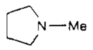
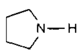
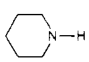
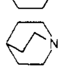
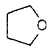
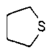
Table I. The UV Absorption Maxima of Silaylides and Their Relative Intensities[a]

substrate	λ_{max}, nm	rel intensities[b] silaylide	silylene	disilene
			0.1	0.9
	324	1		
	334	0.6	<0.1	<0.1
	328	0.2	<0.1	<0.1
	330	1.3		
n-Bu_3P	338	2.7 3.7[c]	0.4	0.2 0.6[c]
	320[d]	<0.1	<0.1	<0.1
	315	<0.1	<0.1	<0.1
PhCl			0.1	0.9

[a] The values in the isopentane/3-methylpentane (4:1) glass matrix at 77 K. [b] The relative values to 1 for the intensity of the absorption of **5a**. [c] The value after the light was interrupted for 1 h. [d] The growth of new band was observed at 385 nm, after the light was interrupted.

weak absorption bands in IP/3MP at low temperature. These are indicative of the instability and high reactivity of the silaylides formed (e.g. C–O or C–S insertion of the silylene).

When a similar photolysis of **1** was carried out in the presence of n-Bu_3P in IP/3MP at 77 K, a intense band with λ_{max} at 338 nm due to silaphosphorus ylide was observed, together with the band due to tetramesityldisilene. The silaphosphorus ylide is significantly more stable under these conditions. The formation of a solution with no bands corresponding to the silylene indicates that formation of the silaphosphorus ylide competes with the dimerization of the silylene.

The observed relative stabilities of silaylides showed a similar trend as complexation energies of the silylene–Lewis base complexes calculated by Gordon (NH_3 > PH_3 > H_2O > H_2S > HCl) show.[5]

Acknowledgment. We are indebted to Shin-etsu Chemical Co., Ltd. for a gift of organochlorosilanes. Financial support of this research by Grant-in-Aid for Special Project Research (No. 62115002) from the Ministry of Education, Science, and Culture is greatly appreciated.

Novel Peroxo- and Oxo-Alkyl Complexes of (Pentamethylcyclopentadienyl)tungsten

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Received September 9, 1987

Summary: Alkylation of Cp*WO_2Cl with RMgCl (R = Me, CH_2SiMe_3) provides a synthetic route to alkyl–dioxo tungsten and trialkyl–oxo tungsten complexes. The Cp*WO_2R complexes are readily converted to the novel Cp*$WO(O_2)R$ peroxy–alkyl complexes.

There have been rapid developments in higher oxidation state organometallic chemistry which have demonstrated substantial stabilities for complexes containing oxo as well as alkyl, olefinic, or acetylenic substituents.[1] Current interest in transition-metal oxo and peroxo complexes as oxidizing agents and for oxygen atom transfer to substrates[2] prompts our report of Cp*$WO(O_2)CH_2SiMe_3$ and Cp*$WO(O_2)CH_3$, which may serve as models for intermediates or as O-atom transfer agents themselves.

Cp*WO_2Cl and $(Cp^*WO_2)_2O$ are readily available via oxidation of $[Cp^*W(CO)_2]_2$[3] and are very useful starting materials in synthesizing oxo–alkyl tungsten complexes. Cp*WO_2Cl reacts at −70 °C with excess methylmagnesium chloride to yield 30% of Cp*$WOMe_3$ (**1**) and 5% of Cp*WO_2Me (**2**), respectively.[4] However, the reaction of Cp*WO_2Cl with Me_3SiCH_2MgCl affords only Cp*$WO_2CH_2SiMe_3$.[3] We did not observe Cp*$WO(CH_2SiMe_3)_3$ in the product, although its formation may have been anticipated by analogy with the reactions with methyl Grignard or the known stability of its cyclopentadienyl analogue which was obtained by oxidation of nitrosyl complexes.[5] Our Grignard route to Cp*WO_2R

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(1) (a) Herrmann, W. A.; Serrano, R.; Bock, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 383. (b) Herrmann, W. A.; Serrano, R.; Kuesthardt, U.; Ziegler, M. L.; Guggolz, E.; Zahn, T. *Ibid.* **1984**, *23*, 515. (c) Herrmann, W. A.; Serrano, R.; Schaeffer, A.; Kuesthardt, U.; Ziegler, M. L.; Guggolz, E.; Zahn, T. *J. Organomet. Chem.* **1984**, *272*, 55. (d) Herrmann, W. *J. Organomet. Chem.* **1986**, *300*, 111. (e) Klahn-oliva, A. H.; Sutton, D. *Organometallics* **1984**, *3*, 1313. (f) Bottomley, F.; Darkwa, J.; Sutin, L.; White, P. S. *Organometallics* **1986**, *5*, 2165. (g) Mayer, J. M.; Tulip, T. H. *J. Am. Chem. Soc.* **1984**, *106*, 3878. (h) Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248. (i) Su, F.-M; Cooper, C.; Geib, S. J.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 3545.

(2) Mimoun, H. *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; p. 465.

(3) Reflux of a chloroform solution of $[Cp^*W(CO)_2]_2$ under an atmosphere of oxygen for 24 h yields a brown solution. Ether extraction of the brown residue obtained upon evaporation of the chloroform provides a 27% yield of pale yellow Cp*WO_2Cl. [Faller, J. W.; Ma, Y. *J. Organomet. Chem.*, in press.]

(4) (a) **Preparations of Cp*WO(Me)$_3$ (1) and Cp*WO$_2$Me (2).** Cp*WO_2Cl (120 mg, 0.31 mmol) was dissolved in 50 mL of diethyl ether and treated with 3 equiv of 2 M MeMgCl in THF at −70 °C for 1 h. The solvent was concentrated, and the residue was extracted with 150 mL of diethyl ether in three fractions. The combined extracts were concentrated to give a light yellow residue that contained both compounds **1** and **2** in addition to some yellow impurities. This mixture was then separated and purified by means of thin-layer chromatography on a 0.25-mm silica gel plate with diethyl ether as an eluent. The yields of **1** and **2** were 34 mg (29%) and 4.5 mg (4%), respectively. Preliminary X-ray results indicate that complex **1** has a four-legged piano-stool structure, but there is disorder between a methyl group and the oxygen. **1**: ^1H NMR ($CDCl_3$, 25 °C, 250 MHz) δ 1.88 (s, 15 H, C_5Me_5), 1.06 (m, 6 H, cis-CH_3, J_{W-H} = 6 Hz), 0.17 (m, 3 H, trans-CH_3, J_{W-H} = 6 Hz); IR (CS_2, $\nu_{W=O}$) 948 cm^{-1} (s). Anal. Calcd for $WOC_{13}H_{24}$: C, 41.07; H, 6.36. Found: C, 41.06; H, 6.38. **2**: ^1H NMR ($CDCl_3$, 25 °C, 250 MHz) δ 2.08 (s, 15 H, C_5Me_5), 0.99 (s, 3 H, J_{W-H} = 10.8 Hz); IR (CS_2, $\nu_{W=O}$) 950, 907 cm^{-1} (s). Anal. Calcd for $WO_2C_{11}H_{18}$: C, 36.09; H, 4.96. Found: C, 36.13; H, 5.00. (b) If more Cp*WO_2Me is desired, using 1.5 equiv of MeMgCl gives about 20% of **1** and 15% of **2** in the final products. (c) **Cp*WO(O$_2$)Me (3).** Compound **2** (20 mg, 0.055 mmol) was dissolved in 15 mL of diethyl ether that tested positive for peroxide, and the solution was stirred for 10 h. The product was purified by TLC in a similar fashion to compounds **1** and **2** to yield 16 mg of compound **3** (76%): ^1H NMR ($CDCl_3$, 25 °C, 250 MHz) δ 2.05 (s, 15 H, C_5Me_5), 1.32 (s, 3 H, J_{W-H} = 8.4 Hz); IR (CS_2) $\nu_{W=O}$ 951 (s), ν_{O-O} 864 (m), ν_{W-O} 588 (w), 572 (s) cm^{-1}. Anal. Calcd for $WO_3C_{11}H_{18}$: C, 34.57; H, 4.75. Found: C, 34.63; H, 4.79. (d) **Cp*WO(O$_2$)CH$_2$SiMe$_3$ (4).** Following that for **3** but with R = CH_2SiMe_3 gave **4** in 80% yield: ^1H NMR ($CDCl_3$, 25 °C, 250 MHz) δ 2.03 (s, 15 H, C_5Me_5), 0.97 (d, 1 H, CH′, $J_{H-H'}$ = 12.6 Hz, J_{W-H} = 10.0 Hz, J_{Si-H} = 7.3 Hz), 0.40 (d, 1 H, CH, $J_{H-H'}$ = 12.6 Hz, J_{W-H} = 7.0 Hz, J_{Si-H} = 7.0 Hz), 0.09 (s, 9 H, $SiMe_3$, J_{Si-H} = 6.6 Hz); IR (CS_2) $\nu_{W=O}$ 945 (s), ν_{O-O} 868 (m), ν_{W-O} 585 (w), 567 cm^{-1}. Anal. Calcd for $WSiO_3C_{14}H_{26}$: C, 37.01; H, 5.77. Found: C, 37.08; H, 5.80. (e) Using *tert*-butyl hydroperoxide as an oxidizing agent was far less effective in giving complexes **3** and **4** over a 10-h period. As (EtO)(Me)HCOOH decomposes upon chromatography and **3** and **4** do not, the potential hazards of evaporating solutions to dryness can be avoided by passing solutions through a short column of alumina before concentration.

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0276-7333/88/2307-0559$01.50/0

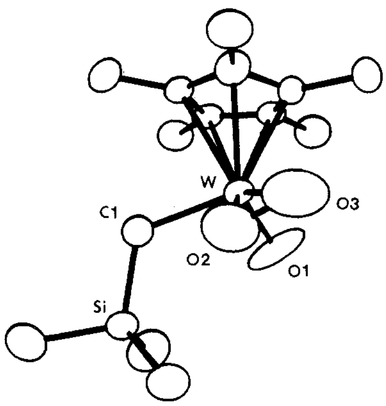

Figure 1. An ORTEP view of 4 showing 30% probability ellipsoids.

appears to allow preparation of some complexes inaccessible by the nitrosyl complex oxidation approach (e.g. R = Me).

A conventional method for the preparation of peroxo metal complexes involves treatment of high-valent early-transition-metal oxo complexes with hydrogen peroxide.[2] Indeed, the remarkably stable W–R bond withstands treatment with H_2O_2 and yields peroxo–alkyl complexes.[6] We have found, however, that a more convenient and milder (though admittedly unconventional) reagent to effect this transformation is hydroperoxide[7] formed by air oxidation of diethyl ether. In either case, Cp*WO_2R complexes react with peroxide[4] in diethyl ether to give a rare class of peroxo–alkyl or "dioxygen alkyl" complexes, Cp*WO(O_2)Me (**3**) and Cp*WO(O_2)CH_2SiMe_3 (**4**).[4,8] An X-ray crystallographic analysis of **4** shows a distorted piano-stool structure, as shown in Figure 1.[10,11]

The IR spectrum in CS_2 shows typically strong W=O stretching frequencies for Cp*$WOMe_3$ at 948 cm^{-1} and for Cp*WO_2Me at 947 and 907 cm^{-1}. Comparison with a well-characterized MO(O_2) system[2,13] suggests that the strong bands at 951 cm^{-1} in **3** and 945 cm^{-1} in **4** are assigned to W=O stretching modes, whereas the bands at 864 and 868 cm^{-1} in **3** and **4**, respectively, correspond to the O–O stretching modes. As expected for W–O stretching modes in the W(O_2) group, there is a relatively strong band at 572 cm^{-1} and a weak one at 588 cm^{-1} in the spectrum of Cp*WO(O_2)Me. The corresponding bands for the (trimethylsilyl)methyl analogue are found at 567 and 585 cm^{-1}.

The ^1H NMR spectrum of **1** exhibits two different methyl resonances in a ratio of 2:1 as expected for the four-legged piano-stool geometry found in CpWO(CH_2SiMe_3)$_3$.[5] Owing to coupling between methyl groups, the two resonances are poorly resolved multiplets. Decoupling each methyl resonance allows the ^{183}W satellites ($J \approx 6$ Hz) of both resonances to be observed. No indication of methyl group scrambling was observed up to 80 °C. The extremely strong W=O bond apparently alters the relative stabilities of the 3:4 ground state and 3:3:1 intermediate and slows the fluxionality typical of 3:4 structures.[14]

Two sets of doublets are observed for the methylene protons in the ^1H NMR spectrum of Cp*WO(O_2)CH_2SiMe_3. Although different heteroatom three-bond couplings are common owing to conformational effects,[14] it is unusual to observe that the two methylene protons have quite different two-bond ^{183}W–H couplings of 10 and 7 Hz, whereas the ^{29}Si–H couplings are nearly the same (~7 Hz). Presumably the extreme asymmetric electronic environment at the metal is sufficient to provide differential correlation between some W 5d orbitals and the C–H σ-bonds. The relative donor character of the oxo ligands apparently affects the magnitude of the ^{183}W couplings, as **1** has the smallest (6 Hz) and **2** the largest (10.8 Hz). Furthermore, Me_6W only exhibits a coupling of 3 Hz.[15] An MO analysis[16] of $OMoX_4$ and O_2MoX_2 systems suggest that the former has substantial triple-bond character in the oxo–metal bond, as opposed to the more normal double-bond character in the two oxo–metal bonds of the latter compound. This argument is strongly supported by crystallographic data for both compounds CpWO(CH_2SiMe_3)$_3$ and Cp$WO_2CH_2SiMe_3$.[5] The W=O bond distance (1.664 Å) of the former is significantly shorter than the average bond distance (1.719 Å) of the latter. Ultimately, a shorter W=O correlates with longer W—C bonds. The longer W—C distance (2.311 vs. 2.134 Å) in the former suggests that Cp*$WOMe_3$ (**1**) has a weaker W—H spin correlation interaction through the C sp^3 hybrids than does Cp*WO_2Me. The increasing trend of $J_{W\text{-}H}$

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(6) As this report was being prepared, we learned from Professor Peter Legzdins and his co-workers that they were pursuing similar lines of research and had prepared 4 via oxidation with 30% H_2O_2 in ether. As their method of precursor preparation does not allow access to the methyl complexes, we have focussed our attention on them. We found from X-ray crystallographic analysis that there was disorder between the O and Me in 1, whereas the Legzdins group found disorder between O and CH_2SiMe_3 in Cp$WO_2CH_2SiMe_3$.

(7) The oxidizing agent is presumably (EtO)(Me)HCOOH. See: Hiatt, R. *Organic Peroxides*; Swern, D., Ed.; Wiley: New York, 1971; Vol. 2, Chapter 1.

(8) There previously was some controversy over the delineation of side-bound M(O_2) complexes as either dioxygen, superoxide, or peroxo complexes. It now appears that most are considered as "peroxo" complexes.[2] The only previously reported complexes containing the M(O_2)R moiety (R = alkyl or aryl) of which we are aware are dioxygen adducts of Vaska complex derivatives.[9]

(9) (a) Dahlenburg, L.; Nast, R. *J. Organomet. Chem.* **1974**, *71*, C49. (b) Drouin, M.; Harrod, J. F. *Can. J. Chem.* **1985**, *63*, 353–360. (c) Mason, M. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 5153.

(10) Crystal data: monoclinic, space group $P2_1/c$; a = 10.845 (2) Å, b = 9.482 (3) Å, c = 16.781 (3) Å, β = 90.52 (1)°, V = 1725.6 (7) Å^3, Z = 4. After correction for decay (26.6% in intensity) and an empirical absorption correction, refinement by full-matrix least squares, with anisotropic temperature factors assigned to W, Si, C, and O atoms and H atoms in calculated positions led to R = 0.036 and R_w = 0.043 (using 1830 data) for which $I > 3\sigma(I)$. A difference Fourier omitting the methylene hydrogen atoms showed only peaks in the expected vicinity for normal hydrogen atoms with no significant agostic interaction with the W. Bond lengths (Å): W=O(1), 1.761 (8) [possibly incorrect, vide infra]; W–O(2) 1.88 (1); W–O(3), 1.92 (1); W–C(1), 2.14 (1); O(2)–O(3), 1.29 (2) (possibly incorrect, vida infra); C(1)–Si, 1.87 (2). Bond angles (deg): O(1)–W–O(2) = 110.5 (5); O(1)–W–O(3), 104.5; O(1)–W–C(1) 98.5 (5); Si–C(1)–W, 119.2 (6). The W=O bond length appears anomalously long for a complex with a single W=O. The peroxy O–O length in most compounds appears to be in the range 1.4–1.5 Å.[6] Only the 1.30-Å O–O bond reported[11] for Ir(O_2)ClCO(PPh_3)$_2$ is as short, and its validity has been questioned owing to problems with anisotropic effects in decay.[12] There does not appear to us to be unusual errors associated with data statistics based on order of collection or h, k, or l. However, the thermal ellipsoids for all of the oxygen atoms are large (B_{eqv} = 11–15 Å^2 for O compared to 7–10 Å^2 for the Si–Me carbons). Considering the propensity of these compounds to disorder, we believe that the short O–O distance and the W–O distances are suspect. In the final difference Fourier, the maximum peak of 1.4 e/Å^3 was located 1.0 Å from the W, as typically found in heavy-atom structures; however, weaker peaks in the vicinity of O(1), O(2), and O(3) suggested the possibility of a disorder between W=O and W(O_2). We were unable to find a suitable disorder model and are planning a low-temperature X-ray study to resolve this issue.

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in the order of compounds Cp^*WOMe_3, $Cp^*WO(O_2)Me$, and Cp^*WO_2Me thus follows increasing C sp^3 and W 5d overlap.

In contrast to the reactivity of the (trimethylsilyl)methyl complexes,[5] heat or irradiation did not effect conversion of Cp^*WOMe_3 to $Cp^*WO({=}CH_2)CH_3$. However, both **3** and **4** apparently act as O transfer agents. Transfer of O from the peroxy compounds to substrates, such as phosphines or olefins, might be anticipated by analogy with Mimoun's work with peroxo molybdenum complexes.[2] We are investigating these possibilities with **3**, **4**, and other analogous chiral peroxides. Although O transfers readily from **3** or **4** to triphenylphosphine at room temperature (<10 min) regenerating **2** or $Cp^*WO_2CH_2SiMe_3$, respectively, we have not yet achieved olefin epoxidations with these tungsten complexes. The thermodynamic stability of both **2** and **3** and presumably their molybdenum analogues would suggest that a catalytic O-atom transfer system could be developed with these systems.

Acknowledgment. We wish to thank the National Science Foundation for support of this work.

Registry No. **1**, 112247-11-7; **2**, 112247-12-8; **3**, 112247-13-9; **4**, 112247-14-0; Cp^*WO_2Cl, 112247-15-1; $Cp^*WO_2CH_2SiMe_3$, 112247-16-2; $[Cp^*W(CO)_2]_2$, 70634-77-4; (EtO)(Me)HCOOH, 18321-53-4; Me_3SiCH_2MgCl, 13170-43-9.

Supplementary Material Available: Tables of experimental procedure, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and calculated hydrogen positions and a complete figure with labels (10 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

Directed Synthesis of Dimetallacyclobutenes: Reaction of $M(CO)_4(\eta^2\text{-}CF_3C{\equiv}CCF_3)$ (M = Ru, Os) with Other 18-Electron Species

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Received July 24, 1987

Summary: Reflecting the strong π-acceptor nature of hexafluorobut-2-yne ($CF_3C{\equiv}CCF_3$, HFB), the compounds $M(CO)_4(\eta^2\text{-HFB})$ (M = Ru, Os) readily react with other 18-electron species, such as $M'(CO)_5$ (M' = Ru, Os) and $Cp^*M''(CO)_2$ (M'' = Co, Rh, Ir; Cp* = C_5Me_5), to give the corresponding dimetallacyclobutenes in good yields.

The chemistry of di- and polynuclear transition-metal alkyne complexes continues to attract a great deal of attention in view of the central role that these complexes occupy in mapping out intermediate steps in alkyne coupling reactions[1] and in providing realistic models for the adsorption and further transformation of surface-bound alkynes.[2] The usual methodology for the synthesis of these species is the reaction of alkynes with preformed multicenter complexes.[3] Only recently has a report[4] appeared on the designed synthesis of bimetallic alkyne complexes from a mononuclear starting material. The products were interesting examples of heterodimetallatetrahedranes (i.e., dimetallic complexes containing a $\mu\text{-}\eta^2,\eta^2$ or perpendicular alkyne bridge[5]). Here we wish to report another example of such a directed synthesis, which however gives rise to dimetallacyclobutenes (i.e., molecules with a $\mu\text{-}\eta^1,\eta^1$ or parallel alkyne bridge[5]).

In a continuation of our efforts to synthesize simple alkyne–tetracarbonyl derivatives of the iron triad transition metals,[6] the photoreaction of $M(CO)_5$ (M = Ru, Os) with hexafluorobut-2-yne ($CF_3C{\equiv}CCF_3$, HFB) was carried out. Careful control of the reaction conditions and isolation procedure, especially with ruthenium, gave the respective $M(CO)_4(\eta^2\text{-HFB})$ (M = Ru, **1a**; M = Os, **1b**) compounds in good yields.[7] Both **1a** and **1b** are extremely volatile, white crystalline materials that can be handled at room temperature, in air for short periods of time. The stability increase of **1a** over its bis(trimethylsilyl)acetylene analogue[6] is noteworthy and reflects the strong π-acceptor nature of HFB. The latter feature is also responsible for the absence of axial–equatorial carbonyl exchange in both **1a** and **1b** at room temperature and above.

In a remarkable development we discovered that the 18-electron complexes $M(CO)_4(\eta^2\text{-HFB})$ (**1a** and **1b**) react further with $M'(CO)_5$ (M' = Ru, Os) to give the corresponding dimetallacyclobutenes in good yields[8] (eq 1).

$$\underset{\textbf{1a,b}}{M(CO)_4(\eta^2\text{-HFB})} + \underset{\textbf{2a,b}}{M'(CO)_5} \xrightarrow[\text{alkane}]{\Delta} \underset{\textbf{3-5}}{MM'(CO)_8(\mu\text{-}\eta^1,\eta^1\text{-HFB})} \quad (1)$$

			Δ	yield
1a, M = Ru	**2a**, M' = Ru	**3**, MM' = Ru_2	25 °C	73%
1b, M = Os	**2b**, M' = Os	**4**, MM' = Os_2	60 °C	66%
1a M = Ru	**2b**, M' = Os	**5**, MM' = RuOs	25 °C	77%

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(7) In a typical experiment 100–200 mg of $M(CO)_5$ and excess HFB dissolved in pentane is photolyzed with filtered radiation (λ ≥ 370 nm) in an immersion type apparatus at −20 °C. The progress of the reaction is followed by IR spectroscopy. At the end of the reaction, the solution is slowly concentrated at low temperature and the product is crystallized at −78 °C. A yield of over 80% can be obtained. Alternatively, after the solvent is removed completely, the products may be purified by room temperature bulb-to-bulb sublimation in a closed vacuum system, the receiving flask being kept at dry-ice temperature. The latter method may become necessary in the ruthenium reaction that is sometimes accompanied by the formation of byproducts, such as $Ru(CO)_4(HFB)_2$. Fuller details on the synthesis and properties, including X-ray structures, of $M(CO)_4(\eta^2\text{-HFB})$ compounds will appear in a forthcoming publication. Spectral and analytical data on compounds **1a**, **1b**, **3**, **4**, **5**, **7**, **8**, and **9** are listed in the supplementary material.

(8) The OsOs compound **4**, obtained via thermal exchange reaction between $Os_2(CO)_8[\mu,\eta^1,\eta^1\text{-}CH_2CH(CO_2Me)]$ and $CF_3C{\equiv}CCF_3$, has been described before (Burke, M. R.; Takats, J. *J. Organomet. Chem.* **1986**, *302*, C25). However the yield of **4** was low and erratic.