

→ Ru₃ or vice versa conversion. Hopefully a better understanding of the details of the rather complicated sequence of reactions can be arrived at by means of in situ high-pressure FTIR studies, which are presently underway in our laboratories.²²

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(22) Our investigations employing mononuclear group 6B pentacarbonyl hydride and formate derivatives as catalysts for HCO₂Me production from CO₂/H₂ in MeOH strongly support a mechanism involving reductive elimination of formic acid from the metal center. Subsequent reactions of formic acid with methanol provide methyl formate.

A Mononuclear, Low-Valent, Electron-Rich Osmium Methylene Complex

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Molecules with transition-metal-carbon multiple bonds are being increasingly recognized as the active species in many catalytic reactions.¹ It is important, therefore, to define the factors that affect the reactivity of these multiple linkages. For the metal-carbon double bond the prototype ligand is methylene, and a mononuclear example of this ligand was first structurally characterized in Ta(=CH₂)(CH₃)Cp₂.² Methylene complexes of metals from groups 6,³ 7,⁴ and 8⁵ also have now been observed, but in many cases their characterization was by spectroscopic methods at low temperatures. Studies of the reactivity of these complexes indicate two distinct patterns of behavior. Ta(=CH₂)(CH₃)Cp₂ and many related molecules⁶ contain nucleophilic methylene centers, a property that has been attributed to extremely effective Ta-C orbital overlap.⁷ On the other hand, cationic methylene complexes from groups 6, 7, and 8 have been shown to contain electrophilic carbene centers.³⁻⁵

We report here (i) the synthesis and X-ray crystal structure of a low-valent methylene complex of osmium, Os(=CH₂)Cl(NO)(PPh₃)₂ (I), in which the methylene ligand is *not* electrophilic, (ii) reactions of I with various electrophilic reagents, (iii) a demonstration that the electron-rich osmium-carbon double bond in I can interact with an electrophilic metal-center [Au(PPh₃)]⁺ forming an osmium-gold μ -methylene complex, and (iv) the crystal structure of Os(CH₂AuI)Cl(NO)(PPh₃)₂.

Diazoalkanes have been extensively studied as transition-metal-carbene precursors but the ultimate products are usually bridging-carbene complexes.⁸ Reaction between diazomethane and IrCl(CO)(PPh₃)₂ led to Ir(CH₂Cl)(CO)(PPh₃)₂.⁹ Four

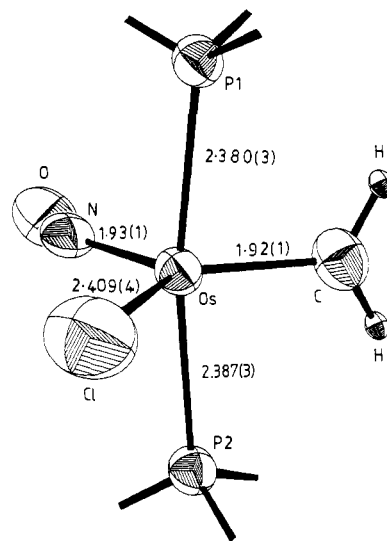
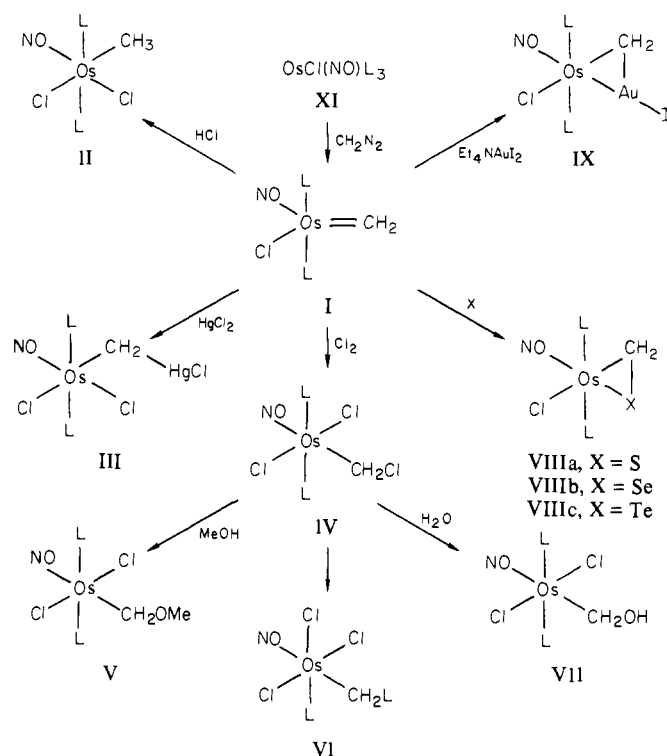


Figure 1. Inner coordination sphere of Os(=CH₂)Cl(NO)(PPh₃)₂ (thermal parameters for the methylene hydrogens have been set artificially small). Interatomic angles: C-Os-Cl, 126.6 (4)°; P1-Os-P2, 170.4 (1)°; C-Os-N, 118.8 (5)°; Cl-Os-N, 114.6 (4)°; Os-N-O, 155.4 (1.6)°.

Scheme I. Synthesis and Some Reactions of an Osmium Methylene Complex (L = PPh₃)¹¹



coordination is much less common for osmium(0) than for iridium(I), and we find that diazomethane with OsCl(NO)(PPh₃)₃¹⁰

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(10) OsCl(NO)(CO)(PPh₃)₂ (1 g) is dissolved in CH₂Cl₂ (100 mL) and EtOH (10 mL). The solution is stirred for 10 min under O₂ (1 atm) while the color changes from brown to yellow. Removal of the solvent under reduced pressure yields a complex of stoichiometry OsCl(CO₂)(NO)(PPh₃)₂ (yield 810 mg, 78%). OsCl(CO₂)(NO)(PPh₃)₂ (810 mg) is dissolved in rigorously degassed benzene (50 mL) with PPh₃ (800 mg). The solution is heated under reflux for 5 min. Dark green crystals of OsCl(NO)(PPh₃)₃ form as the solution cools, and further material is obtained by addition of degassed *n*-hexane (yield 940 mg, 94%). OsCl(NO)(PPh₃)₃ (940 mg) is suspended in benzene (20 mL), and an ethereal solution of CH₂N₂ (20 mL)¹³ is added dropwise. Tan-colored crystals of Os(=CH₂)Cl(NO)(PPh₃)₂ separate as the reaction proceeds. Recrystallization from CH₂Cl₂/EtOH yields orange crystals, 590 mg, 82%.

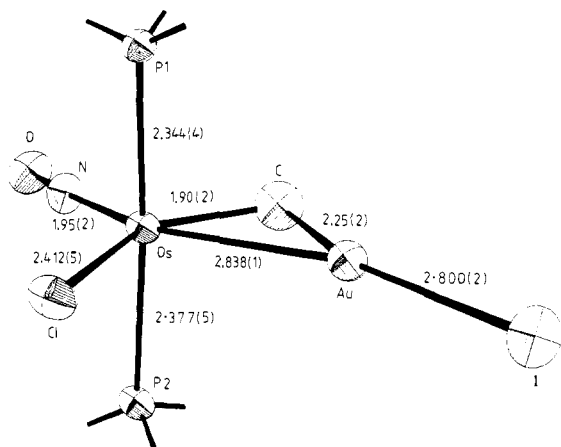


Figure 2. Inner coordination sphere of $\text{Os}(\text{CH}_2\text{AuI})\text{Cl}(\text{NO})(\text{PPh}_3)_2$. Interatomic angles: P1-Os-P2 , $173.9(2)^\circ$; C-Os-Au , $52.4(5)^\circ$; C-Os-N , $104.5(7)^\circ$; N-Os-Cl , $121.0(5)^\circ$; Cl-Os-Au , $82.1(1)^\circ$; Au-C-Os , $85.8(6)^\circ$; C-Au-Os , $41.8(4)^\circ$; Os-Au-I , $156.6(1)^\circ$; C-Au-I , $161.6(4)^\circ$.

gives $\text{Os}(\text{=CH}_2)\text{Cl}(\text{NO})(\text{PPh}_3)_2$, **I**. **I** forms orange crystals, mp $209\text{--}210^\circ\text{C}$, with good air stability. No interaction of **I** with triphenylphosphine or nitrogen bases such as pyridine is detectable. The structure of **I**¹⁴ is shown in Figure 1 and its reactions in Scheme I.¹¹

The geometry of **I** is very similar to $\text{Os}(\text{C-}p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$.¹⁵ Both molecules have large C-Os-Cl angles ($126.6(4)^\circ$ in **I**, 133° in the carbyne complex). The metal-carbon distance, $1.92(1)\text{ \AA}$, is comparable with that found in the osmium vinylidene complex.¹⁶ The methylene hydrogens lie perpendicular to the equatorial plane as expected.¹⁷

I reacts readily with a number of electrophilic reagents as detailed in Scheme I. In the rearrangement of **IV** to **VI** it is attractive to postulate the cationic methylene complex $[\text{Os}(\text{=CH}_2)\text{Cl}_2(\text{NO})(\text{PPh}_3)_2]^+$ as the reactive intermediate. This species, by analogy with $[\text{OsCl}_2(\text{NO})(\text{CO})(\text{PPh}_3)_2]^+$,¹² can be thought of as osmium(II) and hence, in this higher oxidation state complex, the electrophilic property of the carbene ligand returns, and phosphine is coordinated to form **VI**.

Reactions of **I** with sulfur, selenium, and tellurium are slow, giving examples of coordinated thioformaldehyde, selenoformaldehyde, and telluroformaldehyde (**VIII**).¹⁸ These reactions parallel those with the osmium-carbyne system¹⁴ and represent

(11) All complexes analyze satisfactorily for C, H, N. Geometries are assigned by X-ray for **I** and **IX** and by IR and NMR data. Spectral data for **I-XI** are as follows: $\nu(\text{NO})\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3 , 25°C) δ , $J(\text{H-P})\text{ Hz}$. **I**: 1628; 13.8 t, 19.2. **II**: 1805; 1.39 t, 5. **III**: 1815; 2.30 t, 5.6. **IV**: 1780; 3.88 t, 10.1. **V**: 1845; 4.90 t, 5. **VI**: 1815; 3.86 dd, 13, 7. **VII**: 1760; 4.72 dt, 8. **VIIIa**: 1728, 3.60 t, 1.5. **VIIIb**: 1735; 4.03 t, 2. **VIIIc**: 1740; 4.88 t, 3. **IX**: 1757; 8.87 t, 11. **X**: 1745; 10.45 dt, 12, 5. **XI**: 1630.

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(14) Crystal data and refinement results for $\text{Os}(\text{=CH}_2)\text{Cl}(\text{NO})(\text{PPh}_3)_2$: Orthorhombic; $a = 16.874(5)$, $b = 17.956(1)$, $c = 21.979(2)\text{ \AA}$; space group P_{cab} ; $Z = 8$. For $\text{Os}(\text{CH}_2\text{AuI})\text{Cl}(\text{NO})(\text{PPh}_3)_2$ (C_6H_6 solvate): triclinic; $a = 10.032(2)$, $b = 12.936(1)$, $c = 17.545(1)\text{ \AA}$; $\alpha = 103.480(6)^\circ$, $\beta = 96.73(1)^\circ$, $\gamma = 82.45(1)^\circ$; space group $P1$; $z = 2$. Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with monochromated $\text{Mo K}\alpha$ radiation. The structures were solved by conventional methods. Full-matrix least-squares refinement, with anisotropic thermal parameters assigned to all non-hydrogen atoms, has given $R = 0.032$ for 3255 observed reflections for **I** and a present R of 0.065 for 5640 observed reflections for **IX**. Details of the structure determinations will be published elsewhere.

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a new route to these little-studied ligands.

Likewise, PPh_3AuCl ¹⁹ reacts with **I** but adduct formation is readily reversible. However, the AuI (**IX**) and $[\text{AuPPh}_3]^+$ (**X**) adducts are stable compounds.

Figure 2 shows the structure of **IX**.¹⁴ The gold iodide fragment is indeed bridging the double bond but the interaction is weak. Remarkably little structural reorganization accompanies this adduct formation. The osmium-carbon bond length is $1.90(2)\text{ \AA}$, which does not differ significantly from the bond length in **I**, and the C-Os-Cl angle is increased by only 8° upon adduct formation.

We conclude that the reactivity of the linkage $\text{L}_n\text{M}=\text{CH}_2$ is strongly dependent on the oxidation state of the metal. Providing the metal center is sufficiently electron rich, even in 18-electron complexes of group 8 metals the carbene center may be nucleophilic.

The methylene ligand in **I** undergoes coupling reactions with carbon monoxide and isocyanides, and the nature of these products is under investigation.

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Registry No. **I**, 86645-81-0; **II**, 86645-82-1; **III**, 86645-83-2; **IV**, 86645-84-3; **V**, 86645-85-4; **VI**, 86668-00-0; **VII**, 86645-86-5; **VIIIa**, 86645-87-6; **VIIIb**, 86645-88-7; **VIIIc**, 86645-89-8; **IX**, 86668-01-1; **X**, 86668-02-2; **XI**, 86645-90-1; $\text{OsCl}(\text{NO})(\text{CO})(\text{PPh}_3)_2$, 22186-54-5; $\text{OsCl}(\text{CO}_3)(\text{NO})(\text{PPh}_3)_2$, 86645-91-2; HgCl_2 , 7487-94-7; HCl , 7647-01-0; Et_4NAuI_2 , 50481-02-2; PPh_3AuCl , 14243-64-2; CH_2N_2 , 334-88-3; **S**, 7704-34-9; **Se**, 7782-49-2; **Te**, 13494-80-9.

Supplementary Material Available: Listings of atomic coordinates and thermal parameters for **I** and **IX** (32 pages). Ordering information is given on any current masthead page.

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Macrolide Formation via an Isomerization Reaction. An Unusual Dependence on Nucleophile

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One of the major problems associated with the formation of macrolides has been the requirement of relatively high dilutions.^{1,2} We envisioned resolving this problem by use of an isomerization of vinyl epoxides³⁻⁵ such as **I** using polymerically bound transition-metal catalysts.^{4,6} Since neither the nucleophilic nor electrophilic centers are unmasked until the substrate encounters an active site on the polymer, this cyclization should be independent

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