J. Am. Chem. Soc. **1981**, *103*, 7385-7387

are created during the decomposition of the two bimetallic clusters.[23]

The catalytic properties of the materials derived from decomposing the supported clusters have been probed by examining the hydrogenolysis of *n*-butane,[24] the simplest such reaction that offers the possibility of selectivity differences. The resultant data are shown in Table I.[27] The $[Ir_4]$[28] catalyst displayed a high selectivity for scission of the central carbon–carbon bond of butane, forming two molecules of ethane, in agreement with previous studies of highly dispersed Ir/Al_2O_3 catalysts, specifically Anderson's study using $Ir_4(CO)_{12}$ as a precursor.[29] The $[WIr_3]$[28] and $[2W_2 + Ir_4]$[28] catalysts also showed ethane selectivity of 70% or greater, but the $[W_2Ir_2]$[28] catalyst showed less than 50% ethane in the product stream. This substantially different cracking pattern for the $Cp_2W_2Ir_2(CO)_{10}$-derived catalyst is strong evidence for a residual tungsten–iridium interaction that modifies the character of the catalytic site(s). The activities measured were comparable with previous data for Ir/Al_2O_3,[29] but most noteworthy is that the activation energies were lower for both the $[WIr_3]$ and the $[W_2Ir_2]$ catalysts.

Chemisorption data have been collected as partial physical characterization of the cluster-derived catalysts.[30] Freshly activated materials showed irreversibly adsorbed quantities of H_2 and CO corresponding to $H/Ir = 1.5–1.8$ and $CO/Ir = 1.0–1.3$. These values indicate very high dispersions, with particle sizes probably less than 10 Å.[31] The mixed-metal catalysts showed some loss of metal surface area after the hydrogenolysis experiments. However, electron microscopy studies revealed no discernable particles under conditions where ≥20-Å particles were seen in conventionally prepared catalyst samples. The diminished chemisorption was particularly true of the $[W_2Ir_2]$ catalyst and may indicate the formation of carbonaceous residues during the catalytic runs.

Further physical as well as catalytic studies are being conducted with the bimetallic cluster-derived catalysts. Nevertheless, the present work shows that the synthetic and structural methodology of inorganic chemistry can provide suitable precursors to bimetallic catalysts, combining rather disparate elements. More significantly, it indicates that the catalytic properties derived may be uniquely linked to the specific bimetallic precursor.[32] This result offers the possibility of enhanced control and even the effective design of bimetallic catalytic sites.

Acknowledgment. This research was supported at the University of Illinois by NSF Grants DMR 77-23999 and 80-20250 and at SUNY-Buffalo by NSF Grant CHE 80-23448. J.R.S. is grateful for the interest shown in this work by Dr. John Sinfelt and acknowledges very helpful discussions with him, Dr. Gary McVicker, and Al Barnett.

Supplementary Material Available: Lists of positional and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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[23] Cp ligands of the mixed metal clusters were hydrogenated and cracked above 300 °C. However, quantitative data indicate an upper limit of 10% of the CH_4 produced can be due to Cp cracking.

[24] Catalytic activity for *n*-butane hydrogenolysis was monitored by gas chromatography. Conversions were kept less than 5% to eliminate complications due to heat and mass transfer. Catalytic activities at different temperatures were bracketed by runs at standard conditions to minimize possible effects of catalyst deactivation.[25,26] Both activities and product distributions showed good reproducibility at any given temperature and neither varied appreciably with time or after reactivation. A 150-cc/min flow rate, 20:1 H_2–*n*-butane, was employed.

[25] Yates, D. J. C.; Taylor, W. F.; Sinfelt, J. H. *J. Am. Chem. Soc.* **1964**, *86*, 2996.

[26] Vannice, M. A. *J. Catal.* **1975**, *37*, 449.

[27] Neither the decomposed $Cp_2W_2(CO)_6/Al_2O_3$ nor the Al_2O_3 alone was active in the temperature range used (<230 °C).

[28] This abbreviation is meant only to indicate the precursor to the supported metal species, with no implications regarding the actual particle size, shape, or composition.

[29] Foger, K.; Anderson, J. R. *J. Catal.* **1979**, *59*, 325.

[30] Hydrogen and carbon monoxide chemisorption were measured volumetrically by using conventional procedures.[31]

[31] G. B. McVicker, Baker, R. T. K.; Garten, R. L.; Kugler, E. L. *J. Catal.* **1980**, *65*, 207.

[32] Two reports have indicated finding no evidence for bimetallic interactions influencing the activity of cluster-derived catalysts: (a) Thomas, T. J.; Mistalski, G.; Hucul, D. A.; Brenner, A. 179th National Meeting of the American Chemical Society, Houston, TX, March 1980; American Chemical Society: Washington, DC, 1980; Abstr. COLL 11. (b) Shapley, J. R.; Hardwick, S. J.; Foose, D. S.; Stucky, G. D. *Prepr., Div. Pet. Chem., Am. Chem. Soc.* **1980**, *25*, 780. However, for contrary indications, see: (c) McVicker, G. B. U.S. Patent 4 187 168, 1980.

Remarkably Facile Os–Os Bond Cleavage in the Reaction of $H_2Os_3(CO)_{10}$ with a Tungsten Carbyne. Crystal Structures of $CpWOs_3(CO)_{11}[C(O)CH_2C_6H_4Me]$ and $Cp_2W_2Os(CO)_7[C_2(C_6H_4Me)_2]$

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Stone and co-workers have utilized the "isolobal" analogy between an alkyne (RC≡CR) and a metal carbyne complex ($L_nM≡CR$)[1] as motivation for examining the interaction of a variety of reactive low oxidation state compounds with metal carbynes.[2] Intrigued by the success of this analogy, we decided to examine it in the particular instance of $H_2Os_3(CO)_{10}$, which cleanly inserts many alkynes to form the alkenyl derivatives $HOs_3(CO)_{10}(CR{=}CHR)$.[3] We wish to report that $H_2Os_3(CO)_{10}$ indeed reacts easily with a typical carbyne complex, but by two parallel reaction paths, only one of which involves hydrogen transfer. In contrast to the reaction with alkynes, however, both paths involve cleavage of Os–Os bonds under very mild conditions.

A cold (−30 °C) dry dichloromethane solution of $Cp(CO)_2W{\equiv}CC_6H_4Me$ (90 mg, 0.22 mmol) was added to a dry dichloromethane solution of $H_2Os_3(CO)_{10}$ (195 mg, 0.23 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 5 h and then warmed to room temperature. Evaporation of the solvent and preparative TLC (silica gel/3:2 dichloromethane–pentane) provided the two major products,[4] dark red $CpWOs_3(CO)_{12}(CH_2C_6H_4Me)$ (**1**, 59 mg, 21%) and red $Cp_2W_2Os(CO)_7(CC_6H_4Me)_2$ (**2**, 40 mg, 33%), isolated as crystalline solids. These formulations were established by spectroscopic and analytical data,[5] but a reasonable structure could be formulated only for compound **2**. The actual structures of both **1** and **2** have been

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[1] Ashworth, T. V.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1979**, 42.

[2] Ashworth, T. V.; Chetcuti, M. J.; Howard, J. A. K.; Stone, F. G. A.; Wisbey, S. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 763 and references therein.

[3] Clauss, A. D.; Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *Inorg. Chem.* **1981**, *20*, 1528 and references therein.

[4] A third, minor product has been isolated and characterized spectroscopically and structurally as $CpWOs_3(CO)_{10}(CAr)_2H$. Formation of this compound involves cleavage of a W≡C bond as well as an Os–Os bond. Details are still under investigation and will be reported in a full paper.

[5] Compound **1**: IR (CCl_4) ν(CO) 2095 (m), 2063 (vs), 2032 (m), 2021 (s), 2007 (m), 1978 (m), 1939 (vw) cm^{-1}; ^1H NMR (CD_2Cl_2, 25 °C) δ 7.15–7.20 (m, 4 H), 5.43 (s, 5 H), 3.47 (s, 2 H), 2.35 (s, 3 H); mass spectrum (70 eV, ^{192}Os, ^{184}W), *m/z* 1266 (M^+). Anal. Calcd for $C_{25}H_{14}O_{12}WOs_3$: C, 23.82; H, 1.12; W, 14.58; Os, 45.26. Found: C, 24.18; H, 1.21; W, 14.53; Os, 42.64. Compound **2**: IR (CCl_4)ν(CO) 2061 (w), 2046 (vs), 1998 (sh), 1990 (vs), 1977 (vs), 1959 (sh), 1918 (s), 1830 (w) cm^{-1}; ^1H NMR (CD_2Cl_2, 25 °C) δ 6.9–6.7 (m, 8 H), 5.06 (s, 10 H), 2.23 (s, 6 H); mass spectrum (field desorption, ^{192}Os, ^{184}W), *m/z* 1092 (M^+). Anal. Calcd for $C_{33}H_{24}O_7W_2Os$: C, 36.35; H, 2.22; W, 33.72; Os, 17.44. Found: C, 36.17; H, 2.17; W, 33.20; Os, 16.00.

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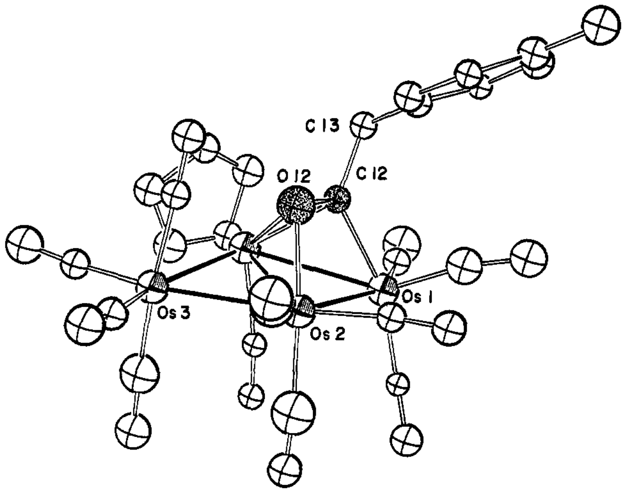

Figure 1. Geometry of the $CpWOs_3(CO)_{11}[C(O)CH_2C_6H_4Me]$ molecule. Intermetallic distances are Os(1)–Os(2) = 2.815 (1) Å, Os(1)–W = 2.867 (1) Å, Os(2)–Os(3) = 2.839 (1) Å, Os(2)–W = 2.741 (1) Å, and Os(3)–W = 2.914 (1) Å.

established by single-crystal X-ray diffraction studies.

Diffraction data (Mo Kα) for **1**[6] and **2**[7] were collected with a Syntex $P2_1$ automated four-circle diffractometer and the structures solved with the (SUNY—Buffalo modified) Syntex XTL system.

The molecular configuration of **1** is shown in Figure 1. This cluster is based upon an almost planar triangulated rhombus (the dihedral angle between Os(1)–Os(2)–W and Os(2)–Os(3)–W planes is 4.0°), as found previously only in $[Re_4(CO)_{16}{}^{2-}]$,[8] $HOs_3Re(CO)_{15}$,[9] and $FeRu_3(CO)_{13}$ (μ-$PPh_2)_2$.[10] A unique feature of this structure, of relevance to chemistry on the surface of heterogeneous metallic catalysts, is the presence of a triply-bridging acyl group [C(12)–O(12)]. Relevant distances in this system include Os(1)–C(12) = 2.037 (22) Å, W–C(12) = 2.184 (22) Å, W–O(12) = 2.155 (14) Å, and Os(2)–O(12) = 2.106 (14) Å. The C(12)–O(12) distance of 1.394 (27) Å suggests significant activation and is close to the C–O single-bond length of ~1.43 Å. The C(12)–C(13) bond length is 1.562 (31) Å, indicating that C(13) is now saturated—i.e., two hydrogen atoms have been transferred to the α carbon of the initial reacting *p*-xylylidyne fragment. [It should be noted that a triply-bridging acyl has also been found in the trinuclear species $[Fe_3(CO)_9(MeCO)^-]$.[11] Here, the C–O distance is only 1.31 (2) Å.]

The structural study of **2** showed that there were two molecules of $Cp_2W_2Os(CO)_7[C_2(C_6H_4Me)_2]$ in the crystallographic asymmetric unit. The two molecules are not identical but are isomers based upon a $2\pi/3$-rad rotation of a $MeC_6H_4C{\equiv}CC_6H_4Me$ moiety about the triangular W_2Os cluster face. The two independent molecules are shown in Figures 2 and 3. They each contain a μ_3-acetylenic ligand obtained by dimerization of $\equiv CC_6H_4Me$ fragments and they correspond to two of the three possible potential minima for rotation of the μ_3-acetylenic moiety on the surface of the triangular W_2Os face. The complex is fluxional at room temperature as is evidenced by the singlet at δ 5.06 for the 10 Cp protons (see footnote 5).

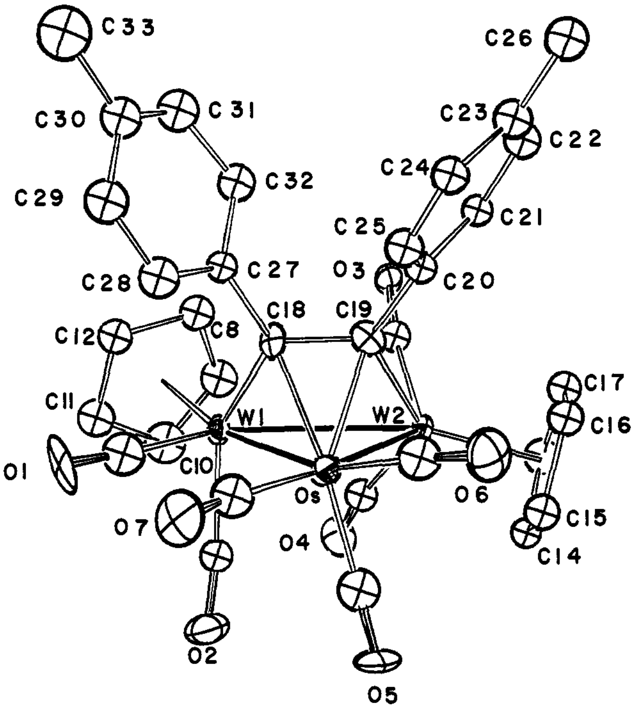

Figure 2. The symmetric molecule in crystalline **2**. Metal–metal distances are W(1)–W(2) = 3.158 (1) Å, W(1)–Os = 2.857 (1) Å, W(2)–Os = 2.836 (2) Å. Important distances involving the $MeC_6H_4C{\equiv}CC_6H_4Me$ ligand are C(18)–C(19) = 1.463 (28) Å, C(18)–Os = 2.229 (19) Å, C(19)–Os = 2.268 (19) Å, C(18)–W(1) = 2.187 (18) Å, and C(19)–W(2) = 2.180 (20) Å.

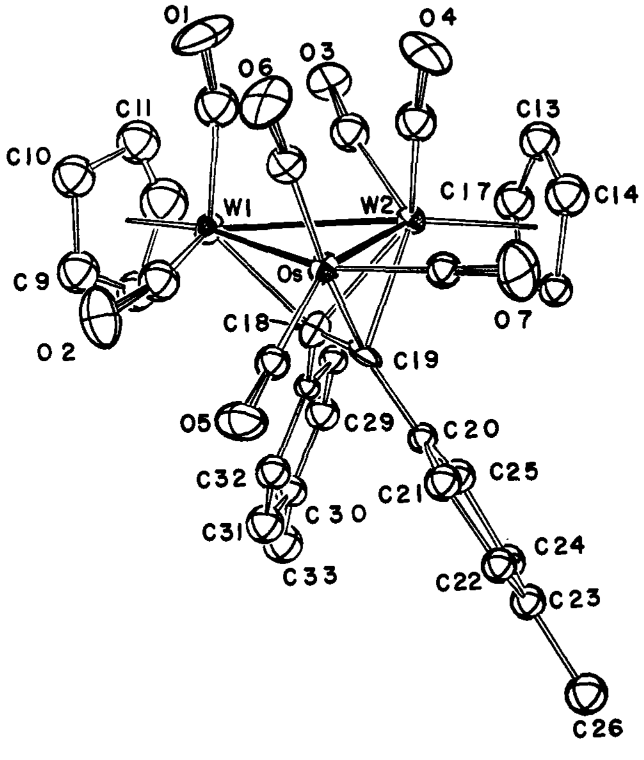

Figure 3. The unsymmetrical isomer in crystalline **2**. Metal–metal distances are W(1)–W(2) = 3.016 (1) Å, W(1)–Os = 2.987 (1) Å, and W(2)–Os = 2.871 (1) Å. Distances involving the $MeC_6H_4C{\equiv}CC_6H_4Me$ ligand include C(18)–C(19) = 1.424 (29) Å, C(18)–W(1) = 2.202 (18) Å, C(18)–W(2) = 2.284 (21) Å, C(19)–Os = 2.090 (21) Å, and C(19)–W(2) = 2.365 (19) Å.

Monitoring the reaction between $Cp(CO)_2W{\equiv}CAr$ and $H_2Os_3(CO)_{10}$ by NMR indicated the relatively rapid formation of **2** followed by slower formation of **1**. Significantly, the appearance of **2** was paralleled by the appearance of an equivalent amount

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(6) **1** (CCl_4 solvate), space group $C2/c$, a = 33.515 (5) Å, b = 11.287 (2) Å, c = 16.630 (3) Å, β = 98.35 (1)°, V: 6224.5 (8) $Å^3$, ρ(calcd) = 2.69 g cm^{-3} for mol wt = 1260.8 and Z = 8. R_F = 7.4% and R_{wF} = 7.1% for all 4063 reflections with $3.5° < 2\theta < 45°$.

(7) **2**, space group $P2_1$, a = 10.242 (3) Å, b = 18.163 (4) Å, c = 16.607 (4) Å, β = 101.22 (2)°, V = 3030.1 (13) $Å^3$, ρ(calcd) = 2.39 g cm^{-3} for mol wt = 1090.7 and Z = 4. R_F = 3.7% and R_{wF} = 3.9% for all 4136 reflections with $3.5° < 2\theta < 45°$. (The model includes $\Delta f'$ and $\Delta f''$ for all nonhydrogen atoms and results from the correct crystal chirality are reported.)

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(11) Wong, W.-K.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1981**, 189.

of $H_2Os_2(CO)_8$. The latter was characterized by its ^1H NMR signal (δ −10.1), the disappearance of this signal upon addition of carbon tetrachloride, and the subsequent isolation of $Os_2(CO)_8Cl_2$.[12] Thus, the overall stoichiometry for the formation of **2** is as shown in eq 1. Neither the source nor the timing for

$$H_2Os_3(CO)_{10} + 2Cp(CO)_2W{\equiv}CAr + CO \rightarrow H_2Os_2(CO)_8 + Cp_2W_2Os(CO)_7(C_2Ar_2) \quad (1)$$

coordination of the extra equivalent of carbon monoxide is known. Yet the overall pathway for formation of **2** likely involves an initial 1:1 adduct, which eliminates $H_2Os_2(CO)_x$ (x = 7 or 8) prior to reaction with a second molecule of carbyne. The possibility of eliminating a relatively stable H_2Os_2 fragment, probably via reductive elimination of Os–H bonds,[13] accounts for the ease of Os–Os bond cleavage.

Detailed speculation concerning the mechanism of formation of **1** is unwarranted, but the likely sequence of steps would involve hydrogen transfer from osmium to the carbyne carbon to form a benzyl group, migration of this group onto a carbonyl to form an acyl, insertion of the tungsten into an Os–Os bond, and multiple coordination of the acyl. In this case Os–Os bond cleavage suggests greater strength for the heterometallic W–Os bonds than for the homometallic Os–Os bonds.

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[13] For facile reductive elimination involving $HRe(CO)_5$, see: Churchill, M. R.; Hollander, F. J.; Lashewycz, R. A.; Pearson, G. A.; Shapley, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 2430. Also see: Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139.

Reaction of $Os_3(CO)_9(C_2Ph_2)$ with Diazomethane. Photoinduced Loss of Dinitrogen and Thermally Activated Coupling of Methylene and Diphenylacetylene on the Triosmium Framework

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In recent years transition-metal compounds with μ-alkylidene ligands have been a subject of increasingly intense study.[1] Such compounds commonly are prepared from diazoalkanes, but the detailed reaction pathway, especially in regard to loss of dinitrogen, is often obscure. There is particular interest in the reactivity of μ-alkylidene compounds toward unsaturated hydrocarbons.[2] For instance, the insertion of alkynes into the metal–carbon bond of dimetallic μ-alkylidenes has recently been reported for complexes of iron and ruthenium, and the implications of this reaction in olefin metathesis and alkyne polymerization have been discussed.[3]

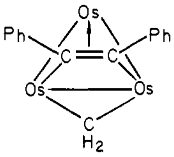
We wish to report that the reaction of diazomethane with coordinatively unsaturated $Os_3(CO)_9(C_2Ph_2)$ proceeds cleanly to yield nearly equal amounts of a thermally stable μ-diazomethane adduct and a μ-methylene complex. Photolysis of the diazomethane complex efficiently converts it into the methylene derivative by loss of dinitrogen. We also report the crystal structure of $Os_3(CO)_9(C_2Ph_2)(CH_2)$ which confirms the presence of a face-bonded diphenylacetylene ligand and an edge-bridging methylene ligand. These cluster-bound hydrocarbon ligands undergo thermally induced coupling, resulting in a face-bonded allyl fragment.

Table I. Selected Bond Lengths (Å) and Bond Angles (Deg) for $Os_3(CO)_9(C_2Ph_2)(CH_2)$

Bond Lengths			
Os(1)–Os(2)	2.765 (1)	Os(2)–C(A1)	2.14 (1)
Os(1)–Os(3)	2.738 (1)	Os(3)–C(A2)	2.13 (2)
Os(2)–Os(3)	2.763 (1)	Os(1)–C(A1)	2.27 (2)
Os(2)–C(10)	2.13 (2)	Os(1)–C(A2)	2.28 (2)
Os(3)–C(10)	2.16 (2)	C(A1)–C(A2)	1.37 (3)

Bond Angles	
Os(2)–C(10)–Os(3)	80.1 (8)
C(10)–Os(2)–C(A1)	83.9 (8)
C(10)–Os(3)–C(A2)	83.4 (8)

Vacuum sublimation (≤10^{-5} torr) of $Os_3(CO)_{10}(C_2Ph_2)$ through a heated Pyrex tube at 250 °C results in efficient decarbonylation to yield $Os_3(CO)_9(C_2Ph_2)$.[4] This intensely red coordinatively unsaturated compound can be washed from the cold finger and is stable in dry hydrocarbon solvents at room temperature. Addition of excess ethereal diazomethane to a cyclohexane solution of $Os_3(CO)_9(C_2Ph_2)$ at room temperature results in an immediate reaction as evidenced by a color change to yellow. After preparative TLC on silica gel $Os_3(CO)_9(C_2Ph_2)(N_2CH_2)$ (39% yield) and $Os_3(CO)_9(C_2Ph_2)(CH_2)$ (32% yield) can be isolated as greenish yellow and orange-yellow solids, respectively.[5] The ^1H NMR and low-temperature ^{13}C NMR spectra of $Os_3(CO)_9(C_2Ph_2)(CH_2)$ indicate a structure containing a μ_3-diphenylacetylene ligand and a μ-methylene ligand (**1**).[6] For $Os_3(CO)_9(C_2Ph_2)(N_2CH_2)$, we propose structure **2** with a μ-diazomethane ligand bound through the terminal nitrogen atom. This assignment is consistent with all available spectroscopic data. An alternative dimetallopyrazolene structure (**3**) is not in agreement with the ^{13}C NMR in the carbonyl region as well as other evidence.[7]



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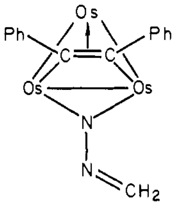

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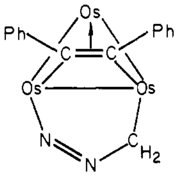

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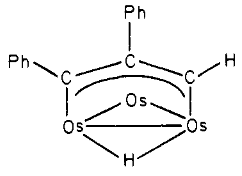

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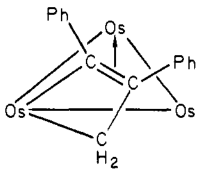

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[4] Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1975**, *97*, 7172.

[5] (a) $Os_3(CO)_9(C_2Ph_2)(N_2CH_2)$: IR ν(CO) (cyclohexane) 2092 (w), 2074 (s), 2050 (m), 2044 (m), 2010 (s), 1997 (m), 1988 (w), 1978 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C) δ 7.1–6.7 (m, 10 H), 6.11 (AB quartet, δ_A 6.13, δ_B 6.10, J_{AB} = 10 Hz); mass spectrum (^{192}Os) m/z 1048 (M^+). (b) $Os_3(CO)_9(C_2Ph_2)(CH_2)$: IR ν(CO) (cyclohexane) 2095 (m), 2065 (vs), 2055 (s), 2024 (vs), 2010 (m), 1995 (m), 1975 (w); ^1H NMR ($CDCl_3$, 25 °C) δ 8.27 (d, 1 H_A), 7.65 (d, 1 H_X, J_{AX} = 5 Hz), 7.0–6.5 (m, 10 H); mass spectrum (^{192}Os) m/z 1020 (M^+).

[6] $^{13}C\{^1H\}$ NMR spectrum of (ca. 50% ^{13}CO enriched) $Os_3(CO)_9(C_2Ph_2)(CH_2)$ ($CDCl_3$, −60 °C): δ 171.20 (s, 2 C), 172.37 (s, 2 C), 173.35 (s, 2 C), 178.55 (s, 1 C), 180.69 (s, 2 C).

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