\rightarrow Ru, 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

Acknowledgment. The financial support of the National Science Foundation through Grant CHE 80-09233 and the Robert A. Welch Foundation is greatly appreciated.

(22) Our investigations employing mononuclear group 6B pentacarbonyl hydride and formate derivatives as catalysts for HCO_2Me production from CO_2/H_2 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 $Ta(=CH_2)(CH_3)Cp_2$.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- $(=CH_2)(CH_3)Cp_2$ 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- $(NO)(PPh_3)_2$ (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 transitionmetal-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

(5) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. J. Am. Chem. Soc. 1980, 102, 1205. Riley, P. E.; Capshew, C. E.; Pettit, R.; Davis, R. E. Inorg. Chem. 1978, 17, 408. Stevens, A. E.; Beauchamp, J. L. J. Am. Chem. Soc. 1978, 100, 2584.

2.380(3) 1.93(1) 1.92(1) 2.40914 ٩s 2,387(3) 02

Figure 1. Inner coordination sphere of $Os(=CH_2)Cl(NO)(PPh_3)_2$ (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 $(L = PPh_3)^{11}$



coordination is much less common for osmium(0) than for iridium(I), and we find that diazomethane with OsCl(NO)(PPh₃)¹⁰

⁽¹⁾ Grubbs, R. H. Prog. Inorg. Chem. 1978, 24, 1. Turner, H. W.; Schrock, R. R. J. Am. Chem. Soc. 1982, 104, 2331. Sancho, J.; Schrock, R. R. J. Mol. Catal. 1982, 15, 75.

⁽²⁾ Schrock, R. R.; Sharp, P. R. J. Am. Chem. Soc. 1978, 100, 2389. Guggenberger, L. J.; Schrock, R. R. Ibid. 1975, 97, 6578.

⁽³⁾ Kegley, S. E.; Brookhart, M.; Husk, G. R. Organometallics 1982, 1,
(3) Kegley, S. E.; Brookhart, M.; Husk, G. R. Organometallics 1982, 1,
(4) Tam, W.; Lin, G.; Wong, W.; Kiel, W. A.; Wong, V. K.; Gladysz, J.
(4) A. Organometallics 1982, 1, 1204. Casey, C. P.; Andrews, M.
(4) Miltere D. P. Pier, L. F. J. L. C. Marchen, Soc. 1990, 102, 1021. A.; McAlister, D. R.; Rinz, J. E. J. Am. Chem. Soc. 1980, 102, 1927.

⁽⁶⁾ Schrock, R. R. Acc. Chem. Res. 1979, 12, 98.

⁽⁷⁾ Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. J. Am. Chem. Soc. 1980, 102, 7667.

⁽⁸⁾ Herrmann, W. A. Adv. Organomet. Chem. 1982, 20, 160.

⁽⁹⁾ Mango, F. D.; Dvoretzky, I. J. Am. Chem. Soc. **1966**, 88, 1654. (10) OsCl(NO)(CO)(PPh₃)₂ 12 (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(CO₃)(NO)(PPh₃)₂ (yield 810 presence yields a complex of solution of y $OSC(CO_3)(10)(11 \text{ H})^2$ (yield solution on the presence of $OSC(CO_3)(NO)(PPh_3)_2$ (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)(PPh_3)_3 form as the solution cools, and further material is obtained by addition of degassed *n* - solution cools, and further material is obtained by addition of degassed *n* - solution cools. because (yield 940 mg, 94%). OsCl(NO)(PPh₃)₃ (940 mg) is suspended in benzene (20 mL), and an ethereal solution of CH_2N_2 (20 mL)¹³ is added dropwise. Tan-colored crystals of Os(=CH₂)Cl(NO)(PPh₃)₂ separate as the reaction proceeds. Recrystallization from $CH_2Cl_2/EtOH$ yields orange crystals, 590 mg, 82%.



Figure 2. Inner coordination sphere of Os(CH₂AuI)Cl(NO)(PPh₃)₂. Interatomic angles: P1-Os-P2, 173.9 (2)°; C-Os-Au, 52.4 (5)°; C-Os-N, 104.5 (7)°; N-Os-Cl, 121.0 (5)°; Cl-Os-Au, 82.1 (1)°; Au-C-Os, 85.8 (6)°; C-Au-Os, 41.8 (4)°; Os-Au-I, 156.6 (1)°; C-Au-I, 161.6 $(4)^{\circ}$.

gives Os(=CH₂)Cl(NO)(PPh₃)₂, I. I forms orange crystals, mp 209-210 °C, with good air stability. No interaction of I with triphenylphosphine or nitrogen bases such as pyridine is detectable. The structure of I¹⁴ is shown in Figure 1 and its reactions in Scheme I.¹¹

The geometry of I is very similar to Os(C-p-tolyl)Cl(CO)- $(PPh_3)_2$ ¹⁵ Both molecules have large C-Os-Cl angles (126.6 (4)° in I, 133° in the carbyne complex). The metal-carbon distance, 1.92 (1) Å, 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 [Os- $(=CH_2)Cl_2(NO)(PPh_3)_2]^+$ as the reactive intermediate. This species, by analogy with $[OsCl_2(NO)(CO)(PPh_3)_2]^+$,¹² can be thought of as osmium(II) and hence, in this higher oxidation state complex, the electrophilic propety 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

(12) Wilson, R. D.; Ibers, J. A. Inorg, Chem. 1979, 18, 336. Laing, K.
 (12) Wilson, R. D.; Ibers, J. A. Inorg, Chem. 1979, 18, 336. Laing, K.
 R.; Roper, W. R. Chem. Commun. 1968, 1556.
 (13) de Boer, Th. J.; Backer, H. J. "Organic Syntheses; Wiley: New York, 1963; Collect. Vol. IV, p 250.

(14) Crystal data and refinement results for Os(=CH₂)Cl(NO)(PPh₁)₂: Orthorhombic; a = 16.874 (5), b = 17.956 (1), c = 21.979 (2) Å; space group

 $P_{cab}; Z = 8$. For $Os(CH_2AuI)Cl(NO)(PPh_3)_2$ (C₆H₆ solvate): triclinic; a = 10.032 (2), b = 12.936 (1), c = 17.545 (1) Å; $\alpha = 103.480$ (6)°, $\beta = 96.73$ (1)°, $\gamma = 82.45$ (1)°; space group $P_1; z = 2$. Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with monochromated Mo K α 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

(15) Clark, G. R.; Marsden, K.; Roper, W. R.; Wright, L. J. J. Am. Chem. Soc. 1980, 102, 6570.

(16) Roper, W. R.; Waters, J. M.; Wright, L. J.; van Meurs, F. J. Organomet. Chem. 1980, 201, C27.

(17) Albright, T. A. Tetrahedron 1982, 38, 1339.

(18) A related series of chalcoformaldehyde complexes, $Os(\eta^2-CH_2X)$ - $(CO)_2(PPh_3)_2$ (X = O, S, Se, Te), has recently been reported. Headford, C. E. L.; Roper, W. R. J. Organomet. Chem. 1983, 244, C53.

a new route to these little-studied ligands.

Likewise, PPh₃AuCl¹⁹ reacts with I but adduct formation is readily reversible. However, the AuI (IX) and $[AuPPh_3]^+$ (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) Å, 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 $L_n M = CH_2$ 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.

Acknowledgment. We thank the N.Z. Universities Grants Committee for the award of a Postgraduate Scholorship to A.H.W. and for grants toward equipment and Johnson Matthey Ltd. for a generous loan of osmium tetroxide.

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; OsCl(NO)(CO)(PPh₃)₂, 22186-54-5; OsCl(CO₃)(NO)(PPh₃)₂, 86645-91-2; HgCl₂, 7487-94-7; HCl, 7647-01-0; Et₄NAuI₂, 50481-02-2; PPh₃AuCl, 14243-64-2; CH₂N₂, 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.

(19) Clark, G. R.; Cochrane, C. M.; Roper, W. R.; Wright, L. J. J. Organomet. Chem. 1980, 199, C35.

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 1 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

(1) Galli, C.; Mandolini, L. J. Chem. Soc., Chem. Commun. 1982, 251. Nicolaou, K. C. Tetrahedron 1977, 33, 683. Masamune, S.; Bates, G. S.; Corcoran, J. W. Angew. Chem., Int. Ed. Engl. 1977, 16, 585. Back, T. G. Tetrahedron 1977, 33, 3041. Newkome, G. R.; Sauer, J. D.; Roper, J. M.; Hager, D. C. Chem. Rev. 1977, 77, 513.

(5) Takahashi, T.; Kataoka, H.; Tsuji, J. J. Am. Chem. Soc. 1983, 105, 147

(6) For polystyrene-supported palladium catalysts see: Trost, B. M.; Keinan, E. J. Am. Chem. Soc. 1978, 100, 7779. Pittman, C. U., Jr.; Ng, Q. J. Organomet. Chem. 1978, 153, 85. Terasawa, M.; Kaneda, K.; Imanaka, T.; Teranishi, S. Ibid. 1978, 162, 403.

⁽¹¹⁾ All complexes analyze satisfactorily for C, H, N. Geometries are (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: $\nu(NO) \text{ cm}^{-1}$; ¹H NMR (CDCl₃, 25 °C) δ , J(H-P) 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.

⁽²⁾ Also see: Regen, S. L.; Kumura, Y. J. Am. Chem. Soc. 1982, 104, 2064. These authors report substrate concentrations of <0.003 M.

⁽³⁾ For neutral alkylations with vinyl epoxides see: Trost, B. M.; Molander, G. A. J. Am. Chem. Soc. 1981, 103, 5969. Tsuji, J.; Kataoka, H.; Kobayashi, Y. Tetrahedron Lett. 1981, 22, 2575.
(4) Trost, B. M.; Warner, R. W. J. Am. Chem. Soc. 1982, 104, 6112.