiE<sub>5</sub> (E = S, Se) permitted similar conversions with a unique metallocycle, 1,4-[(MeCp)<sub>2</sub>Ti]<sub>2</sub>S<sub>4</sub>, co-produced with the Ir-S<sub>2</sub> complex. In the formation of the Ir-Se<sub>2</sub> compound, a significant rate enhancement (x 1000) was noted, as compared to the Se<sub>8</sub> method. The Ir-S<sub>2</sub> and -Se<sub>2</sub> complexes reacted with potent electrophiles such as CH<sub>3</sub>SO<sub>3</sub>F and CF<sub>3</sub>SO<sub>3</sub>H to form [Ir( $\eta^2$ -E<sub>2</sub>R)(dppe)<sub>2</sub>]<sup>2+</sup> (R = CH<sub>3</sub>, H and E = S, Se) [8]. The pyramidal nature of the alkylated chalcogen atom was demonstrated by the observation of resonances for diastereomeric complexes in the 360 MHz <sup>1</sup>H NMR spectra. The  $\eta^2$ -S<sub>2</sub>CH<sub>3</sub> complex is very reactive toward nucleophiles (CH<sub>3</sub>NC, CN<sup>-</sup>, and PPh<sub>3</sub>) and a variety of reaction pathways have been elucidated. In particular, the reaction involving CH<sub>3</sub>NC was shown to involve at least two steps (eq. 1) and serves as a model for the Oxirane olefin epoxidation process (eq. 2) [9].



The use of organoperacids permitted rapid, clean oxidations of the Ir-S<sub>2</sub> and Se<sub>2</sub> complexes to the corresponding  $\eta^2$ -S<sub>2</sub>O, S<sub>2</sub>O<sub>2</sub>, and Se<sub>2</sub>O compounds. Similarly, oxidation of Cp<sub>2</sub>Nb( $\eta^2$ -S<sub>2</sub>)Cl produced an  $\eta^2$ -S<sub>2</sub>O unit. Peracids were also used to effect the facile conversion of  $\mu_3$ -S to  $\mu_3$ -SO ligands in the syntheses of Fe<sub>3</sub>(CO)(S)(CO)<sub>9</sub> and Fe<sub>2</sub>Pt(SO)(S)(CO)<sub>6</sub>(PPh<sub>3</sub>)<sub>2</sub>, which represent the only sulfur-monoxide complexes presently known [10]. Only the triiron complex has been previously reported and was a by-product from the synthesis of Fe<sub>3</sub>(S)<sub>2</sub>(CO)<sub>9</sub> [11]. Reactivity studies on the E<sub>2</sub>O, S<sub>2</sub>O<sub>2</sub> and SO ligands indicated transfer of the exocyclic oxygen atom to be very

difficult in sulfur-based systems but relatively facile for the  $\eta^2$ -Se<sub>2</sub>O ligand.

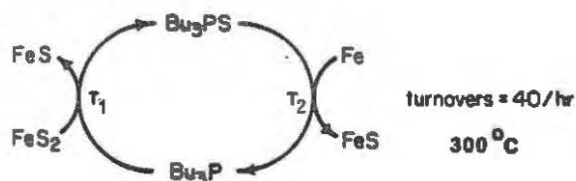
Attempted syntheses of complexes containing the elusive  $\eta^2$ -EO (E=S,Se) ligands by abstraction of the unsubstituted chalcogen in the  $\eta^2$ -E<sub>2</sub>O groups were not successful. However, the analogous and previously unknown  $\eta^2$ -SeS ligand was synthesized with [Ir(dppe)<sub>2</sub>]<sup>+</sup> and the chalcogen-transfer reagent, Cp<sub>2</sub>TiS<sub>x</sub>Se<sub>5-x</sub> (x≈2). A stabilized form of the SO unit, the O-methyl thioperoxide ligand, was observed in [Ir( $\eta^1$ -SOCH<sub>3</sub>)(CH<sub>3</sub>NC)(dppe)<sub>2</sub>]<sup>2+</sup> and was synthesized from the  $\eta^2$ -S<sub>2</sub>O complex by O-alkylation, followed by abstraction of the unsubstituted sulfur atom with CH<sub>3</sub>NC (eq. 3).



The appearance of high-field shifted ortho-phenyl resonance(s) for all cis-[Ir(X)(Y)(dppe)<sub>2</sub>]<sup>n+</sup> complexes [12] is particularly distinctive. A new theory based on mutual shielding effects of the aromatic rings is proposed from solution and solid-state structural studies of the cis-iridium complexes.

The research on monomeric  $\eta^2$ -dichalcogenide complexes has been extended to desulfurization of solid-state, extended-lattice metal sulfides, particularly pyrite (FeS<sub>2</sub>). The formation of pollutants, such SO<sub>2</sub>, from the decomposition of pyrite has remained a major barrier to increased use of coal as a fuel source. We found that pyrite is desulfurized at ~260°C with (n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>P to an equilibrium mixture of FeS and Fe<sub>0.95</sub>S (pyrrhotite), as determined by x-ray powder diffraction and Mössbauer spectroscopy [13,14]. The phosphine desulfurization reaction was successfully applied to a sample of Illinois coal (1.9% FeS<sub>2</sub>) with x-ray powder diffraction revealing complete conversion of pyrite to pyrrhotite. Also, partial desulfurization of a spectrum of metal sulfides (MoS<sub>3</sub>, CoS<sub>2</sub>, and Cu<sub>2</sub>S) was successful. Addition of a sulfur-receptor, such as metallic iron, created a catalytic cycle (shown below) with 40 turnovers/hour observed for an 100:1 ratio of FeS<sub>2</sub> to (n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>P at ~300°C. The desulfurization of FeS<sub>2</sub> with Fe under a CO atmosphere at 400°C indicated other catalytic cycles, such as the CO-COS couple [15,16], may exist and be potentially useful in future coal desulfurization processes.

#### Desulfurization Cycle



References

1. Müller, A.; Jaegermann, W.; Enemark, J. H. Coord. Chem. Rev. 1982, 46, 245.
2. Ibers, J. A. Chem. Soc. Rev. 1982, 11, 57.
3. Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. J. Chem. Soc., Dalton Trans. 1979, 1612.
4. Calderazzo, F. Angew. Chem., Int. Ed. Engl. 1977, 16, 299.
5. Collins, T. J.; Roper, W. R. J. Organomet. Chem. 1978, 159, 73.
6. Ginsberg, A. P.; Osborne, J. H.; Sprinkle, C. R. Inorg. Chem. 1983, 22, 254.
7. Ginsberg, A. P.; Lindsell, W. E.; Sprinkle, C. R.; West, K. W.; Cohen, R. L. Inorg. Chem. 1982, 21, 3666.
8. Only the  $S_2CH_3$  complex has been synthesized previously. Plute, L. K.; Haltiwanger, R. C.; Dubois, M. R. Inorg. Chem. 1979, 18, 3246.
9. Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidations of Organic Compounds," Academic Press: New York, 1981, pp. 56-62.
10. Lesch, D. A. Ph.D. Thesis, University of Illinois, 1983.
11. Markó, L.; Markó-Monostory, B.; Madach, T.; Vahrenkamp, H. Angew. Chem., Int. Ed. Engl. 1980, 19, 226.
12. Ginsberg, A. P.; Lindsell, W. E. Inorg. Chem. 1973, 12, 1983.
13. Vaughan, D. J.; Craig, J. R. "Mineral Chemistry of Metal Sulfides," Cambridge University Press: New York, 1978, Chapter 8, pp. 279-280.
14. Montano, P. A. Adv. Chem. Ser. 1981, 194, 137-175.
15. Hadjisavvas, P.; Caillet, M.; Galerie, A.; Besson, J. J. Electrochem. Soc. 1980, 127, 569.
16. Smith, G. V.; Hinckley, C. C.; Zahraa, O.; Nishizawa, T.; Saporoschenko, M.; Shiley, R. H. J. Catalysis 1982, 78, 262.