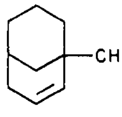
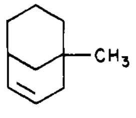


14



15

The greater stability of the platinum–pyridine complex 5 relative to the palladium–nitrile complexes is not fully understood but may be due to the metal (Pt vs. Pd) or the enhanced lability of the nitrile that can more readily create coordinatively unsaturated, reactive species.

We are currently broadening our studies of these complexes to include additional anti-Bredt olefins and metals (Fe, Ir, Rh) as well as further investigations into the reactivity of these unique complexes. In particular, these species are well suited to mechanistic studies of insertions because of their clear propensity to undergo such reactions and because of their inability to participate in competitive processes involving direct ligand attack, and we are focusing additional studies in this area.

Acknowledgment. We wish to thank the National Institutes of Health, Grant GM-27328, for support of this research. In addition, we wish to thank Mr. Frank Feher of the University of Rochester for considerable assistance in obtaining a number of the NMR spectra. We are also indebted to Prof. M. Anders of the Pharmacology Department, University of Rochester, Medical School, and Dr. Jonas Dedinnas of Kodak Research Laboratories for providing GC–MS services.

Registry No. 3, 17530-61-9; 4, 86508-21-6; 5, 86508-19-2; 6, 86560-60-3; 8, 86508-22-7; 9, 86508-23-8; 14, 86508-24-9; 15, 86508-25-0; (ethylene)$PtCl_2$(pyridine), 12078-66-9; $Pd(OAc)_2$, 3375-31-3; $Pd(CH_3CN)_2Cl_2$, 14592-56-4; $Pd(PhCN)_2Cl_2$, 14220-64-5; $Pd(Me)_2(PPh_3)_2$, 36485-69-5; $Pd(CD_3)_2(PPh_3)_2$, 86508-20-5.

Synthesis of Open Metal Carbonyl Cluster Compounds. The Reactions of *closo*-Sulfido Metal Carbonyl Cluster Compounds with H_2S. Synthesis and Crystal and Molecular Structure of $H_2Os_5(CO)_{14}(\mu_3\text{-}S)_2$

Richard D. Adams,* István T. Horváth, and Li-Wu Yang

Department of Chemistry, Yale University
New Haven, Connecticut 06511

Received April 15, 1983

Summary: The reactions of the *closo*-sulfido osmium carbonyl cluster compounds $Os_4(CO)_{12}(\mu_3\text{-}S)$, I, and $Os_5(CO)_{15}(\mu_4\text{-}S)$, II, with H_2S yield the open cluster compounds $H_2Os_4(CO)_{12}(\mu_3\text{-}S)_2$, III, and $H_2Os_5(CO)_{14}(\mu_3\text{-}S)_2$, IV, in yields of 55% and 94%, respectively. In each reaction one H_2S molecule has been converted into a triply bridging sulfido ligand and two hydride ligands.

The reaction of metal carbonyl cluster compounds with electron pair donors produces usually either ligand substitution or degradation of the cluster via cleavage of the metal–metal bonds.[1-4] However, if the added donor can serve as a bridging ligand, it could help to preserve the integrity of the molecule even in the presence of extensive cleavage of the metal–metal bonds.[5]

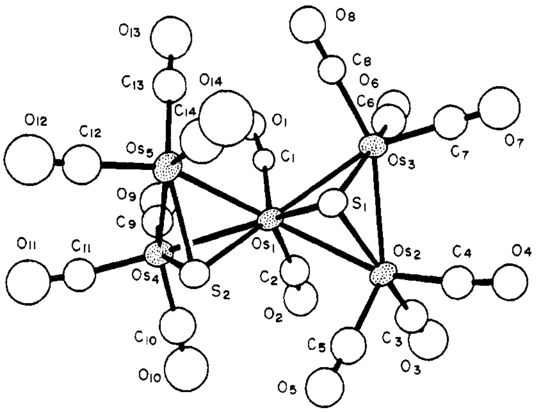
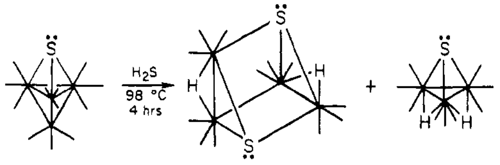


Figure 1. An ORTEP plot of $H_2Os_5(CO)_{14}(\mu_3\text{-}S)_2$, IV, showing 50% probability thermal-motion ellipsoids.

The reactions of H_2S with transition-metal complexes often yield complexes containing thiol or sulfido ligands as a result of cleavage of hydrogen–sulfur bonds in the H_2S ligand.[6-10] Sulfido ligands frequently coordinate as bridging, multielectron pair donors.[11] We have now found that the *closo*-sulfido osmium carbonyl clusters $Os_4(CO)_{12}(\mu_3\text{-}S)$, I,[12] and $Os_5(CO)_{15}(\mu_4\text{-}S)$, II,[13] react with H_2S to yield the open disulfido osmium carbonyl clusters $H_2Os_4(CO)_{12}(\mu_3\text{-}S)_2$, III, and $H_2Os_5(CO)_{14}(\mu_3\text{-}S)_2$, IV, respectively.

When refluxed for 4 h in heptane solvent under an atmosphere of H_2S, I is converted into the known compounds III and $H_2Os_3(CO)_9(\mu_3\text{-}S)$ in yields of 55% and 35%, respectively.[14] The structure of the selenium analogue of III has been determined previously.[14] The molecule consists of a trigonal prismatic cluster containing four osmium atoms and two sulfido ligands. Hydride ligands bridge two of the three metal–metal bonds. In this addition, the H_2S molecule is converted into one triply bridging sulfido and two bridging hydride ligands. Collectively, these ligands donate six electrons to the cluster. Accordingly, compound I which contains six metal–metal bonds is converted into the open cluster III which contains only three.



I III

---

[1] Muetterties, E. L.; Burch, R. R.; Stolzenberg, A. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 89.

[2] Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 379.

[3] Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285.

[4] Meyer, T. J. *Prog. Inorg. Chem.* **1975**, *19*, 1.

[5] Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113.

[6] Deeming, A. J.; Underhill, M. *J. Organomet. Chem.* **1972**, *42*, C60.

[7] Morelli, D.; Segre, A.; Ugo, R.; La Monica, G.; Cenini, S.; Conti, F.; Bonati, F. *Chem. Commun.* **1967**, 524.

[8] Collman, J. P.; Rothrock, R. K.; Stark, R. A. *Inorg. Chem.* **1977**, *16*, 437.

[9] Schmidt, M.; Hoffman, G. G.; Holler, R. *Inorg. Chem. Acta* **1979**, *32*, L19.

[10] Klumpp, E.; Marko, L.; Bor, G. *Chem. Ber.* **1964**, *97*, 926.

[11] Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 322.

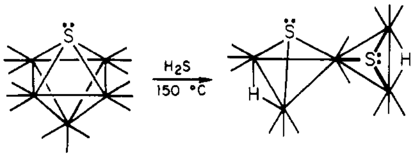
[12] Adams, R. D.; Foust, D. F.; Mathur, P. *Organometallics*, in press.

[13] Adams, R. D.; Horváth, I. T.; Segmüller, B. E.; Yang, L. W. *Organometallics* **1983**, *2*, 144.

[14] Johnson, B. F. G.; Lewis, J.; Lodge, P. G.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1979**, 719.

0276-7333/83/2302-1257$01.50/0

When refluxed in nonane solvent under an atmosphere of H_2S, II adds 1 mol of H_2S and eliminates 1 mol of CO to form the new compound IV in 94% yield.[15]



II

IV

The structure of IV was determined by X-ray crystallographic methods, and an ORTEP diagram of the molecule is shown in Figure 1.[16,17] The molecule consists of a "bow-tie" cluster of five metal atoms arranged in the form of two triangular Os_3 groupings which share the central metal atom Os(1).[18] Each triosmium group contains a triply bridging sulfido ligand and one bridging hydride ligand. The Os–Os and Os–S internuclear separations are similar to those in $H_2Os_3(CO)_9(\mu_3\text{-}S)$.[19] The elongated exterior Os–Os bonds Os(2)–Os(3) = 2.891 (1) Å and Os(4)–Os(5) = 2.885 (1) Å probably contain the bridging hydride ligands. Overall, the molecule has C_2 symmetry (not crystallographically imposed); thus, the hydride ligands are equivalent. The Os_5 bow tie is not planar but is twisted to give a dihedral angle of 56.3° between the Os(1), Os(2), Os(3) and Os(1), Os(4), Os(5) planes. The cluster compounds $Os_5(CO)_{19}$ and $Os_5(CO)_{16}[P(OMe)_3]_3$ contain bow-tie structures in which the dihedral angles between the Os_3 triangles are 21.2° and 24.8°, respectively.[20]

As in the reaction with I, the H_2S molecule in this reaction is converted into one triply bridging sulfido ligand and two hydride ligands which collectively donate six electrons to the cluster. However, due to the loss of the one CO ligand, the net increase in the number of cluster electrons is only four, and the conversion of II into IV results in the cleavage of only two metal–metal bonds. It is significant that the opening up of these closo clusters by H_2S does not lead to their degradation. In contrast, Lewis et al. have recently reported that the cluster $Os_6(CO)_{20}$ is converted into $H_2Os_3(CO)_9(\mu_3\text{-}S)$ upon reaction with H_2S.[21] Further studies on the addition of H_2S to *closo*-metal carbonyl clusters are in progress.

Acknowledgment. This work was supported by the National Science Foundation and the Alfred P. Sloan Foundation through a fellowship to R.D.A. NMR studies were supported by Grant no. CHE-7916210 to the Northeast Regional NSF-NMR Facility from the National Science Foundation. We wish to thank Engelhard Industries for a loan of osmium tetroxide.

Registry No. I, 82080-90-8; II, 86456-36-2; III, 72314-28-4; IV, 86456-37-3; $H_2Os_3(CO)_9(\mu_3\text{-}S)$, 38979-82-7.

Supplementary Material Available: Tables of structure factor amplitudes fractional atomic coordinates, bond distances, and bond angles (17 pages). Ordering information is given on any current masthead page.

---

[15] IR (hexane solvent): δ(CO) 2090 (vs), 2086 (s, sh), 2027 (s, sh), 2024 (s), 2013 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ −19.44 (s).

[16] Crystal data: space group $P\bar{1}$, No. 2; a = 9.147 (5) Å, b = 9.913 (4) Å, c = 14.920 (5) Å, α = 86.75 (3)°, β = 89.14 (4)°, γ = 70.09 (4)°, M_r 1409.3, Z = 2, ρ_{calcd} = 3.69 g/cm³. The structure was solved by the heavy-atom method. After correcting for absorption (μ = 251.9 cm^{-1}, for Mo Kα), full-matrix least-squares refinement (3672 reflections, $F^2 \geq 3.0\sigma(F^2)$, $2\theta \leq 50°$) yielded the final residuals R_F = 0.055 and R_{wF} = 0.056.[17]

[17] Intensity data were collected on an Enraf-Nonius CAD-4 automatic diffractometer by using ω scans. All calculations were performed on a Digital Equipment Corp. PDP 11/45 computer by using the Enraf-Nonius SDP program library, version 18.

[18] Selected internuclear distances (Å) and angles (deg) are as follows: Os(1)–Os(2) = 2.836 (1), Os(1)–Os(3) = 2.830 (1), Os(1)–Os(4) = 2.809 (1), Os(1)–Os(5) = 2.795 (1), Os(2)–Os(3) = 2.891 (1), Os(4)Os(5) = 2.885 (1); Os(2)–Os(1)–Os(3) = 61.38 (2), Os(1)–Os(2)–Os(3) = 59.21 (2), Os(1)–Os(3)–Os(2) = 59.41 (2); Os(4)–Os(1)–Os(5) = 61.98 (2), Os(1)–Os(4)–Os(5) = 58.78 (2), Os(1)–Os(5)–Os(4) = 59.24 (2), Os(2)–Os(1)–Os(4) = 138.06 (3), Os(2)–Os(1)–Os(5) = 139.67 (3), Os(3)–Os(1)–Os(4) = 157.89 (3), Os(3)–Os(1)–Os(5) = 111.82 (3), S(1)–Os(1)–S(2) = 90.16 (14).

[19] Johnson, B. F. G.; Lewis, J.; Pippard, D.; Raithby, P. R.; Sheldrick, G. M.; Rouse, K. D. *J. Chem. Soc., Dalton Trans.* **1979**, 616.

[20] Farrar, D. H.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc., Dalton Trans.* **1982**, 2051.

[21] Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Witmire, K. H. *J. Chem. Soc., Chem. Commun.* **1983**, 246.

Activation of Heteronuclear Triple Bonds by Cluster Compounds. The Cleavage of the C–N Triple Bond of an Isocyanide Ligand by a Ruthenium Cluster

Richard D. Adams,* Pradeep Mathur, and Brigitte E. Segmüller

Department of Chemistry, Yale University
New Haven, Connecticut 06511

Received May 3, 1983

Summary: Pyrolysis of the compound $Ru_5(CO)_{14}(CN\text{-}t\text{-}Bu)(\mu_5\text{-}CN\text{-}t\text{-}Bu)$, I, in nonane solvent for 2 h leads to formation of the hexaruthenium carbide cluster $Ru_6(C)(CO)_{15}(CN\text{-}t\text{-}Bu)(\mu\text{-}CO)$, II.

Considerable attention has been focused on the nature of the activation of small molecules by transition-metal cluster compounds.[1-3] It has been suggested that the reduction of triple bonds will be facilitated by multinuclear coordination interactions.[4] The activation of carbon monoxide, in particular, is a problem of great interest and importance,[5,6] and it has been shown that certain carbido clusters can be made by the abstraction of carbon from carbonyl ligands. However, the importance of polynuclear coordination in the activation of the ligand has not been ascertained.[7-9]

Herein we report the synthesis of a hexaruthenium carbido cluster in which the carbide carbon atom was abstracted from an isocyanide ligand and the importance of polynuclear coordination of the isocyanide ligand is strongly implied.

The compound $Ru_5(CO)_{14}(CN\text{-}t\text{-}Bu)(\mu_5\text{-}CN\text{-}t\text{-}Bu)$, I, was recently synthesized by Bruce et al. and shown to contain a quintuply bridging isocyanide ligand.[11] When heated

---

[1] Adams, R. D. *Acc. Chem. Res.* **1983**, *16*, 67.

[2] Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7238.

[3] Johnson, B. F. G.; Lewis, J. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 225.

[4] Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451.

[5] Tkatchenko, I. B. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: London, 1982; Chapter 50.

[6] Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

[7] (a) Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2606. (b) Bradley, J. S.; Ansell, G. G.; Hill, E. W. *J. Organomet. Chem.* **1980**, *184*, C33.

[8] Tachikawa, M.; Muetterties, E. L. *Prog. Inorg. Chem.* **1981**, *28*, 203.

[9] Shriver has recently demonstrated the importance of polynuclear metal centers in the proton-induced reduction of CO to methane.[10]

[10] Drezdgon, M. A.; Whitmire, K. H.; Battacharyya, A. A.; Wen-Liang, H.; Nagel, C. C.; Shore, S. G.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 5630.

[11] Bruce, M. I.; Matisons, J. G.; Rodgers, J. R.; Wallis, R. C. *J. Chem. Soc., Chem. Commun.* **1981**, 1070.