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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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]

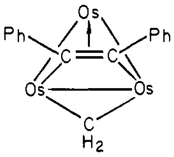
We wish to report that the reaction of diazomethane with coordinatively unsaturated $Os_3(CO)_9(C_2Ph_2)$ proceeds cleanly to yield nearly equal amounts of a thermally stable μ-diazomethane adduct and a μ-methylene complex. Photolysis of the diazomethane complex efficiently converts it into the methylene 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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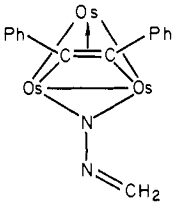

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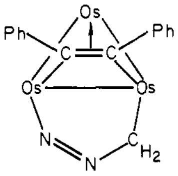

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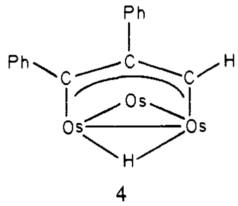

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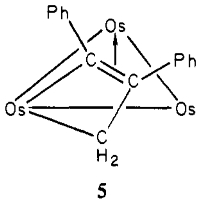

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[4] Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1975**, *97*, 7172.

[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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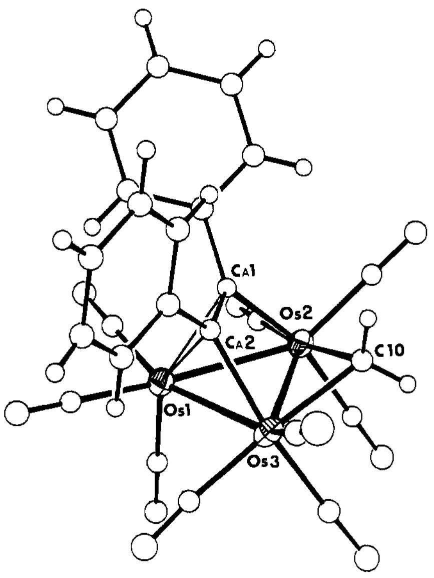

Figure 1. Perspective view of $Os_3(CO)_9(C_2Ph_2)(CH_2)$. The hydrogen atoms are shown in idealized positions.

The diazomethane derivative, $Os_3(CO)_9(C_2Ph_2)(N_2CH_2)$, is thermally stable in solution up to 80 °C; at higher temperatures it decomposes to give products that have not yet been characterized. No $Os_3(CO)_9(C_2Ph_2)(CH_2)$ is formed. The conversion of $Os_3(CO)_9(C_2Ph_2)(N_2CH_2)$ to $Os_3(CO)_9(C_2Ph_2)(CH_2)$ does, however, readily occur by photolysis.[8] This is the first example in which a stable coordinated diazoalkane ligand is photochemically converted to the corresponding alkylidene. A dissociative mechanism involving the intermediacy of $Os_3(CO)_9(C_2Ph_2)$ can be ruled out from the fact that the presence of excess carbon monoxide in solution does not inhibit the formation of $Os_3(CO)_9(C_2Ph_2)(CH_2)$.[9] The dimetallopyrazolene structure (**3**) remains under consideration as a likely intermediate in the conversion of $Os_3(CO)_9(C_2Ph_2)(N_2CH_2)$ to $Os_3(CO)_9(C_2Ph_2)(CH_2)$ although there is no direct evidence for it at this time. A similar cyclic structure has recently been proposed as a transition state in the conversion of $Cp_2Mo_2(CO)_4(N_2CR_2)$ to $Cp_2Mo_2(CO)_4(CR_2)$ (R = Ph, *p*-MeC_6H_4), where the X-ray crystal structure of the reactant confirmed a μ-η^1-bonding mode for the diazo ligand.[10] In contrast to the triosmium system, $Cp_2Mo_2(CO)_4$ reacts with the diaryldiazomethanes at room temperature to yield only the diazoalkane adducts which are thermally converted to alkylidene complexes under mild conditions (60 °C).

Although spectroscopic data on $Os_3(CO)_9(C_2Ph_2)(CH_2)$ indicated structure **1**, this compound was further characterized by a single-crystal X-ray diffraction study to determine the precise relative positions of the hydrocarbon ligands as well as other details of the structure.[11] The molecular structure is illustrated in Figure 1 and selected bond lengths and bond angles are given in Table I. The molecule consists of a triangular array of osmium atoms each bonded to three terminal carbonyls. The diphenylacetylene ligand is coordinated to all three osmium atoms, forming a π bond to Os(1) and σ bonds to Os(2) and Os(3). The Os(2)–Os(3) edge is also bridged by the methylene ligand, which is tilted 21° out of the triosmium plane toward the diphenylacetylene. This results in a separation of only 2.86 (3) Å between the methylene carbon and either of the acetylenic carbons. Although the molecule has no crystallographically imposed symmetry in the solid state, it exhibits the expected idealized C_s symmetry in solution as evidenced by the limiting low-temperature ^{13}C NMR spectrum in the carbonyl region.[6]

Heating a solution of $Os_3(CO)_9(C_2Ph_2)(CH_2)$ (xylenes, 135 °C) results in clean conversion to a new compound, which has been isolated and characterized as $HOs_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C_3Ph_2H)$ (structure **4**).[12] This isomerization (**1** $\rightarrow$ **4**) requires carbon–carbon bond formation and oxidative addition of a methylene C–H bond to the cluster. A reasonable mechanism would involve initial carbon–carbon bond formation resulting in a coordinatively unsaturated intermediate, **5**, which rearranges to **4** following C–H oxidative addition. It was not apparent, however, which step is responsible for the rather high temperature required to effect the isomerization. In order to elucidate the mechanism, the reaction of 1,2-diphenylcyclopropene[14] with $Os_3(CO)_{10}(CH_3CN)_2$[15] was investigated and found to produce $HOs_3(CO)_9(C_3Ph_2H)$ in high yield under milder conditions (refluxing cyclohexane). This reaction pathway involves opening of the cyclopropene ring, loss of carbon monoxide, and C–H oxidative addition. The higher temperature required for the isomerization of **1** to **4** indicates that initial carbon–carbon bond formation is the rate-determining step in this process.

The reactions of $Os_3(CO)_9(C_2Ph_2)$ with other diazoalkanes (N_2CHR; R = CH_3, Ph, CO_2Et, CF_3, $CHCHMe_2$) have also been investigated. In all cases stable diazoalkane adducts are isolated as the major products and smaller amounts of the corresponding alkylidenes are usually observed. The thermal and photochemical reactivity of these compounds is currently being studied.

Acknowledgment. This work has been supported by a grant from the National Science Foundation (No. CHE 81-00140).

Supplementary Material Available: A list of positional and thermal parameters for $Os_3(CO)_9(C_2Ph_2)(CH_2)$ (4 pages). Ordering information is given on any current masthead page.

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(7) 90-MHz $^{13}C\{^1H\}$ NMR for (ca. 50% ^{13}CO enriched) $Os_3(CO)_9(C_2Ph_2)(N_2CH_2)$: (acetone-$d_6$, 25 °C) δ 173.60 (s, 2 C), 176.60 (s, 3 C), 176.89 (s, 2 C), 180.88 (s, 2 C). Only these resonances were observed down to −85 °C, although the lowest field resonance was very broad and the other resonances were slightly broadened at −85 °C. Structure **3** with C_1 symmetry would be expected to show nine separate carbonyl resonances whereas structure **2** with C_s symmetry would be expected to show four resonances for the equivalent pairs of carbonyls and one resonance for the unique carbonyl. The spectrum is consistent with structure **2** assuming the unique carbonyl to be isochronous with one of the symmetry-related pairs. To check this assignment, $Os_3(CO)_9(C_2Ph_2)(N_2CHCHMe_2)$ was synthesized from $Os_3(CO)_9(C_2Ph_2)$ and $N_2CHCHMe_2$. In this derivative the methyl groups would be diasterotopic in structure **3** but could be enantiotopic in structure **2**. The observed ^1H NMR spectrum [($CDCl_3$, 25 °C) δ 7.1–6.6 (m, 10 H), 6.37 (d, 1 H, J = 6 Hz), 3.55 (m, 1 H), 1.10 (d, 6 H, J = 7 Hz)] shows one doublet for the methyl groups, as expected for structure **2**.

(8) Photolyses were carried out on cyclohexane solutions in Pyrex glassware with an Ace-Hanovia 450-W high-pressure quartz mercury-vapor lamp.

(9) Photolysis of $Os_3(CO)_9(C_2Ph_2)(N_2CH_2)$ under argon flush for 12 h results in formation of $Os_3(CO)_9(C_2Ph_2)(CH_2)$ (42% yield) as the only product isolated after TLC. If carbon monoxide is bubbled through the solution during photolysis, no appreciable amount of $Os_3(CO)_{10}(C_2Ph_2)$ is formed and the yield of $Os_3(CO)_9(C_2Ph_2)(CH_2)$ is enhanced (68%).

(10) Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 7789.

(11) $Os_3(CO)_9(C_2Ph_2)(CH_2)$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with a = 15.831 (3) Å, b = 16.910 (5) Å, c = 11.386 (3) Å, α = 104.00 (2)°, β = 106.72 (2)°, γ = 110.47 (2)°, V = 2528 (1) Å^3, and ρ_{calcd} = 2.666 g/cm^3 for Z = 4. Diffraction data were collected in the range $3.5° \leq 2\theta \leq 50.0°$ using Mo Kα radiation on a Syntex P2$_1$ diffractometer and were numerically corrected for absorption. The structure was solved by a combination of direct methods (SHELX 76) and Fourier and difference Fourier syntheses and was refined via full-matrix least-squares to R_F = 4.4% and R_{wF} = 5.6%. The osmium atoms were refined by using anisotropic thermal parameters. All other nonhydrogen atoms were refined by using isotropic thermal parameters. The phenyl rings were refined as rigid groups with ideal bond lengths and angles. Each of the asymmetric units contains two independent molecules with essentially the same structural features. Only one of the molecules is described here.

(12) $HOs_3(CO)_9(C_3Ph_2H)$: IR ν(CO) (cyclohexane) 2098 (m), 2072 (s), 2048 (vs), 2020 (s), 2008 (sh), 2004 (s), 1991 (w), 1985 (w), 1956 (w, br); ^1H NMR ($CDCl_3$, 25 °C) δ 8.75 (s, 1 H), 7.2–6.7 (m, 10 H), −19.15 (s, 1 H); mass spectrum (^{192}Os) m/z 1020 (M^3). The IR and ^1H NMR data are in close agreement with those of $HOs_3(CO)_9(C_3H_2OH)$ and $HOs_3(CO)_9(C_3H_2OCH_3)$, which have recently been characterized by single-crystal X-ray diffraction to contain face-bonded ($2\sigma + \pi$)-allyl ligands.[13]

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