

Organometallic and Inorganic Derivatives of the Tetrathiomallates

Kevin E. Howard

Final Seminar

June 2, 1988

The coordination chemistry of the tetrathiomallates, especially of MoS_4^{2-} and WS_4^{2-} , has been of great interest because of its implied relevancy [1] to the nitrogen-fixing enzyme nitrogenase [2], biological copper/molybdenum antagonism [3], and the industrially important hydrodesulfurization process [4]. The tetrathiomallates are also important as potential precursors to useful materials [5]. A large number of inorganic coordination complexes of MoS_4^{2-} and WS_4^{2-} have been reported, yet few organometallic derivatives have been prepared [1].

In an effort to study the tetrathiomallates as ligands in heterometallic complexes, which may bind π -acidic coligands, the preparation of a number of low-valent organometallic derivatives of MoS_4^{2-} and WS_4^{2-} was undertaken. The complex $[(\text{COD})\text{Rh}]_2\text{WS}_4$ (Figure 1), 1, was prepared from the direct reaction of equimolar amounts of $[(\text{COD})\text{RhCl}]_2$ and $(\text{Ph}_4\text{P})_2\text{WS}_4$ [6].

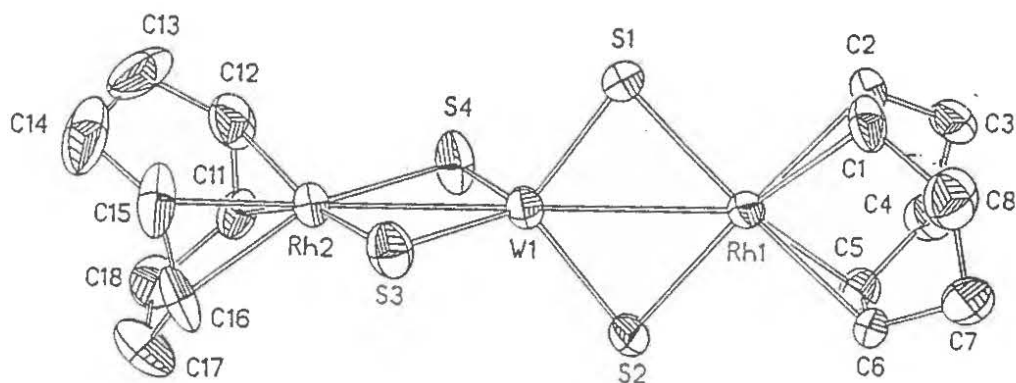


Figure 1

Compound 1 was found to exhibit extensive ligand substitution chemistry, involving organophosphines, CO, and *t*-BuNC. It was found that 1 could only support two strongly π -acidic CO ligands; $[(\text{PPh}_3)(\text{CO})\text{Rh}]_2\text{WS}_4$ was found to be the stable species. The reaction of $\text{Pd}(\text{WS}_4)_2^{2-}$ with an equimolar amount of $[(\text{COD})\text{RhCl}]_2$ gave the insoluble species, $(\text{COD})\text{Rh}(\mu\text{-S})_2\text{W}(\mu\text{-S})_2\text{Pd}(\mu\text{-S})_2\text{W}(\mu\text{-S})_2\text{Rh}(\text{COD})$. This complex reacted with excess PPh_3 , giving the CH_2Cl_2 -soluble species: $(\text{PPh}_3)_2\text{-Rh}(\mu\text{-S})_2\text{W}(\mu\text{-S})_2\text{Pd}(\mu\text{-S})_2\text{W}(\mu\text{-S})_2\text{Rh}(\text{PPh}_3)_2$.

Complexes of general formula $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Ru}(\text{PPh}_3)]_2\text{ME}_4$ (where $\text{R} = \text{H}, \text{CH}_3$; $\text{M} = \text{Mo}, \text{W}$; $\text{E} = \text{S}, \text{Se}$) were synthesized from two equivalents of $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Ru}(\text{PPh}_3)_2\text{Cl}$ and one equivalent of the corresponding $(\text{Ph}_4\text{P})_2\text{ME}_4$ [7]. The WSe_4 derivative was prepared using $(\text{t-BuNH}_3)_2\text{WSe}_4$, which was obtained from the reaction of $\text{W}(\text{NH-t-Bu})_2(\text{NH}_2\text{-t-Bu})_2$ with H_2Se . These compounds undergo single one electron oxidations in their cyclic voltammograms. Trialkylphosphines, carbon monoxide, and isocyanides (RNC , $\text{R} = \text{t-Bu}, \text{Me}, \text{and Bz}$) were found to displace the PPh_3 ligands in $[\text{CpRu}(\text{PPh}_3)]_2\text{WS}_4$ 2. In the case of CO however, substitution was

observed to occur at only one ruthenium center. A kinetic study of the substitution of PPh_3 by $t\text{-BuNC}$ in 2 revealed that the rate was independent of $[t\text{-BuNC}]$, indicating a dissociative mechanism.

A number of $[\text{L}_n\text{M}']_2\text{WS}_4$ complexes were prepared from WS_4^{2-} and compounds of the type $[\text{L}_n\text{M}(\mu\text{-Cl})]_2$. These included complexes where L_nM was $(\text{NBD})\text{Rh}$, $(\text{COD})\text{Ir}$, $(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}$, and $(\text{allyl})\text{Pd}$ [8]. The $\text{Rh}(\text{III})$ and $\text{Pd}(\text{II})$ derivatives were characterized by X-ray crystallography which showed M-W distances of $2.90\text{\AA}(\text{av.})$ and $2.80\text{\AA}(\text{av.})$ respectively. Poorly soluble complexes of the type $(\text{COD})\text{PtMS}_4$ ($\text{M} = \text{Mo}, \text{W}$) were prepared from the reaction of $(\text{COD})\text{PtCl}_2$ and $(\text{Ph}_4\text{P})_2\text{MS}_4$. The thermal gravimetric analyses of $[(\text{COD})\text{Rh}]_2\text{MS}_4$ and $(\text{COD})\text{PtMS}_4$ over temperature ranges of $50 - 900^\circ\text{C}$ indicate the formation of MRh_2S_x ($x = 2$ or 2.5) and PtMS formulas. We suggest that these complexes should be examined as precursors to new ternary metal sulfides.

The first tris-tetrathiometalate complexes, $\text{M}'(\text{WS}_4)_3^{3-}$, have been prepared from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ or $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ and three equivalents of $(\text{Et}_4\text{N})_3\text{WS}_4$. The rhodium complex was characterized by solution conductivity, IR, ^{183}W NMR, and elemental analysis.

The arene ruthenium thiometalate derivatives [9] $[(p\text{-cymene})\text{RuCl}]_2\text{WS}_4$ and $[(\text{C}_6\text{Me}_6)\text{RuCl}]_2\text{WS}_4$ were prepared from the reaction of $[(\text{arene})\text{RuCl}_2]_2$ with $(\text{Ph}_4\text{P})_2\text{WS}_4$. The complex $(p\text{-cymene})\text{Ru}(\text{PPh}_3)\text{WS}_4$ was prepared from $(p\text{-cymene})\text{-Ru}(\text{PPh}_3)\text{Cl}_2$ and $(\text{Ph}_4\text{P})_2\text{WS}_4$ and exhibits two distinct W-S distances (2.15 and 2.24\AA) in its structure (Figure 2) [9].

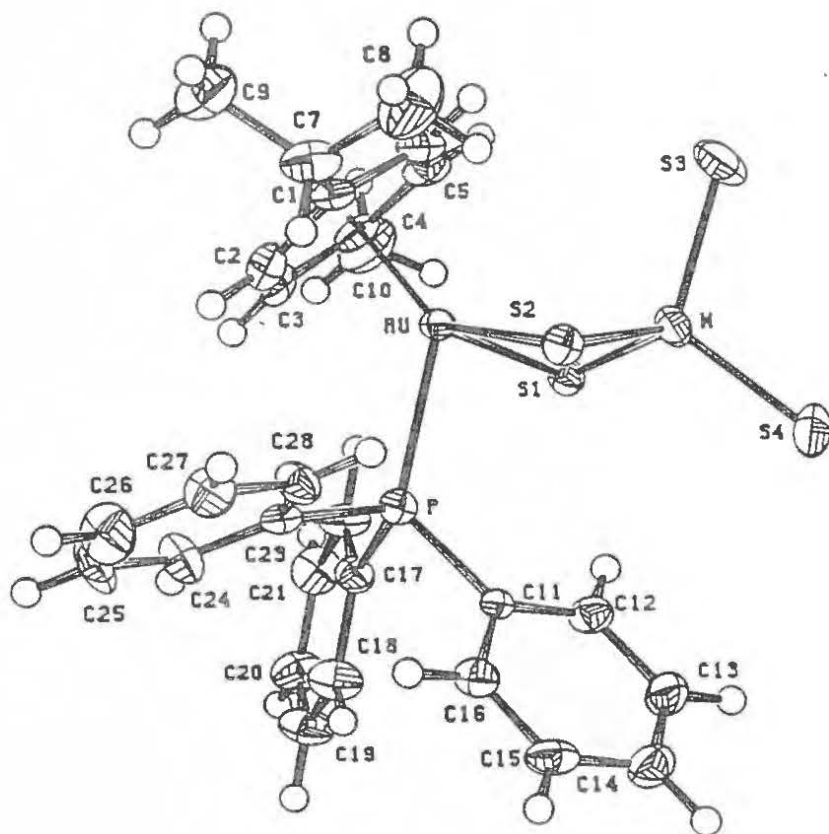


Figure 2

References

1. (a) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. Angew. Chem., Int. Ed. Engl. 1981, 20, 934.
(b) Coucouvanis, D. Acc. Chem. Res. 1981, 14, 201.
(c) Holm, R. H. Chem. Soc. Rev. 1981, 10, 455.
2. Zumft, W. G. Eur. J. Biochem. 1978, 91, 345.
3. Williams, D. F. Systemic Aspects of Biocompatibility 1981, 1, 166.
4. Chianelli, R. R.; Pecoraro, T. A.; Halbert, T. R.; Pan, W.-H.; Stiefel, E. I. J. Catal. 1984, 86, 226.
5. (a) Engelken, R. D.; Van Doren, T. P.; Boone, J. L.; Berry, A. K.; Shahnazary, A. Mat. Res. Bull. 1985, 20, 1173.
(b) Cramer, S. P.; Liang, S. K.; Jacobson, A. J.; Chang, C. H.; Chianelli, R. R. Inorg. Chem. 1984, 23, 1215.
(c) Nanjundaswamy, K. S.; Vasanthacharya, N. Y.; Gopalakrishnan, J.; Rao, C. N. R. Inorg. Chem. 1987, 26, 4286.
6. Howard, K. E.; Rauchfuss, T. B.; Rheingold, A. L. J. Am. Chem. Soc. 1986, 108, 297.
7. Howard, K. E.; Rauchfuss, T. B.; Wilson, S. R. Inorg. Chem. 1988, 27, 1710.
8. Howard, K. E.; Rauchfuss, T. B.; Wilson, S. R., submitted to Inorg. Chem. 1988.
9. Howard, K. E.; Rauchfuss, T. B.; Wilson, S. R., manuscript in preparation.