Journal of the Chinese Chemical Society, **1994**, *41*, 621-625

Communication

Synthesis of Thiolato Heterometallic Clusters from the Reaction of $Os_3(CO)_9(NCMe)(\mu\text{-}H)(\mu\text{-}SMe)$ with $CpW(CO)_3H$

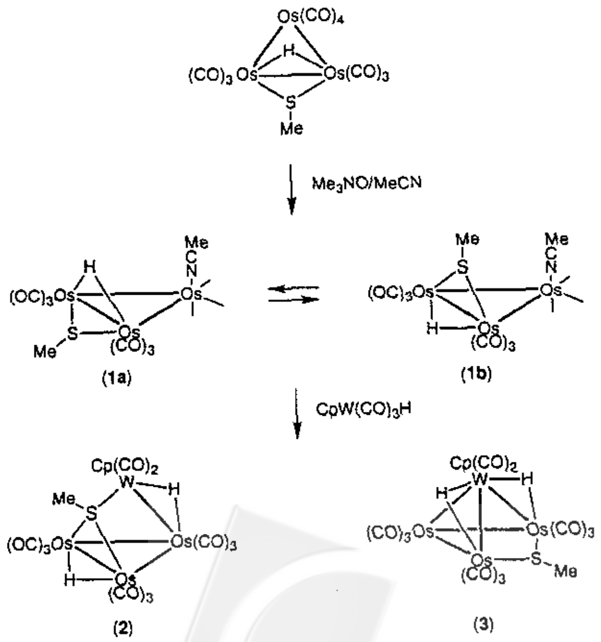
Chyuan-Wu Tsay[a] (蔡全武), Wen-Cheng Tu[a] (杜文正), Yun Chi*[a] (季　昀),
Shie-Ming Peng*[b] (彭旭明), Gene-Hsiang Lee[b] (李錦祥)
[a]*Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, R.O.C.*
[b]*Department of Chemistry, National Taiwan University, Taipei, Taiwan 107, R.O.C.*

Decarbonylation of triosmium methylthiolato cluster $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SMe)$ with Me_3NO in acetonitrile solution gave cluster $Os_3(CO)_9(NCMe)(\mu\text{-}H)(\mu\text{-}SMe)$ **(1)**, in which one axial CO on the non-bridged Os atom is replaced by an acetonitrile ligand. Crystal data for **2**: space group P bca, a = 14.491(1), b = 16.107(5), c = 16.639(5) Å, Z = 8; $R_F = 0.037$, $R_w = 0.033$. Treatment of **2** with $CpW(CO)_3H$ in refluxing THF solution yielded two cluster compounds with formula $CpWOs_3(CO)_{11}(\mu\text{-}H)_2(\mu_3\text{-}SMe)$ **(2)** and $CpWOs_3(CO)_{11}(\mu\text{-}H)_2(\mu\text{-}SMe)$ **(3)** as the principle products. The first possesses a spiked-triangular geometry with a triply bridging thiolato ligand and the second adopts a butterfly metal core arrangement with an edge-bridging thiolato grouping. The structure of **2** was characterized by single-crystal X-ray diffraction. Crystal data: space group P $\bar{1}$, a = 8.865(5), b = 8.959(3), c = 16.688(4) Å, α = 103.49(2), β = 93.58(3), γ = 113.03(4)°, Z = 2, $R_F = 0.034$, $R_w = 0.035$.

The chemistry of mixed-metal cluster complexes has been the subject of intensive research for many years,[1] due to the potential of these systems in studying the bonding and reactivity of organic hydrocarbon ligands by varying the transition-metal elements. With the objective to find a systematic method for the preparation of heterometallic cluster complexes, our research group have examined the condensation of mononuclear tungsten hydrides $LW(CO)_3H$, L = Cp and Cp*, and group 8 trinuclear clusters containing a heteroatom bridging ligand, such as $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}COMe)$,[2] $Ru_3(CO)_{10}(\mu_3\text{-}NPh)$[3] and $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}PPh_2)$.[4] As a result, we obtained several polynuclear heterometallic cluster compounds containing methoxymethylidyne, phenylimido and phosphinidene ligands. In order to extend these cluster assembling reactions to the compounds containing thiolato or sulfido ligand, we have carried out the reaction of osmium complex $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SMe)$ with $CpW(CO)_3H$ in the presence of Me_3NO reagent. In this preliminary report, we describe the X-ray crystal structure of $Os_3(CO)_9(NCMe)(\mu\text{-}H)(\mu\text{-}SMe)$, which was obtained from direct treatment of $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SMe)$ with Me_3NO in acetonitrile solution, and the characterization of two other heterometallic thiolato complexes prepared from the specified reactions.

Treatment of the triosmium thiolato complex $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SMe)$ with 1.2 equivalent of freshly sublimed Me_3NO in a dichloromethane-acetonitrile solution (10 : 1) produced an acetonitrile substituted cluster compound $Os_3(CO)_9(NCMe)(\mu\text{-}H)(\mu\text{-}SMe)$ **(1)** in 65% yield (Scheme I). This cluster compound was isolated by thin-layer chromatography on silica gel and fully characterized

Scheme I



Dedicated to Professor Sung-Mao Wang (王松茂) on the occasion of his seventieth birthday.

by spectroscopic methods.[5] Compound **1** and related derivatives of the type $Os_3(CO)_9(NCMe)(\mu\text{-}H)(\mu\text{-}ER)$, E = O or S, R = Et and Ph, have been synthesized by Lewis and Johnson using the same method, but no crystal structure is reported.[6] Thus, a single-crystal X-ray diffraction study of **1** was performed to establish the ligand arrangement.[7]

The molecular structure is depicted in Fig. 1, which also provides the selected data of bond lengths and angles. The molecule has an isosceles triangular geometry, the longest Os-Os edge is bridged by both the methylthiolato group and a hydride ligand. The bridged Os(2)-Os(3) distance of 2.856(1) Å is slightly longer than the other Os-Os distances within this molecule (Os(1)-Os(2) = 2.821(1) Å and Os(1)-Os(3) = 2.827(1) Å), which are comparable to distances 2.841 - 2.871 Å observed in the clusters containing $Os_2(\mu\text{-}H)(\mu\text{-}SR)$ fragment.[8] The non-bridged Os(1) atom is associated with three CO ligands and an acetonitrile ligand. The latter occupies an axial coordination site located on the same side of the bridging hydride ligand. The axial Os-C(carbonyl) distance *trans* to the acetonitrile ligand (Os(1)-C(2) = 1.86(2) Å) is shorter than the equatorial Os-C(carbonyl) distances (Os(1)-C(1) = 1.91(2) and Os(1)-C(3) = 1.89(2) Å) of the same Os atom. The shortening of the axial Os-C distance is a result of π-bond competition because the acetonitrile ligand is a good σ-donor but poor π-acceptor. Therefore, the *trans*-carbonyl ligand, which is a better π-acceptor, receives most of the back-donated electron density from the metal and this results in the short axial Os-C bond. Similar variation in Os-C(carbonyl) distances has been noted for the parent acetonitrile derivatives $Os_3(CO)_{10}(NCMe)_2$ and $Os_3(CO)_{11}(NCMe)$.[9]

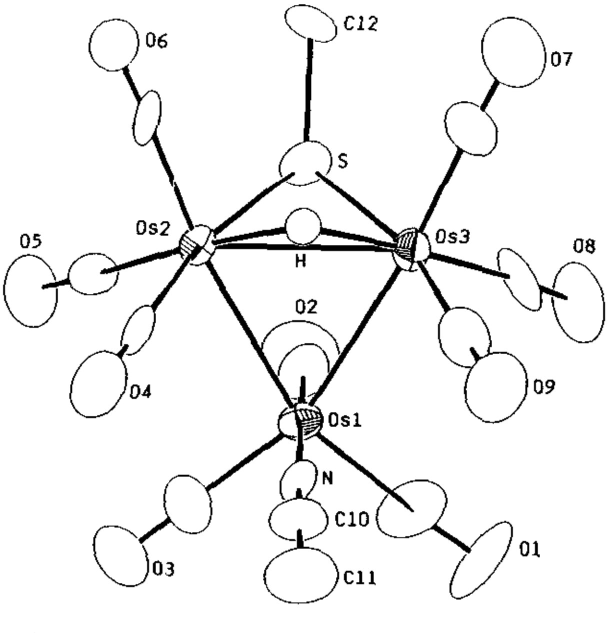


Fig. 1. Molecular structure of **1** and selected bond lengths and angles: Os(1)-Os(2) = 2.821(1), Os(1)-Os(3) = 2.827(1), Os(2)-Os(3) = 2.856(1), Os(2)-S = 2.400(5), Os(3)-S = 2.422(5), Os(2)-H = 1.73(1), Os(3)-H = 1.78(1), Os(1)-N = 2.12(1), N-C(10) = 1.18(2), Os(1)-C(1) = 1.91(2), Os(1)-C(2) = 1.86(2), Os(1)-C(3) = 1.89(2) Å; Os(2)-S-Os(3) = 72.6(4), Os(1)-N-C(10) = 177(8), N-C(10)-C(11) = 173(2)°. Thermal ellipsoids are shown at the 50% level.

Complex **1** forms two isomers in solution, as revealed by ^1H and ^{13}C NMR spectra. The ^1H NMR spectrum displays one set of NCMe, μ-SMe and hydride signals at δ 2.53, 2.48 and -16.29 ($J_{Os\text{-}H}$ = 34 Hz), and a second set of signals at δ 2.54, 2.49 and -16.49 ($J_{Os\text{-}H}$ = 34 Hz), respectively. The relative ratio of the two sets of signals was 1:2. The low intensity satellites of the hydride ligands were clearly discernible for both isomers, as a result of coupling with ^{187}Os nuclei (I = 1/2, 1.6% natural abundance). These $J_{Os\text{-}H}$ couplings fall in the range expected for osmium hydrido clusters.[10] The ^{13}C NMR spectrum exhibits one set of five Os-CO signals at δ 181.4, 181.1, 180.8, 175.1 and 172.3 with a ratio 1:2:2:2:2, and a less intense second set of five CO signals at δ 181.8, 180.1, 178.6, 176.1 and 173.7 with a ratio 2:1:2:2:2. These ^{13}C NMR data indicate that both isomers contain C_s point group symmetry in solution. Based on these ^{13}C NMR data and the fact that its parent complex $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SMe)$ shows only one isomer in solution,[11] we propose that isomerization is a result of interchange of the acetonitrile ligand at both axial positions of the non-bridged $Os(CO)_3(NCMe)$ center, as indicated in Scheme I. Thus, the CO signals occurring at δ 181.4 and 180.1 with an intensity corresponding to one CO are apparently due to the axial CO *trans* to the acetonitrile ligand. The presence of the third isomer, in which the acetonitrile is coordinated to one of the Os atoms bridged by thiolate and hydride ligands, was not observed in this system.

Reactions of $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SMe)$ and **1** with $CpW(CO)_3H$ were next carried out in attempts to synthesize the anticipated WOs_3 thiolato cluster compounds. Direct treatment of **1** with $CpW(CO)_3H$ in refluxing THF solution failed to produce any isolable cluster compounds. However, when complex **1** was first reacted with freshly sublimed Me_3NO (1.3 eq.) in acetonitrile-dichloromethane mixture followed by treatment with $CpW(CO)_3H$ (2 eq.) in refluxing THF (10 min), we isolated two WOs_3 thiolato clusters $CpWOs_3(CO)_{11}(\mu\text{-}H)_2(\mu_3\text{-}SMe)$ **(2)** and $CpWOs_3(CO)_{11}(\mu\text{-}H)_2(\mu\text{-}SMe)$ **(3)** in 18% and 12% yields, respectively. These cluster compounds were separated by thin-layer chromatography and characterized by microanalysis, spectroscopic methods and X-ray diffraction studies.[12] Similar results were obtained by using $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-SMe})$ and approximately 2.5 equiv. of Me_3NO instead of the preceding system, suggesting that the initialization of cluster condensation requires removal of two CO ligands on triosmium cluster $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-SMe})$.

The FAB mass spectrum of **2** indicates a parent ion at *m/z* 1182, corresponding to a composition $C_{17}H_{10}O_{11}S_1W_1Os_3$. Its solution IR spectrum shows CO stretching bands at the regime 2089 - 1890 cm^{-1} indicating the presence of terminal CO ligands. The ^1H NMR spectrum exhibits Cp and methyl resonances at δ 5.73 (5H) and 2.68 (3H) in addition to two hydride signals at δ -16.16 (1H) and -22.35 (1H, $J_{W\text{-}H}$ = 49 Hz). The ^{13}C NMR spectrum clearly shows the presence of 11 CO ligands; two signals of equal intensity at δ 243.2 and 235.9 are due to the W-CO ligands. Nine other CO signals in the highfield region of δ 182.1-169.5 are assigned to the Os-CO ligands. Based on these spectral data, a formula $CpWOs_3(CO)_{11}(\mu\text{-H})_2(\mu\text{-SMe})$, which involves a $CpW(CO)_2$, three $Os(CO)_3$ fragments, two bridging hydrides and a methylthiolato grouping, is proposed for this complex.

Complex **2** was further characterized by single crystal X-ray diffraction.[13] As indicated in Fig. 2, this molecule adopts a spiked-triangular core arrangement, in which each Os atom is associated with three orthogonal terminal CO ligands, whereas the tungsten bears a cyclopentadienyl and two terminal CO ligands. The methylthiolato ligand is coordinated to three metal atoms, Os(1), Os(3) and W. The W-S distance (2.468(3) Å) is much shorter than that of the W-S distances in dinuclear complex $CpW(CO)_3(\mu\text{-SMe})W(CO)_5$ which contains no direct W-W bond,[14] whereas the Os-S distances (2.380(3) Å and 2.367(3) Å) are comparable with those of the Os-S single bonds in the μ_3-sulfido clusters.[15] The bridging hydrides, located by the difference Fourier method, are associated with the longest and the second longest metal-metal bonds within the molecule (Os(1)-Os(3) = 2.882(2) Å and W-Os(1) = 3.436(1) Å). The positions of hydrides are also in accordance with the observed $J_{W\text{-}H}$ coupling in the ^1H NMR spectrum. Two other Os-Os distances are nearly equal (Os(1)-Os(2) = 2.824(2) Å and Os(2)-Os(3) = 2.824(1) Å), which are similar to those observed in sulfido cluster $CpWOs_3(CO)_{11}(\mu\text{-H})(\mu_3\text{-S})$.[16] Finally, assuming that the μ_3-SMe ligand serves as a five-electron donor, this molecule contains 64 valence electrons, which agrees with the electron counting of tetranuclear clusters with four metal-metal bonds.

The second cluster product isolated is complex **3** which possesses a molecular formula identical with that of **2**, indicated by FAB mass analysis and elemental analysis. The ^1H NMR spectrum of this compound exhibits only one hydride signal at δ -14.12 (2H, $J_{W\text{-}H}$ = 43.6Hz), in addition to the expected Cp and μ-SMe signals at δ 5.80 (5H) and 2.38 (3H). The W-CO ligands appear at δ 214.2 (2C, $J_{W\text{-}C}$ = 148Hz) and other Os-CO ligands resonate at δ 187 (br), 181 (br), 178.3, 180.0 and 172.1 with a ratio 2:1:2:2:2 in the ^{13}C NMR spectrum at room temperature. These sepctral data suggests that complex **3** contains a C_s symmetry and both hydride ligands are coordinated to the equivalent W-Os edges. The structure shown in Scheme I is consistent with these spectroscopic data. An X-ray analysis of the related derivative $Cp^*WOs_3(CO)_{11}(\mu\text{-H})_2(\mu\text{-SPh})$ confirmed the above structural assignment.[17]

In summary, the condensation reaction reported in this article provides a convenient strategy for preparation of WOs_3 clusters with a bridging thiolato group. The successful isolation of these two WOs_3 cluster compounds confirms the ability of thiolato ligands in adopting the various coordination modes and the potential to serve as a protecting group that can hold together the metal atoms. We are currently examining the reactivity of these thiolato clusters. According to our preliminary results, upon heating in refluxing toluene solution we observed that complexes **2** and **3** failed to inter-

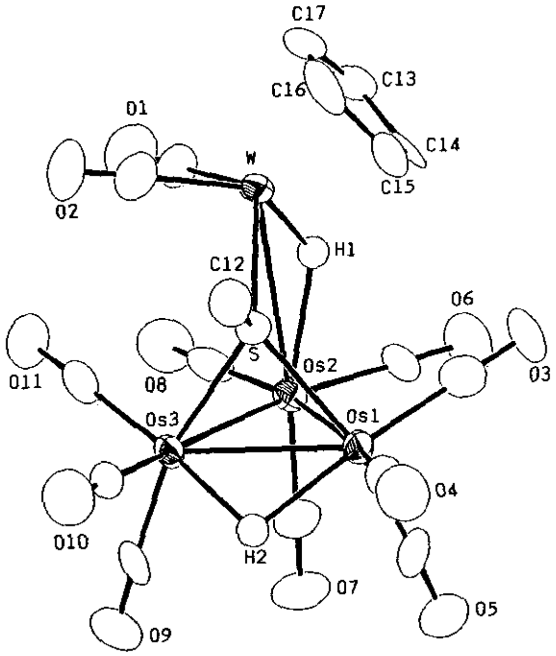


Fig. 2. Molecular structure of **2** and selected bond lengths and angles: Os(1)-Os(2) = 2.824(2), Os(1)-Os(3) = 2.882(2), Os(2)-Os(3) = 2.824(1), W-Os(2) = 3.436(1), Os(1)-S = 2.380(3), Os(3)-S = 2.367(3), W-S = 2.468(3), W-H(1) = 1.64(1), Os(2)-H(1) = 2.18(1), Os(1)-H(2) = 2.01(1), Os(3)-H(2) = 1.78(1) Å; W-S-Os(1) = 120.4(1), W-S-Os(3) = 115.8(7), Os(1)-S-Os(3) = 74.8(1)°. Thermal ellipsoids are shown at the 50% level.

convert with each other, but generate a third heterometallic WOs_3 cluster $CpWOs_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}SMe)$ by elimination of one CO ligand. The crystal structure and solution dynamics of this new cluster compound will be presented in a separate paper.

ACKNOWLEDGMENT

We thank the National Science Council of the Republic of China under the grant (NSC 83-0208-M007-43) for financial support.

Received September 9, 1994.

Key Words
Osmium; Tungsten; Thiolato; Heterometallic clusters; Acetonitrile.

REFERENCES

1. (a) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W. Eds.; Pergamon: Oxford, **1982**; Vol. 6, Chapter 40. (b) Adams, R. D. In *The Chemistry of Metal Clusters*; Shriver, D. F.; Kaesz, H. D.; Adams, R. D. Eds.; VCH: New York, **1990**; Chapter 3.
2. Chi, Y.; Chuang, S.-H.; Chen, B.-F.; Peng, S.-M.; Lee, G.-H. *J. Chem. Soc. Dalton Trans.* **1990**, 3033.
3. (a) Chi, Y.; Liu, L.-K.; Huttner, G.; Zsolnai, L. *J. Organomet. Chem.* **1990**, *390*, C50. (b) Chi, Y.; Hsu, H.-F.; Liu, L.-K.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1992**, *11*, 1763.
4. (a) Chi, Y.; Lin, R.-C.; Peng, S.-H.; Lee, G.-H. *J. Cluster Sci.* **1992**, *3*, 333. (b) Lin, R.-C.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Inorg. Chem.* **1992**, *31*, 3818. (c) Wang, J.-C.; Lin, R.-C.; Chi, Y.; Peng, S.-H.; Lee, G.-H. *Organometallics* **1993**, *12*, 4061.
5. Spectral data for **1**: MS (FAB, ^{192}Os) *m/z* 917 (M^+); IR (C_6H_{12}): ν (CO), 2079 (vw), 2050 (vs), 2032 (vs), 1990 (vs), 1981 (vs), 1973 (m), 1960 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 294K): isomer **a**, 35%; δ 2.53 (s, MeCN, 3H), 2.48 (s, SMe, 3H), -16.29 (s, 1H, $J_{Os\text{-}H}$ = 34 Hz); isomer **b**, 65%; δ 2.54 (s, MeCN, 3H), 2.49 (s, SMe, 3H), -16.49 (s, 1H, $J_{Os\text{-}H}$ = 34 Hz). ^{13}C NMR ($CDCl_3$, 294K): isomer **a**, 35%; δ 181.8 (2CO), 180.1 (1CO), 178.6 (2CO), 176.1 (2CO), 173.7 (2CO), 122.9 (CH_3*C*N), 36.2 (*C*H_3CN), 3.9 (SCH_3); isomer **b**, 65%; δ 181.4 (1CO), 181.1 (2CO), 180.8 (2CO), 175.1 (2CO), 172.3 (2CO), 126.3 (CH_3*C*N), 38.6 (*C*H_3CN), 3.9 (SCH_3). Elemental analysis: Found: C, 15.76; H, 0.80. $C_{12}H_7N_1O_9S_1Os_3$ calcd.: C, 15.81; H, 0.77%.
6. Ditzel, E. J.; Gómez-Sal, M. P.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc. Dalton Trans.* **1987**, *1623*.
7. Orange crystals of **1** suitable for X-ray diffraction were obtained from a mixture of dichloromethane-methanol. Crystal data: $C_{12}H_7N_1O_9S_1Os_3$, M = 911.84, orthorhombic, space group P bca, a = 14.491(1), b = 16.107(5), c = 16.639(5) Å, V = 3384(2) $Å^3$, Z = 8, D_c = 3.119 g/cm^3, F (000) = 3215, Mo-K_α radiation with λ = 0.70930 Å, 3414 unique reflections were measured of which 2378 were considered observed with $I > 2\,\sigma(I)$. The structure was solved and refined by using the NRCC-SDP-VAX packages. Final R = 0.037, R_w = 0.033, GOF = 1.97. Tables of bond distances and angles, tables of positional parameters and anisotropic thermal parameters, and listings of the observed and calculated structural factors are available from an author (S.-M. P).
8. (a) Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 1306. (b) Allen, V. F.; Mason, R.; Hitchcock, P. R. *J. Organomet. Chem.* **1977**, *140*, 297.
9. Dawson, P. A.; Johnson, B. F. G.; Lewis, J.; Puga, J.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc. Dalton Trans.* **1982**, 233.
10. Constable, E. C.; Johnson, B. F. G.; Lewis, J.; Pain, G. N.; Taylor, M. J. *J. Chem. Soc. Chem. Commun.* **1982**, 754.
11. Crooks, G. R.; Johnson, B. F. G.; Lewis, J.; Williams, I. G. *J. Chem. Soc. (A)* **1969**, 797.
12. Spectral data for **2**: MS (FAB, ^{192}Os, ^{184}W), *m/z* 1182 (M^+); IR (C_6H_{12}): ν (CO), 2089 (m), 2061 (vs), 2035 (vs), 2014 (s), 2000 (m), 1985 (s, br), 1978 (m), 1967 (w), 1890 (w, br) cm^{-1}; ^1H NMR ($CDCl_3$, 294K): δ 5.73 (s, 5H), 2.68 (s, 3H), -16.16 (s, 1H), -22.35 (s, 1H, $J_{W\text{-}H}$ = 49Hz). ^{13}C NMR (acetone-d_6, 294K): CO, δ 243.2, 235.9, 182.1, 181.9, 181.8, 181.4, 180.0, 178.7, 173.4, 170.1, 169.5; d 95.5 (*C*$_5H_5$, 5C), 53.9 (CH_3). Elemental analysis: Found: C, 17.20; H, 0.83%. $C_{17}H_{10}O_{11}S_1W_1Os_3$ calcd.: C, 17.35; H, 0.86.
Spectral data for **3**: MS (FAB, ^{192}Os, ^{184}W), *m/z* 1182 (M^+); IR (C_6H_{12}): ν (CO), 2087 (m), 2064 (s, br), 2032 (vs), 2014 (s), 1983 (s, br), 1964 (w) cm^{-1}; ^1H NMR (CD_2Cl_2, 294K): δ 5.80 (s, 5H), 2.38 (s, 3H), -14.12 (s, 2H, $J_{W\text{-}H}$ = 43.6Hz). ^{13}C NMR (acetone-d_6, 294K): CO, δ 214.2 (2C, $J_{W\text{-}C}$ = 148Hz), 187 (2C, br), 181 (1C, br),

178.3 (2C), 180.0 (2C), 172.1 (2C); d 89.0 (C_5H_5, 5C), 35.3 (CH_3). Elemental analysis: Found: C, 17.35; H, 0.80. $C_{17}H_{10}O_{11}S_1W_1Os_3$ calcd.: C, 17.35; H, 0.86%.

13. Crystal data for **2**: $C_{17}H_{10}O_{11}S_1W_1Os_3$, M = 1176.76, triclinic, space group $P\bar{1}$, a = 8.865(5), b = 8.959(3), c = 16.688(4) Å, α = 103.49(2), β = 93.58(3), γ = 113.03(4)°, V = 1168.5(8) $Å^3$, Z = 2, D_c = 3.345 g/cm^3, F (000) = 1008, Mo-K_α radiation with λ = 0.70930 Å, 4147 unique reflections were measured of which 3652 were considered observed with $I > 2\sigma(I)$. Final R = 0.034, R_w = 0.035, GOF = 2.81. Tables of bond distances and angles, tables of positional parameters and anisotropic thermal parameters, and listings of the observed and calculated structural factors are available from the author (S.-M. P).

14. Guerchais, J. E.; LeQuéré, J. L.; Pétillon, F. Y.; Manojlovic-Muir, L.; Muir, K. W.; Sharp, D. W. A. *J. Chem. Soc. Dalton Trans.* **1982**, 283.

15. (a) Adams, R. D.; Foust, D. F.; Mathur, P. *Organometallics* **1983**, *2*, 990. (b) Adams, R. D. *Polyhedron* **1985**, *4*, 2003.

16. Süss-Fink, G.; Thewalt, U.; Klein, H.-P. *J. Organomet. Chem.* **1984**, *262*, 315.

17. This compound was obtained from treatment of $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}SPh)$ with $Cp^*W(CO)_3H$ and Me_3NO in refluxing THF solution. Selected spectral data: IR (C_6H_{12}): v (CO), 2083 (m), 2062 (vs), 2031 (vs), 2010 (s), 2001 (w), 1984 (s, br), 1962 (w, br) cm^{-1}; ^1H NMR (CD_2Cl_2, 294K): δ 7.30 - 7.11 (m, 5H), 2.17 (s, 15H), -12.65 (s, 2H, $J_{W\text{-}H}$ = 43.9 Hz). Selected crystal data: monoclinic, space group $P2_1/n$, a = 10.001(2), b = 18.188(5), c = 17.352(5) Å, β = 91.49(2)°.