Synthesis and Reactivity of Polysulfido Metal Complexes

Robert J. Pafford, IV Final Seminar June 15, 2000

Polysulfidometalates have been known for almost 100 years. In the seminal work of Hofmann and Höchlen, they reported on a number of novel compounds including $[NH_4]_3[IrS_{15}]$ and $[NH_4]_2[PtS_{15}]\cdot 2H_2O$.[1,2] These compounds bridge the gap between main group and coordination chemistry.[3,4] Ninety years later, however, the $[NH_4]_3[IrS_{15}]$ complex was shown by single-crystal X-ray diffraction to be $[NH_4]_3[IrS_{16}]$.[5] The size of the metallopolysulfido ring can be roughly predicted with geometry. As the S-M-S angle increases, the polysulfide chain length increases.

Our group has previously shown that neutral zinc polysulfido amine complexes of the formula $ZnS_6(N\text{-donor})_2$ can be readily made in large quantities (where *N*-donor is pyridine, methylimidazole, or 1/2 tetramethylethylenediamine).[6] These zinc polysulfide complexes were shown to be reactive towards electrophiles. The initial goal of this project was to coordinate a third amine to the zinc center and observe the effect this would have on the structure and reactivity.

The tridentate amines pentamethyldiethylenetriamine (PMDETA) and 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3TACN)[7] were chosen as coligands for the zinc polysulfide moiety. Ligand substitution reactions of these amines with ZnS_6(TMEDA) yielded $ZnS_4(N\text{-donor})_3$ (where *N*-donor is PMDETA and Me_3TACN). These tridentate amine complexes adopt a distorted trigonal bipyramidal geometry in the solid state (Figure 1).

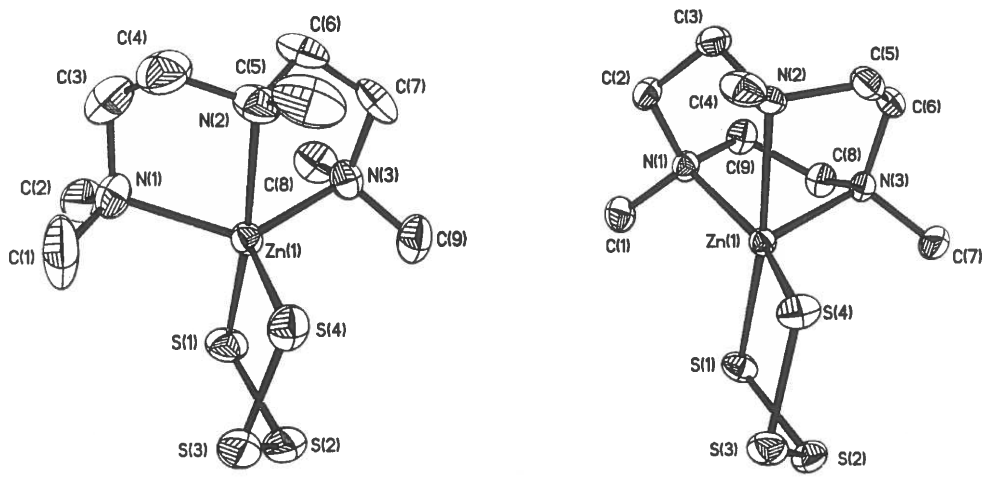

Figure 1. ZnS_4(PMDETA) (left) and $ZnS_4(Me_3TACN)$ (right)

ZnS_4(PMDETA) is about 100x more reactive than ZnS_6(TMEDA) towards the same electrophiles. Moreover, $ZnS_4(Me_3TACN)$ is about 5x more reactive than ZnS_4(PMDETA). Zinc dithiolenes can be prepared from the dehydrogenation of olefins by ZnS_4(PMDETA) (eq 1).

$$ZnS_4(PMDETA) \xrightarrow{+\ C_2H_3CN} ZnS_2C_2H(CN)(PMDETA) \qquad (1)$$

Desulfurization of $(NBu^n_4)Ir(S_6)_3$ (**1**) with excess PPh_3 yields a 30 e^- dimer $Ir_2S_2(PPh_4)_4$ (**2**). Crystallographic analysis of $Ir_2S_2(PPh_4)_4$ reveals a bitetrahedral structure with a pair of μ-S atoms (Figure 2).

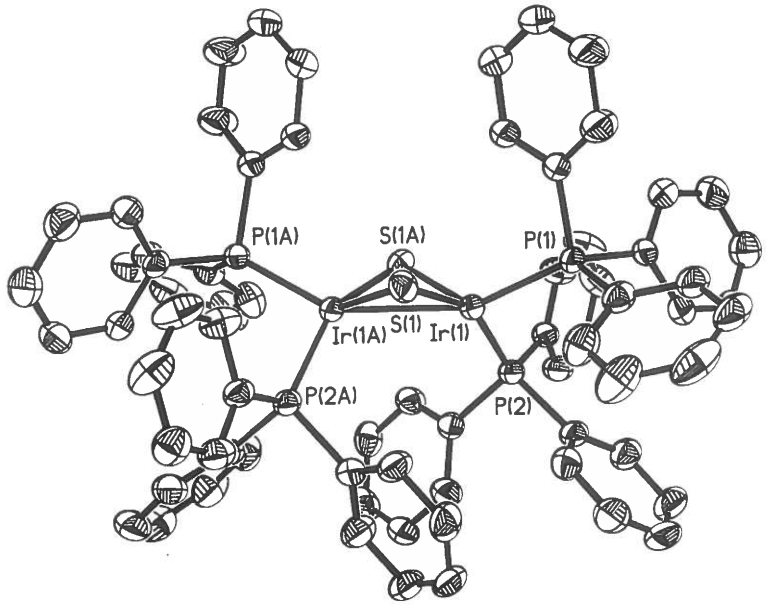

Figure 2

Two equiv of H_2 add to $Ir_2S_2(PPh_4)_4$ to yield $Ir_2S(SH)H_3(PPh_3)_4$ (**4**). The first addition of H_2 to $Ir_2S_2(PPh_4)_4$ proceeds homolytically while the second addition proceeds heterolytically. $Ir_2S(SH)H_3(PPh_3)_4$ had been previously made via a different method.[8] One equiv of H_2 adds to $Ir_2S_2(PPh_4)_4$ to yield $Ir_2S_2H_2(PPh_3)_4$ (**3**) (Scheme 1).

Scheme 1

$$Ir_2S_2(PPh_3)_4 \xrightarrow{+\,H_2} Ir_2S_2H_2(PPh_3)_4 \xrightarrow{+\,H_2} Ir_2S(SH)H_3(PPh_3)_4$$

Low temperature H_2 addition to $Ir_2S_2(PPh_4)_4$ reveals an intermediate (**4***). This intermediate is a kinetic isomer of compound **4**. The conversion of **4*** to **4** is a first-order reaction with an approximate rate constant (k_2) of 5 x 10^{-5} s^{-1} at -20 °C. With a 50 fold excess of H_2, the production of **4** by the addition of H_2 to **3** is also a first-order reaction with an approximate rate constant (k_1) of 3 x 10^{-5} s^{-1}.

Scheme 2

$$\mathbf{3} \xrightarrow{k_1} \mathbf{4^*} \xrightarrow{k_2} \mathbf{4}$$

References

1. Hofmann, K. A.; Höchtlen, F. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 3090.
2. Hofmann, K. A.; Höchtlen, F. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 245.
3. Draganjac, M. E.; Rauchfuss, T. B. *Angew. Chem. Int., Ed. Engl.* **1985**, *24*, 742.
4. Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89.
5. Albrecht-Schmitt, T. E.; Ibers, J. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2010.
6. Verma, A. K.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1995**, *34*, 3072.
7. Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1988**, *35*, 329.
8. Mueting, A. M.; Boyle, P. D.; Wagner, R.; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 271.