

can be seen that the two aryl oxides and enediamide chelate generate a pseudotetrahedral coordination about the zirconium atom. The lack of planarity of the 5-membered chelate ring is clearly evident although the distances from the metal to the carbon atoms of this ring are long, lying between 2.6 and 2.8 Å. It is interesting to note that the enediamide ligand is less distorted from planarity in the solid state than the analogous enamidolate⁴ (folding angles of 37.8 (7)° and 50.0 (6)°, respectively) although the latter shows much more rapid chelate "inversion" in solution.

Preliminary kinetic measurements on this coupling process at zirconium, **1b** → **2b**, show the reaction to be a unimolecular process with activation parameters $\Delta H^\ddagger = 24.4 \pm 1.0$ kcal mol⁻¹ and $\Delta S^\ddagger = -16 \pm 5$ eu (105–145 °C temperature range). The moderately large and negative entropy of activation possibly reflects the necessity of the η^2 -iminoacyl groups to both rotate into a coplanar geometry prior to coupling.

In contrast to this behavior, the monocyclometalated complex Ti(OC₆H₃-*t*-BuCMe₂CH₂)(OAr')(CH₂SiMe₃)¹⁰ will rapidly insert 2 equiv of xyNC (as indicated both by mass spectrometry and microanalysis) to give high yields of a coupled product (**3**) immediately (Scheme I). The ¹H NMR spectrum of this compound is considerably more complex than that of the coupled products previously isolated. However, the spectrum is consistent with the molecular geometry shown (Scheme I) in which the titanium metal atom is surrounded by an aryl oxide group (OAr') as well as an unusual *tris*-anionic, multidentate ligand coordinated to the metal through oxygen, nitrogen, and carbon atoms forming both a five- and eight-membered chelate ring. Preliminary X-ray diffraction data on complex **3** confirms this molecular structure in the solid state.¹¹ There are a number of possible pathways that can lead to this product following initial insertion into both of the metal-carbon bonds. One possibility is the isomerization of an intermediate, chelating enediamide by activation of the carbon-hydrogen bonds of the CH₂SiMe₃ substituent on the chelate ring,¹² while a second possibility involves an intramolecular trans coupling of the η^2 -iminoacyls¹³ followed by a metal-mediated hydrogen transfer from the CH₂SiMe₃ group to the nitrogen atom. The final product **3** can be described as containing an azametallocyclopentene ring with an amine substituent on the backbone.

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Supplementary Material Available: Listings of atomic coordinates and temperature factors (5 pages). Ordering information is given on any current masthead page.

Synthesis and Crystal Structure of $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\eta^1\text{-C}(\text{OMe})_2)(\mu_3\text{-CPh})$, a Mixed Carbene-Carbyne Cluster Complex

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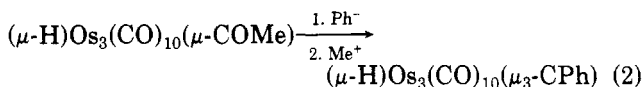
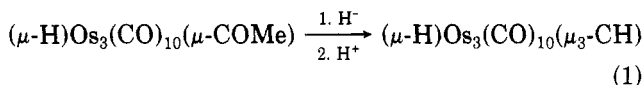
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Summary: The complex $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\eta^1\text{-C}(\text{OMe})_2)(\mu_3\text{-CPh})$ (**1**) is formed by sequential treatment of $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-COMe})$ with PhLi and MeOSO₂CF₃ at 0 °C. The osmium triangle is semi-triply-bridged by a benzyldiene ligand (Os(2)–C(3) = 2.074 (14) Å, Os(3)–C(3) = 2.040 (15) Å, and Os(1)···C(3) = 2.286 (12) Å), and a dimethoxycarbene ligand takes up an equatorial site on Os(1). Further treatment of **1** with MeOSO₂CF₃ yields $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CPh})$ and $\text{Os}_3(\text{CO})_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$.

The COMe → CH transformation shown in eq 1 proceeds through the isolable intermediate $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-CHOMe})^-]$, demonstrating nucleophilic attack at the carbyne center.¹ Recently, we showed that an analogous set of nucleophilic/electrophilic treatments can effect the COMe → CPh transformation shown in eq 2.²



However, by modifying the reaction conditions in (2), we have now isolated and characterized an intermediate, the structure of which is not only unusual but indicates an entirely different pathway for (2) compared with (1).

Slow addition of PhLi (1.8 M, benzene/ether, 2.5 equiv) to a solution of $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-COMe})$ (330 mg, 0.37 mmol) in freshly distilled diethyl ether (150 mL) at 0 °C under nitrogen produced an orange-red, cloudy solution. MeOSO₂CF₃ (4 equiv) was then added via a syringe. The solution was concentrated to ca. 10 mL under vacuum, then placed under nitrogen, and stirred for 30 min at 0 °C, at which point the solution became clear. The volatile materials were removed under vacuum, and the orange residue was purified by preparative TLC (silica gel), eluting with *n*-pentane/dichloromethane (4:1, v/v). Crystallization

(1) Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 140.

(2) Yeh, W.-Y.; Shapley, J. R.; Li, Y.-J.; Churchill, M. R. *Organometallics* **1985**, *4*, 767.

(3) **1**: mp 121–123 °C; mass spectrum (field desorption), *m/z* 992 (M⁺, ¹⁹²Os); IR (C₆H₁₂) ν (CO) 2091 (m), 2081 (s), 2053 (s), 2029 (s), 2000 (s), 1989 (m), 1980 (m), 1966 (sh), 1955 (sh) cm⁻¹; ¹H NMR (CD₂Cl₂, 17 °C, mixture of two isomers, A and B, A:B = 0.7:1) δ 7.57–7.13 (m, C₆H₅), 4.00 (s, CH₃(B)), 3.88 (s, CH₃(A)), -16.66 (s, $\mu\text{-H(A)}$), -17.40 (s, $\mu\text{-H(B)}$); ¹³C NMR (THF-*d*₆ + THF (1:1), 17 °C) δ 252.0 (=C(B)), 238.4 (=C(A)), 222.6 (=C(A)), 214.8 (=C(B)), 185–170 (CO). Anal. Calcd for Os₃C₁₉H₁₂O₁₁: C, 23.12; H, 1.22; Os, 57.82. Found: C, 23.32; H, 1.23; Os, 57.6.

(10) Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.*, in press.

(11) Huffman, J. C., private communication.

(12) Isomerization of an azametallocyclopentene ring by a titanium metal atom mediated hydrogen shift between nitrogen and carbon has been reported; see: Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006.

(13) The comparable stability and interconvertibility of *cis*- and *trans*-butadiene ligands bound to Cp₂Zr units has been well documented; see: Erker, G.; Wicker, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Kruger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344.

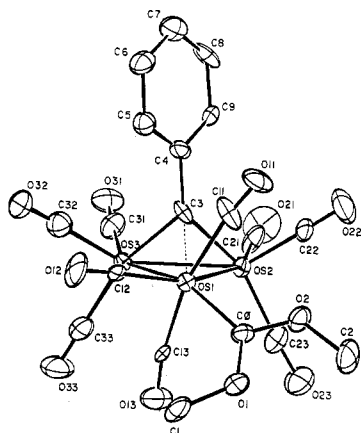


Figure 1. ORTEP diagram of $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\eta^1\text{-C}(\text{OMe})_2)(\mu_3\text{-CPh})$. Significant distances are as follows: $\text{Os}(1)\text{-Os}(2) = 2.782$ (1), $\text{Os}(2)\text{-Os}(3) = 2.884$ (1), $\text{Os}(3)\text{-Os}(1) = 2.867$ (1), $\text{Os}(1)\text{-C}(3) = 2.286$ (12), $\text{Os}(2)\text{-C}(3) = 2.074$ (14), $\text{Os}(3)\text{-C}(3) = 2.040$ (15), $\text{Os}(1)\text{-C}(\text{O}) = 2.039$ (18), $\text{C}(\text{O})\text{-O}(1) = 1.311$ (17), and $\text{C}(\text{O})\text{-O}(2) = 1.318$ (22) Å.

of the orange-yellow band from *n*-hexane yielded air-stable crystals formulated as $\text{HOs}_3(\text{CO})_9(\text{C}(\text{OMe})_2)(\text{CPh})^3$ (**1**) (315 mg, 0.32 mmol, 87%).

The crystal of **1** found suitable for X-ray analysis⁴ was grown from dichloromethane/methanol solution at -20°C . The resulting structure is illustrated in Figure 1. The bridging hydride ligand was not located but is believed to span the $\text{Os}(2)\text{-Os}(3)$ edge. The dimethoxycarbene ligand takes up an essentially equatorial position on $\text{Os}(1)$, although atom $\text{C}(\text{O})$ lies 0.904 (13) Å below the triosmium plane. The dihedral angle between the triosmium plane and the $\text{O}(1)\text{-C}(\text{O})\text{-O}(1)$ system is 131.7° . The osmium-carbon distance in the carbene (2.039 (18) Å) is significantly longer than in the carbonyls (range 1.862 (19)–2.010 (18) Å). The carbon-oxygen distances are equivalent; however, the angle $\text{Os}(1)\text{-C}(\text{O})\text{-O}(1) = 132.5$ (11) $^\circ$ is some 14.1° larger than the angle $\text{Os}(1)\text{-C}(\text{O})\text{-O}(2) = 118.4$ (11) $^\circ$. (The remaining angle is $\text{O}(1)\text{-C}(\text{O})\text{-O}(2) = 109.0$ (13) $^\circ$.) Kaesz and co-workers⁶ have established a terminal configuration for the methoxymethylcarbene ligand in $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\eta^1\text{-C}(\text{OMe})\text{Me})(\mu\text{-}\eta^2\text{-C}(\text{O})\text{Me})$, although bridging configurations have been indicated for other types of triosmium carbene complexes involving $\text{CH}(\text{OMe})$,¹ CH_2 ,⁷ and CHR ⁸ ligands. Recently, Singh and Angelici⁹ have prepared a triruthenium bis(dioxy-carbene) complex, $\text{Ru}_3(\text{CO})_{10}(=\text{COCH}_2\text{CH}_2\text{O})_2$, for which terminal coordination also is indicated.

The benzylidyne ligand in **1** adopts a semi-triply-bridged configuration,¹ interacting strongly with $\text{Os}(2)$ and $\text{Os}(3)$

(4) Complex **1** crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 14.6783$ (18) Å, $b = 10.3281$ (14) Å, $c = 16.8542$ (25) Å, $\beta = 112.184$ (10) $^\circ$, $V = 2365.9$ (5) Å³, and $Z = 4$. Diffraction data ($\text{Mo K}\alpha$, $2\theta = 4.0\text{-}40.0^\circ$) were collected with a Syntex $P2_1$ diffractometer⁵ and corrected for the effects of absorption and Lorentz-polarization factors. The structure was solved by using MULTAN and was refined to $R_F = 4.8\%$ and $R_{wF} = 4.1\%$ for 298 parameters refined against all 2215 independent reflections. ($R_F = 2.9\%$ and $R_{wF} = 3.6\%$ for those 1858 reflections with $|F_o| > 3\sigma(|F_o|)$.)

(5) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

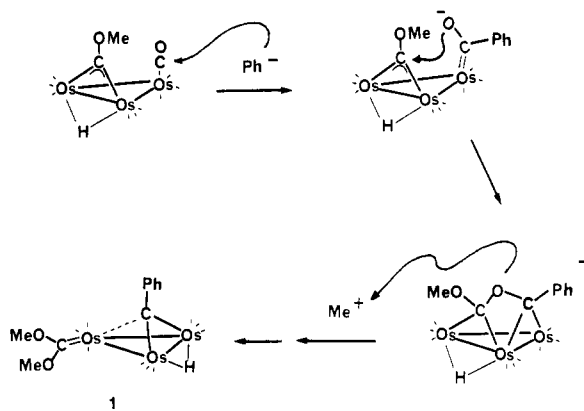
(6) (a) Jensen, C. M.; Lynch, T. J.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1982**, *104*, 4680. (b) Jensen, C. M.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 5926.

(7) (a) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 825. (b) Schultz, A. J.; Williams, J. M.; Calvert, R. B.; Shapley, J. R.; Stucky, G. D. *Inorg. Chem.* **1979**, *18*, 319.

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Scheme I



and weakly with $\text{Os}(1)$. The same configuration has been established previously for $\text{HOs}_3(\text{CO})_{10}(\mu_3\text{-CR})$, $\text{R} = \text{H}, \text{Ph}, \text{and } \text{CH}_2\text{CHMe}_2$.¹⁰ However, the distance between the unique osmium atom and the carbyne carbon is shorter in **1** than in any of the previous complexes, in particular, 0.30 Å shorter than in $\text{HOs}_3(\text{CO})_{10}(\mu_3\text{-CPh})$.² This decrease substantiates the bonding picture originally proposed for $\text{HOs}_3(\text{CO})_{10}(\mu_3\text{-CH})$,¹ i.e., that the unique osmium acts as an electron pair donor to the carbyne carbon, since replacing a carbonyl ligand by a more nucleophilic dimethoxycarbene ligand should make the osmium center a better donor. Consistent with the short $\text{Os}(1)\text{-C}(3)$ distance in **1**, the dihedral angle between $\text{Os}(1)\text{-Os}(2)\text{-Os}(3)$ and $\text{Os}(2)\text{-C}(3)\text{-Os}(3)$ planes, 66.6° , is the most acute yet observed (cf. 78.2° for $\text{HOs}_3(\text{CO})_{10}(\mu_3\text{-CPh})$).² The benzylidyne ligand also causes displacements of the axial carbonyl groups on $\text{Os}(1)$, such that $\text{Os}(3)\text{-Os}(1)\text{-C}(11) = 118.0$ (5) $^\circ$ vs. $\text{Os}(3)\text{-Os}(1)\text{-C}(13) = 68.4$ (4) $^\circ$, the $\text{Os}(3)\cdots\text{C}(13)$ distance being only 2.811 (15) Å.

The crystal structure of **1** shows that the carbene ligand occupies an equatorial position on the unique atom $\text{Os}(1)$. However, room-temperature ^{13}C and ^1H NMR spectroscopy of **1** in solution show the presence of two species.³ Low-temperature spectra reveal that the major species is actually a mixture of two equilibrating forms; dissolving crystals of **1** at -78°C gives only this mixture. These results suggest that the carbene ligand displays positional as well as conformational isomerism in **1**; details will be described in a full paper.

The ^{13}C NMR spectrum of $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-COMe})$ combined with PhLi in THF ¹¹ shows three methoxy-carbyne signals at δ 374.1, 360.3, and 358.4 as well as three signals at δ 243.1, 242.5, and 241.6 assignable to benzoyl carbons.⁶ This suggests that initial attack occurs at a carbonyl ligand to generate the species $[(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu\text{-COMe})(\eta^1\text{-C}(\text{O})\text{Ph})]^-$. Protonation of this species regenerates the starting material, and methylation gives **1**. Intramolecular attack of the acyl oxygen at the carbyne center followed by oxygen transfer in the presence of the methylating agent would form **1**. This mechanism is shown in Scheme I.

Extended treatment of **1** with $\text{MeOSO}_2\text{CF}_3$ in diethyl ether gives $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CPh})$, which was described previously,² together with a coproduct, which has now been

(10) Green, M.; Orpen, A. G.; Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1984**, 37.

(11) The sample was dissolved in THF and placed in a NMR tube under nitrogen. After 3 equiv of phenyllithium was added at 0°C , the solution was cooled to -70°C , at which temperature the spectrum was taken. Owing to the poor solubility of the anionic product in diethyl ether, THF was chosen as the solvent in the NMR study. However, the IR spectra observed are identical in diethyl ether and THF.

characterized as $\text{Os}_3(\text{CO})_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$.¹² The ratio of these two products depends on the temperature at which the methylation is conducted; a higher temperature (35 °C) favors the latter whereas a lower temperature (<25 °C) favors the former. In the absence of methylating agent 1 undergoes other rearrangements involving both the carbene and carbyne centers. The details of these reactions are under investigation.

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Registry No. 1, 98015-25-9; $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-COMe})$, 69048-01-7; $[(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu\text{-COMe})(\eta^1\text{-C}(\text{O})\text{Ph})]$, 98015-26-0; $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CPh})$, 95122-80-8; $\text{Os}_3(\text{CO})_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$, 98015-27-1.

Supplementary Material Available: Tables of final positional parameters, anisotropic thermal parameters, and observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

(12) X-ray structure: Churchill, M. R.; Li, Y.-J.; unpublished results. Spectroscopic data: mass spectrum, m/z 960 (M^+ , ^{192}Os); IR (C_6H_6) $\nu(\text{CO})$ 2065 (vs), 2060 (vs), 2024 (s), 2003 (m, br) cm^{-1} ; ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 20 °C) δ 7.90-7.82 (m, 2 H), 7.40-7.16 (m, 3 H), 4.62 (s, 3 H); ^{13}C NMR (CD_2Cl_2 , 20 °C) δ 319.4 (s, 1 C, $\equiv\text{COMe}$), 234.6 (s, 1 C, $\equiv\text{CPh}$), 173.9 (s, 9 C, CO).

Reversible Alkyne Ligand Scission: Formation and Reactivity of $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_5(\mu\text{-CTol})(\mu_3\text{-CTol})$

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Summary: Decarbonylation of $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_7(\mu_3\text{-}\eta^2\text{-C}_2\text{ToI}_2)$ (1) in refluxing methylcyclohexane induces cleavage of the alkyne C-C bond, giving $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_5(\mu\text{-CTol})(\mu_3\text{-CTol})$ (2). This transformation is reversed upon exposure to CO (1 atm, 25 °C, 5 min), but reaction with H_2 (1 atm, 101 °C, 15 min) provides $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_4(\mu\text{-CTol})(\mu_3\text{-CTol})(\mu\text{-H})\text{H}$ (4). Treatment of 4 with CCl_4 gives $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_4(\mu\text{-CTol})(\mu_3\text{-CTol})(\mu\text{-H})\text{Cl}$ (5).

The scission of alkyne ligands is of considerable current interest, as shown by recent reports involving dinuclear,¹ trinuclear,² and tetranuclear³ complexes. Irreversible formation of alkynes from alkyldiene ligands is frequently observed.⁴ However, strong inferential evidence for reversible alkyne scission/alkyldiene coupling equilibration has only been presented recently, by Vollhardt and co-

workers for dialkyldynetricobalt complexes⁵ and by Chisholm and co-workers for alkyneditungsten complexes.⁶ We now report direct observation of reversibly related alkyne and dialkyldiene mixed-metal trinuclear complexes.

Thermolysis of $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_7(\mu_3\text{-}\eta^2\text{-C}_2\text{ToI}_2)$ (1) in refluxing methylcyclohexane flushed with argon (101 °C, 20 min) provides mildly air sensitive $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_5(\mu\text{-CTol})(\mu_3\text{-CTol})$ (2) (>95% by ^1H NMR). The compound is isolated in 88% yield as a dark brown crystalline solid by cooling the concentrated solution to -20 °C; the formulation is established by analytical and spectroscopic data.⁸ The key structural features for 2 are revealed in its ^{13}C NMR spectrum.⁹ Resonances at δ 384.1 ($^1J_{\text{C-W}} = 135$ Hz) and δ 244.5 ($^1J_{\text{C-W}} = 89$ Hz) are assigned to the doubly bridging and the triply bridging alkyldiene centers, respectively. These signals are well downfield of the signals for the alkyne carbons in the two isomers of 1 (δ 136-162) and show no evidence for C-C coupling.¹¹ Furthermore, these chemical shifts are compatible with those reported by Stone and co-workers for two related ditungsten-rhenium clusters, $\text{Cp}_2\text{W}_2\text{Re}(\text{CO})_3(\mu\text{-Br})(\mu\text{-X})(\mu\text{-CTol})(\mu_3\text{-CTol})$ [$\text{X} = \text{O}$, δ 341.4, 294.5; $\text{X} = \text{CO}$, δ 364.9, 305.2], the structures of which have been established by X-ray crystallography.¹²

Complex 2 reacts readily with carbon monoxide (1 atm, 5 min) at room temperature to generate alkyne complex 1 (95% recovery from 1 \rightarrow 2 \rightarrow 1 cycle). A reasonable picture of the probable reaction sequence linking 1 and 2 can be constructed (see Scheme I), based largely on the structures of related compounds characterized by Stone and co-workers.^{12,13} The $\mu_3\text{-}\eta^2$ (\parallel) alkyne configuration shown by 1⁷ is that expected for a 48e complex, and loss of one CO ligand should give a 46e species, $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_6(\text{C}_2\text{ToI}_2)$ (3), with a $\mu_3\text{-}\eta^2$ (\perp) configuration.¹⁴ In fact, the iron analogue of 3, namely, $\text{Cp}_2\text{W}_2\text{Fe}(\text{CO})_6(\mu_3\text{-}\eta^2\text{-C}_2\text{ToI}_2)$, has been isolated and shown to have the perpendicular configuration,¹⁵ no analogue of 1 was observed. However, this osmium/iron stability reversal has been evident before: 48e $\text{Os}_3(\text{CO})_{10}(\text{C}_2\text{Ph}_2)$ is stable,¹⁶ whereas

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(8) $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_5(\mu\text{-CTol})(\mu_3\text{-CTol})$: FD mass spectrum (^{184}W , ^{192}Os), m/z 1036 (M^+), 1004 ($\text{M}^+ - \text{CO}$); IR (C_6H_6) $\nu(\text{CO})$ 2040 (vs), 1979 (s), 1951 (m) cm^{-1} ; ^1H NMR (360 MHz, C_6D_6) δ 7.24-6.46 (8 H, m), 4.88 (10 H, s), 2.40 (3 H, s), 2.01 (3 H, s). Anal. Calcd for $\text{W}_2\text{Os}_2\text{C}_{31}\text{H}_{24}\text{O}_5$: C, 35.99; H, 2.34; W, 35.55. Found: C, 35.85; H, 2.30; W, 35.55.

(9) 2: ^{13}C NMR (90.4 MHz, C_6D_6 , -75 °C) δ 384.1 ($\mu\text{-CR}$, $^1J_{\text{C-W}} = 135$ Hz), 244.5 ($\mu_3\text{-CR}$, $^1J_{\text{C-W}} = 89$ Hz), 231.5 (W-CO , $^1J_{\text{C-W}} = 165$ Hz), 186.4, 182.4 (1:2, Os-CO). The intensity of the tungsten satellites for both alkyldiene carbon resonances indicates the alkyldienes are connected to two identical tungsten centers. The carbon-13 enriched samples were obtained from the reaction of the $\text{CpW}(\text{CO})_2\text{*CTol}$ and $\text{H}_2\text{Os}_3(\text{*CO})_{10}$.

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(2) Clauss, A. D.; Shapley, J. R.; Wilker, C. N.; Hoffmann, R. *Organometallics* **1984**, *3*, 619 and references therein.

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(4) Vollhardt, K. P. C.; Walborsky, E. C. *J. Am. Chem. Soc.* **1983**, *105*, 5507. Also see Allison et al.⁵ especially ref 4 therein.