Synthesis of New Selenium- and Oxygen-Containing Tungsten Acetylide Complexes [(η^5-C_5Me_5)W(O)(Se_2)(CCPh)] and [(η^5-C_5Me_5)W(Se_5CCPh)]

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*Summary: Thermolysis of a mixture of [(η^5-C_5Me_5)W-$(CO)_3$(CCPh)] and [$Fe_3(CO)_9(\mu_3\text{-}Se)_2$] in toluene solvent at 90 °C in air yields the unusual diselenaoxoacetylide compound [(η^5-C_5Me_5)W(O)(Se_2)(CCPh)] (**1**). When the same reaction is carried out under nitrogen atmosphere, the pentaselenaacetylide compound [(η^5-C_5Me_5)W(Se_2)(Se_3-CCPh)] (**2**) and the previously reported cluster [(η^5-C_5Me_5)$_2W_2Fe_3(CO)_6(\mu_3\text{-}Se)_2(\mu_4\text{-}CC(Ph)C(Ph)C)$] (**3**) are formed. Structures of **1** and **2** have been established crystallographically.*

Introduction

In recent times, the use of mononuclear acetylide precursors for preparation of heterometallic compounds has been quite rewarding.[1−5] As part of our interest in chalcogen-bridged clusters, we have investigated some reactions between chalcogen-bridged iron carbonyl clusters [$Fe_3(CO)_9(\mu_3\text{-}E)_2$] (E = S, Se, Te) and the metal acetylide complex [(η^5-C_5Me_5)W$(CO)_3$(CCPh)]. A novel tail-to-tail carbon−carbon bond coupling of acetylides on S- and Se-bridged mixed W/Fe clusters was observed when a toluene solution containing [$Fe_3(CO)_9(\mu_3\text{-}E)_2$] (E = S or Se) and [($\eta^5$-$C_5Me_5$)W$(CO)_3$(CCPh)] was refluxed under nitrogen for 2 h.[6] Also observed in that reaction were minute quantities of another product, which we were unable to isolate in sufficient amounts for a complete and unambiguous characterization. We observed that the yield of this compound increased when the reaction was carried out under aerobic conditions, thus indicating that it could be a metal−oxo compound. Serendipitously therefore we shifted our interest in the hope of obtaining a complex containing both an oxo and an acetylide ligand. Such complexes, which contain oxo and hydrocarbon ligands, are of particular interest as models for metal-mediated oxidations and other reactions in which high-valent metal species are employed as catalysts.[7,8] Furthermore, the presence of the oxo ligand may give rise to novel types of reactivity which would otherwise be inhibited in its absence. Here we report on the synthesis and characterization of two novel mononuclear complexes, one that contains the oxo, acetylide, and selenium ligands and the other which bears an unusual array of five selenium atoms and an acetylide group.

Results and Discussion

When a toluene solution of [(η^5-C_5Me_5)W$(CO)_3$(CCPh)] and [$Fe_3(CO)_9(\mu_3\text{-}Se)_2$] was refluxed in air, rapid decomposition occurred. However, when the mixture was heated at 90 °C, in the presence of air, after 4 h, a new orange compound (**1**) could be isolated after chromatographic workup of the reaction mixture (Scheme 1). The structural features of **1** were identified on the basis of IR and ^{1}H and ^{77}Se NMR spectroscopy. The most notable feature in the IR spectrum of **1** is the absence of any ν(CO) bands and the presence of a strong ν(W=O) band. Its ^{1}H NMR spectrum showed a single peak for the C_5Me_5 protons and a multiplet for the phenyl group protons. The ^{77}Se NMR spectrum showed a single peak. The structure of **1** was confirmed by single-crystal X-ray diffraction. Dark red crystals of **1** were grown from a hexane/dichloromethane solvent mixture at −4 °C, and a single-crystal X-ray diffraction analysis was carried out. The molecular structure of **1**, shown in Figure 1, consists of a (η^5-C_5Me_5)W(C≡CPh) unit, with an oxo and a side-on bonded Se_2 ligand attached to the W atom. The W−O bond distance of 1.702(4) Å in **1** is similar to the 1.709(5) Å reported for the W−O(terminal) double bond, but shorter than the 1.793(5) Å for the W−O(bridging) single bond distance in [(η^5-C_5Me_5)W$(O)_2$-$Ru_4(CO)_{10}(\mu_4\text{-}PPh)$(CCPh)].[9] The W$Se_2$ unit of **1** has a Se−Se bond distance of 2.3156(12) Å, which is longer than the Se=Se double-bond distance of 2.19 Å, but closer to the normal Se−Se single-bond distance of 2.336 Å.[10] It is only slightly beyond the range reported for μ-η^2-Se_2 ligands in other complexes, $[W_2Cl_8Se(Se_2)]^{2-}$, 2.255(8) Å; [(η^5-$CH_3C_5H_4$)$_2V_2Se_5$], 2.290(2) and 2.295(2) Å; [$Fe_2(CO)_6(\mu\text{-}Se_2)$], 2.293(2) Å; $[FeW(Se_2)(CO)_8]^{2+}$, 2.281(3) Å,[11] but close to the average Se−Se bond distance of 2.318 Å observed in $[Fe_3(Se_2)_2(CO)_{10}][SbF_6]_2$.[12] It is slightly shorter than the Se−Se bond distance of 2.362(11) Å in the FeSe_2 unit of [$CrFe_2(CO)_{10}Se_4$].[13] From this reaction we have not been able to isolate any iron-containing product, and we assume that under the

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(1) Delgado E.; Chi, Y.; Wang, W.; Hogarth, G.; Low, P. J.; Enright, G. D.; Peng, S.-M.; Lee, G.-H.; Carty, A. J. *Organometallics* **1998**, *17*, 2936.

(2) Wu, C.-H.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *J. Chem. Soc., Dalton Trans.* **1990**, 3025.

(3) Blenkiron, P.; Enright, G. D.; Carty, A. J. *Chem. Commun.* **1997**, 483.

(4) Carty, A. J.; Enright, G. D.; Hogarth, G. *Chem. Commun.* **1997**, 1883.

(5) Chi, Y.; Carty, A. J.; Blenkiron, P.; Delgado, E.; Enright, G. D.; Wang, W.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1996**, *15*, 5269.

(6) Mathur, P.; Ahmed, M. O.; Dash, A. K.; Walawalkar, M. G. *J. Chem. Soc., Dalton Trans.* **1999**, 1795.

(7) Yamamoto, J. H.; Enright, G. D.; Carty, A. J. *J. Organomet. Chem.* **1999**, *577*, 126.

(8) Shiu, C.-W.; Su, C.-J.; Pin, C.-W.; Chi, Y.; Peng, P. S−M.; Lee, G.-H. *J. Organomet. Chem.* **1997**, *545*, 151.

(9) Blenkiron, P.; Carty, A. J.; Peng, S.-M.; Lee, G.-H, Su, C.-J.; Shiu, C.-W.; Chi, Y. *Organometallics* **1997**, *16*, 519.

(10) Wells, A. F. In *Structural Inorganic Chemistry*, 4th ed.; Clarendon: Oxford, 1975; pp 571−573.

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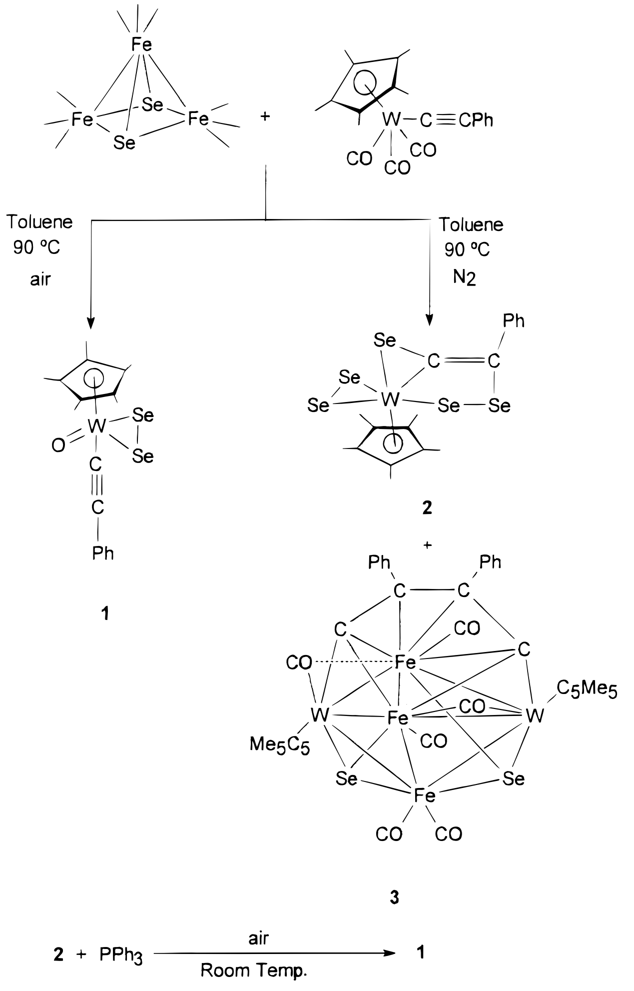
Scheme 1



reaction conditions used such compounds are unstable and undergo decomposition.

When a toluene solution containing [(η^5-C_5Me_5)W(CO)$_3$(CCPh)] and [$Fe_3(CO)_9(\mu_3$-$Se)_2$] was heated at 90 °C, under a nitrogen atmosphere, for 4 h, a new pentaselenaacetylide complex [(η^5-C_5Me_5)W(Se$_2$)(Se$_3$-CCPh)] (**2**) was formed. Also obtained from this reaction was the previously reported cluster, [(η^5-$C_5Me_5)_2W_2Fe_3(CO)_6(\mu_3$-$Se)_2(\mu_4$-CC(Ph)C(Ph)C] (**3**) (Scheme 1). Formation of **2** is sensitive to the temperature used in the thermolysis reaction. For instance, when the same reaction mixture was refluxed in toluene, even after several hours, formation of **2** was not observed. At temperatures lower than 90 °C also, compound **2** is not obtained. The infrared spectrum of **2** was devoid of any ν(CO) bands. Its ^{1}H NMR spectrum confirmed the presence of (η^5-C_5Me_5) and phenyl groups. The ^{77}Se NMR spectrum showed five signals for the Se atoms spread over a range of 1164 ppm. Dark red crystals of **2** were grown from its hexane/dichloromethane solvent mixture at −4 °C, and an X-ray structural analysis was undertaken. The molecular structure of **2** is shown in Figure 2. It consists of a (η^5-C_5Me_5)W unit to which is attached a sideways bonded Se$_2$ ligand, as in **1**. The most striking feature of **2** is the presence of an unusual Se$_3$(CCPh) group, in the form of two fused rings: a five-membered WSe$_2$CC(Ph) ring and a three-membered WSeC ring. The Se−Se bond distance of 2.3156(12) Å in the WSe$_2$ triangle of **2** is similar to that in **1.** The W−Se bond distances of this unit differ by about 0.2 Å (2.4511(11) and 2.6695(14) Å), which contrasts with the somewhat closer W−Se bond lengths in **1** (2.4915(8) and

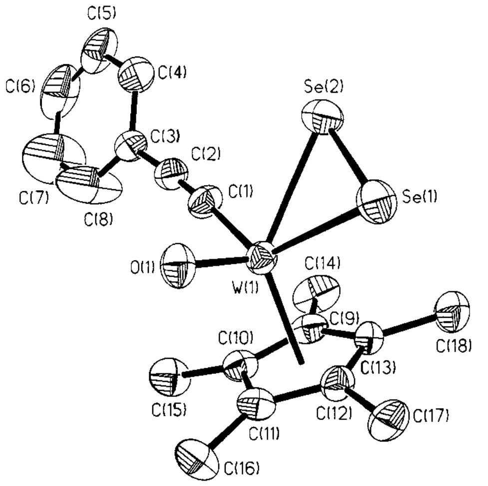


Figure 1. Molecular structure of **1** with 30% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): W(1)−O(1) = 1.702(4), W(1)−C(1) = 2.074(6), C(1)−C(2) = 1.207(8), C(2)−C(3) = 1.454(9), W(1)−Se(1) = 2.5517(8), W(1)−Se(2) = 2.4915(8), Se(1)−Se(2) = 2.3156(12), W(1)−C(1)−C(2) = 175.9(6), W(1)−Se(1)−Se(2) = 61.35(3), W(1)−Se(2)−Se(1) = 64.00(3), O(1)−W(1)−C(1) = 97.2(2).

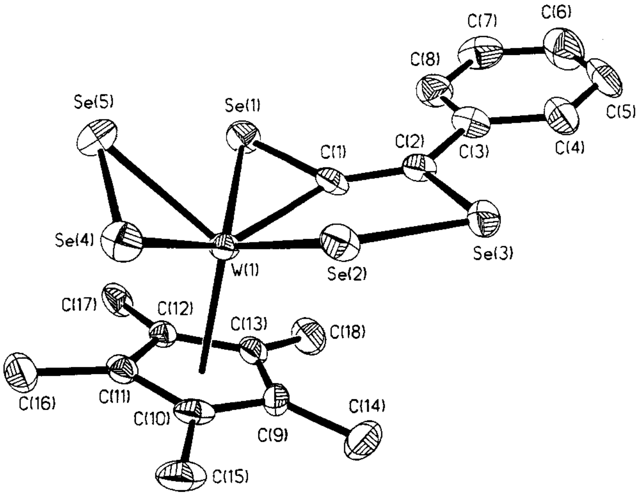


Figure 2. Molecular structure of **2** with 30% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): W(1)−C(1) = 2.086(10), C(1)−C(2) = 1.348(12), W(1)−Se(1) = 2.5903(12), W(1)−Se(2) = 2.4622(12), W(1)−Se(4) =2.6695(12), W(1)−Se(5) = 2.4511(11), Se(1)−C(1) = 1.887(8), Se(2)−Se(3) = 2.378(2), Se(3)−C(2) = 1.914(9), Se(4)−Se(5) = 2.319(2), W(1)−Se(1)−C(1) = 52.8(3), W(1)−Se(4)−Se(5) = 58.35(4), W(1)−Se(5)−Se(4) = 67.99(4), W(1)−Se(2)−Se(3) = 105.00(5), Se(2)−Se(3)−C(2) = 93.1(3), Se(3)−C(2)−C(1) = 114.4(7), W(1)−C(1)−C(2) = 143.0(7), C(1)−C(2)−C(3) = 128.4(9).

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(11) (a) Drew, M. G. B.; Fowles, G. W. A.; Page, E. M.; Rice, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5827. (b) Rheingold, A. L.; Bolinger, C. M.; Rauchfuss, T. B. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1986**, *42*, 1878. (c) Campana, C. F.; Lo, F. Y−K.; Dahl, L. F. *Inorg. Chem.* **1979**, *18*, 3060. (d) Signeurin, A.; Makani, T.; Jones, D. J.; Roziere, J. *J. Chem. Soc., Dalton Trans.* **1987**, 2111.

(12) Drake, G. W.; Schimek, G. L.; Kolis, J. W. *Inorg. Chim. Acta* **1995**, *240*, 63.

(13) Mathur, P.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* **1997**, *16*, 142

2.5517(8) Å). The Se−Se bond distance in the WSe_2CC(Ph) unit is 2.378(2) Å, consistent with a Se−Se single bond, and the C−C bond in this ring is 1.348(12) Å, indicative of a double bond.

On room temperature stirring of a toluene solution of a mixture of **2** and PPh_3, in the presence of air, compound **1** was formed in 15% yield. Whereas formation of the previously reported **3** can be understood as involving a formal addition of two tungsten acetylide units to an opened Fe_3Se_2 cluster, the formation of **1** and **2** is more complicated. Preparation of **1** by our reaction contrasts with that of another metal oxo−acetylide complex recently reported in the literature; reaction of $[(C_5H_5)W(CO)_3(CCR)]$ (R = Ph, CH_2OMe or Pr^n) with an acidic solution of hydrogen peroxide forms the oxo−peroxo acetylide complexes $(C_5H_5)W(O)(O_2)$(CCR), which on treatment with PPh_3 affords the dioxo complexes, $(C_5H_5)W(O)_2(CCR)$.[8] Investigations are in progress to explore the potential of **1** and **2** as precursors for obtaining heterometallic clusters which are stabilized by Se ligands and contain oxo and acetylide groups.

Experimental Section

Reactions and manipulations were performed using standard Schlenk techniques under an atmosphere of prepurified nitrogen, unless otherwise stated. Solvents were purified, dried, and distilled under an argon or nitrogen atmosphere prior to use. Infrared spectra were recorded on a Nicolet Impact 400 FT spectrometer as dichloromethane solutions in 0.1 mm path length cells; NMR spectra, on a Varian VXR-300S spectrometer in $CDCl_3$. The ^{77}Se NMR measurements were made at an operating frequency of 57.23 MHz using 90° pulses with 1.0 s delay and 1.0 s acquisition time and referenced to Me_2Se (δ 0). Elemental analyses were performed on a Carlo-Erba automatic analyzer. The compounds $[Fe_3(CO)_9(\mu_3\text{-}Se)_2]$[14] and $[(\eta^5\text{-}C_5Me_5)W(CO)_3(C{\equiv}CPh)]$[15] were prepared by established procedures.

Reaction of $[Fe_3(CO)_9(\mu_3\text{-}Se)_2]$ with $[(\eta^5\text{-}C_5Me_5)W(CO)_3(C{\equiv}C(Ph)]$ in the Presence of Air. A toluene solution (50 mL) containing $[Fe_3(CO)_9(\mu_3\text{-}Se)_2]$ (320 mg, 0.56 mmol) and $[(\eta^5\text{-}C_5Me_5)W(CO)_3(C{\equiv}C(Ph)]$ (140 mg, 0.28 mmol) was heated at 90 °C for 4 h in the presence of air. The solution was cooled to room temperature, and the solvent was removed in vauco. The residue was dissolved in dichloromethane and subjected to chromatographic workup using silica gel TLC plates. Elution with 40/60 (v/v) hexane−dichloromethane mixture afforded a single dark orange band **1** (35 mg, 25%).

1. IR [(ν(W = O), cm^{-1}]: 911(s). ^1H NMR (δ, ppm): 7.26−7.95 (m, 5H, C_6H_5), 2.24 (s, $(C_5(CH_3)_5)$. ^{13}C NMR (δ, ppm): 11.98 (CH_3), 109.21 ($C_5(CH_3)_5$), 128.23−129.24 (C_6H_5). ^{77}Se NMR (δ, ppm): 334 ppm. Anal. Calcd (Found) for $C_{18}H_{20}WOSe_2$: C, 36.15 (36.38); H, 3.37 (3.59).

Reaction of $[Fe_3(CO)_9(\mu_3\text{-}Se)_2]$ with $[(\eta^5\text{-}C_5Me_5)W(CO)_3(C{\equiv}CPh)]$ in the Presence of N_2. To a solution of $[Fe_3(CO)_9(\mu_3\text{-}Se)_2]$ (320 mg, 0.56 mmol) in dry toluene (30 mL) was added $[(\eta^5\text{-}C_5Me_5)W(CO)_3(C{\equiv}C(Ph)]$ (140 mg, 0.28 mmol). The reaction mixture was heated at 90 °C for 4 h under an atmosphere of nitrogen. The solution was cooled to room temperature, and the solvent was removed in vacuo. The residue was dissolved in a minimal amount of CH_2Cl_2 and was chromatographed by TLC on silica gel. A dark green band eluted first and was characterized spectroscopically as $(\eta^5\text{-}C_5Me_5)$ $(CO)_6W_2Fe_3(\mu_3\text{-}S)_2(\mu_4\text{-}CCPhCPhC)$ (**3**) (42 mg, 30%). The second dark brown band was identified as $[(\eta^5\text{-}C_5Me_5)WSe_5C_2Ph]$ (**2**) (28 mg, 20%). A trace amount of a third band was also observed and identified as $(\eta^5\text{-}C_5Me_5)WOSe_2C_2Ph$ (**1**).

2. ^1H NMR (δ, ppm): 7.27−8.03 (m, 5H, C_6H_5), 2.07 (s, $(C_5(CH_3)_5)$. ^{13}C NMR (δ, ppm): 12.19 (CH_3), 111.4 ($C_5(CH_3)_5$), 127.9−130.8 (C_6H_5). ^{77}Se NMR (δ, ppm): 1162, 992, 864, −2, −132 ppm. Anal. Calcd (Found) for $C_{18}H_{20}WSe_5$: C, 26.50 (26.71); H, 2.46 (2.65).

3. IR [(ν(CO), cm^{-1}]: 1968 (m), 1936 (vs) and 1777 (m), 1734 (m). ^1H NMR (δ, ppm): 7.3−7.1 (m, 10H, C_6H_5), 1.92 (s, 15H, $(C_5(CH_3)_5)$, 1.87 (s, 15H, $(C_5(CH_3)_5)$. ^{13}C NMR (δ, ppm): 11.1 (CH_3), 11.6 (CH_3), 105.7 ($C_5(CH_3)_5$), 107.1 ($C_5(CH_3)_5$), 127.6−131.1 (C_6H_5), 135.1 (C_4Ph_2), 136.9 (C_4Ph_2), 214.2, 214.4, 216.5, 220.3, 222.6 (CO). ^{77}Se NMR (δ, ppm): 872, 800. Anal. Calcd (found) for $C_{42}H_{40}Fe_3O_6Se_2W_2$: C, 37.8 (37.5); H, 3.00 (3.21).

Reaction of 2 with PPh_3. A mixture of $[(\eta^5\text{-}C_5Me_5)W(Se_2)(Se_3C_2Ph)]$ (**2**) (50 mg, 0.016 mmol) and PPh_3 (16 mg, 0.106 mmol) in toluene (30 mL) was stirred at room temperature in the presence of air for 5 min. The solvent was removed in vacuo, and the residue was redissolved in dichloromethane and subjected to chromatographic workup using silica gel TLC plates. Elution with a 40/60 (v/v) hexane/dichloromethane mixture yielded **1** (7.5 mg, 15%).

X-ray Crystal Structure Determinations. X-ray crystallographic data for **1** and **2** were collected from single-crystal samples (0.21 × 0.18 × 0.11 mm and 0.32 × 0.16 × 0.08 mm, respectively) mounted on glass fibers. Data were collected using a P4 Siemens diffractometer, equipped with a Siemens SMART 1K charge coupled device (CCD) area detector (using the program SMART[16]) and a rotating anode, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystal-to-detector distance was 3.991 cm, and the data collection was carried out in 512 × 512 pixel mode, utilizing 2 × 2 pixel binning. The initial unit cell parameters were determined by a least-squares fit of the angular settings of the strong reflections, collected by a 4.5° scan in 15 frames over three different sections of reciprocal space (45 frames in total). One complete hemisphere of data was collected, to better than 0.8 Å resolution. Upon completion of the data collection, the first 50 frames were recollected in order to improve the decay corrections analyses. Processing was carried out using the program SAINT,[17] which applied Lorentz and polar corrections to the three-dimensionally integrated diffraction spots. The program SADABS[18] was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The structure was solved by using the direct-methods procedure in the Siemens SHELXTL program library[19] and refined by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the carbon atom to which they are bonded.

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Supporting Information Available: Details of the structure determinations for **1** and **2**, including tables listing atomic coordinates, thermal parameters, and bond distances and angles, and figures showing structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) (a) Mathur P.; Chakrabarty, D.; Hossain, M. M.; Rashid, R. S.; Rugmini, V.; Rheingold, A. L. *Inorg. Chem*. **1992**, *31*, 1106. (b) Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem*. **1981**, *20*, 3583.

(15) Bruce, M. I.; Humphery, M. G.; Matisons, J. G.; Roy, S. K.; Swincer, A. G. *Aust. J. Chem*. **1984**, *37*, 1955.

(16) *SMART, Release 4.05*; Siemens Energy and Automation Inc.: Madison, WI 53719, 1996.

(17) *SAINT, Release 4.05*; Siemens Energy and Automation Inc.: Madison, WI 53719, 1996.

(18) Sheldrick, G. M. *SADABS Siemens Area Detector Absorption Corrections*; 1996.

(19) Sheldrick, G. M. *Siemens SHELXTL, Version 5.03*; Siemens Crystallographic Research Systems, Madison, WI 53719, 1994.