

Interconversion of Methylene and Ketene Ligands on a Triosmium Cluster. Crystal and Molecular Structure of the Ketene Complex $\text{Os}_3(\text{CO})_{12}(\eta^2(\text{C},\text{C}),\mu\text{-CH}_2\text{CO})$

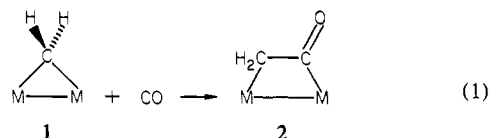
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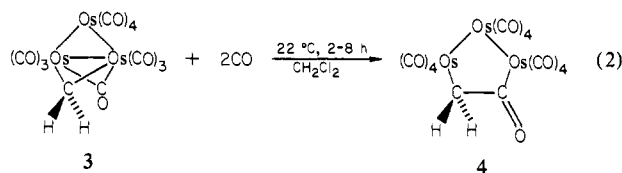
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A relatively large number of methylene-bridged transition-metal compounds (**1**) have now been prepared and characterized, and their chemistry is under active exploration.² However, one important reaction that has not been well documented for this class of compounds is the insertion of CO into a metal-methylene bond to yield a coordinated ketene, e.g., eq 1.³⁻⁵ Such reactions may



be of relevance to the mechanism of chain growth during CO reduction over heterogeneous catalysts where surface-bound methylene ligands are believed important.⁶ Also obvious is the probable stabilization of the reactive ketene moiety in **2** by simultaneous coordination to two metals, a feature that could allow the use of such complexes in synthetic chemistry. We describe herein an example of the transformation of eq 1 that involves the interconversion of methylene and ketene ligands on a triosmium cluster, including the first structural details of a complex of an unsubstituted ketene ligand.

$\text{Os}_3(\text{CO})_{11}(\mu\text{-CH}_2)$, **3**,⁷ was previously found to lose CO upon heating ($\sim 80^\circ\text{C}$) to yield $\text{Os}_3\text{H}_2(\text{CO})_9(\mu_3\text{-CCO})$.⁸ We have since found that **3** readily adds two CO's to yield the new ketene derivative $\text{Os}_3(\text{CO})_{12}(\eta^2(\text{C},\text{C}),\mu\text{-CH}_2\text{CO})$ (**4**, eq 2). This species



has been spectroscopically⁹ and structurally characterized,¹⁰ see

(1) (a) The Pennsylvania State University. (b) The University of Delaware.

(2) For a recent review see: Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 160.

(3) The conversion of mononuclear alkylidene complexes to ketene derivatives via reaction with CO has been demonstrated in two instances: Herrmann, W. A.; Plank, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 525. Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 7789.

(4) The first stable ketene complex, $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_2\text{O})]_n$, prepared from the reaction of a titanium- η^2 -acetyl complex with CH_2PPh_3 , was recently described: Strauss, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499.

(5) (a) Such a binuclear transformation was suggested in the reaction of $\text{Fe}_2(\text{CO})_8(\mu\text{-CH}_2)$ with CO in the presence of alcohols, but the ketene intermediate was not isolated nor fully characterized: Roper, M.; Strutz, H.; Keim, W. *J. Organomet. Chem.* **1981**, 219. (b) After this paper was submitted a binuclear Ru_2 ketene complex was described: Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679.

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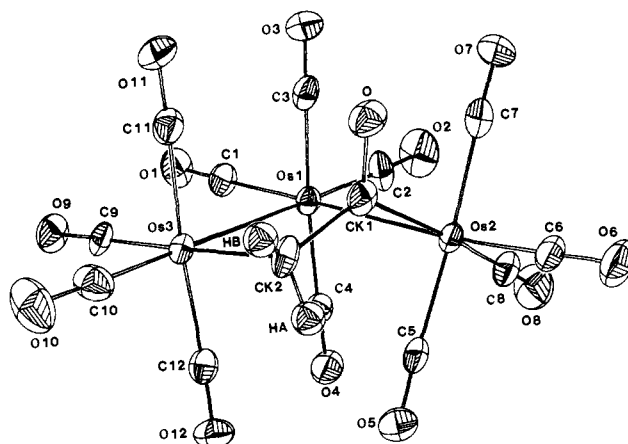


Figure 1. ORTEP drawing of the molecular structure of $\text{Os}_3(\text{CO})_{12}(\eta^2(\text{C},\text{C}),\mu\text{-CH}_2\text{CO})$. Relevant bond distances (\AA) and angles ($^\circ$) are as follows: Os1-Os3, 3.011 (1); Os1-Os2, 2.939 (1); Os2-CK1, 2.162 (10); CK1-O, 1.256 (11); CK1-CK2, 1.470 (14); CK2-Os3, 2.218 (9); Os2-Os3, 4.259 (2); Os3-Os1-Os2, 91.4 (1); Os1-Os2-CK1, 80.1 (2); Os2-CK1-O, 120.6 (7); Os2-CK1-CK2, 121.4 (6); O-CK1-CK2, 117.9 (9); CK1-CK2-Os3 112.2 (6); CK2-Os3-Os1, 89.6 (3).

below, but it is not particularly stable and slowly decomposes to yield $\text{Os}_3(\text{CO})_{12}$. Thus, when a red CH_2Cl_2 solution of **3** is exposed to CO, the color changes to the yellow color of **4** over 2-8-h period and a precipitate of $\text{Os}_3(\text{CO})_{12}$ gradually forms. The yield of $\text{Os}_3(\text{CO})_{12}$ increases with reaction time, eventually reaching $\sim 100\%$ after ~ 8 days. Solid samples of **4** can be obtained in 16-20% yields by removing the CO atmosphere when IR monitoring indicates complete consumption of **3**, filtering to remove the precipitated $\text{Os}_3(\text{CO})_{12}$, and then evaporating the solvent. However, such samples are usually contaminated with small amounts of $\text{Os}_3(\text{CO})_{12}$, but recrystallization from CH_2Cl_2 /cyclohexane at $+4^\circ\text{C}$ gave crystals suitable for an X-ray diffraction study.

An ORTEP drawing of the molecular structure of **4** is shown in Figure 1. The ketene ligand bridges between two nonbonded Os atoms ($\text{Os}\cdots\text{Os} = 4.259(2) \text{\AA}$) with a carbon bound to each and with each Os coordinated by four terminal CO's. The structural parameters (Figure 1) imply the hybridization of the two carbons of the ketene ligand to be essentially sp^3 (CH_2) and sp^2 (CO), and the molecule is best viewed as a trimetallacyclopentanone derivative. The spectroscopic properties⁹ of the ketene carbonyl is in the region typical of metal acyls. The ^{13}C resonance for this carbon ($\delta 219.5$) is only slightly upfield of the normal metal acyl range ($\delta 240\text{-}350$).¹¹ The ketene CH_2 ^{13}C resonance ($\delta 32.8$) falls within the usual range for sp^3 hybridized methylene carbons adjacent to carbonyls ($\delta 27\text{-}46$).¹² Likewise the ^1H resonance for the methylene hydrogens ($\delta 2.77$ (br s)) is in the typical sp^3 CH_2 range. The single resonance observed for the methylene

(9) **4**: IR (CH_2Cl_2) νCO 2107 s, 2071 s, 2054 sh, 2046 s, 2020 m, $\{1573 \text{ m (KBr)}\} \text{cm}^{-1}$; m/e (EI) 948 (M^+ , ^{190}Os), 906 ($\text{M}^+ - \text{CH}_2\text{CO}$), and fragment ions corresponding to successive loss of the 12 CO ligands; ^1H NMR (CD_2Cl_2) δ 2.77 (br s); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 219.4, 181.2, 180.0, 178.3, 170.0, 169.8, 169.5, 169.0, 165.0, 164.8, 32.8; ^{13}C NMR δ 32.8 (t, $J_{\text{C-H}} = 136 \text{ Hz}$).

(10) **4** crystallizes in the space group $P2_1/n$ with $a = 9.414(2) \text{\AA}$, $b = 15.369(3) \text{\AA}$, $c = 13.940(4) \text{\AA}$, $\beta = 107.9(2)^\circ$, $V = 1918.6(7) \text{\AA}^3$, and $Z = 4$. The intensities of 3331 unique reflections were collected by using an automated diffractometer. Of these, 3015 had $I_o > \sigma(I_o^2)$ and were included in the refinement of the structure. Least-squares refinement of the complete structure converged with $R = 0.033$ and $R_w = 0.034$. The hydrogen atoms were calculated by using a riding model ($d(\text{C-H}) = 0.96 \text{\AA}$, $U = 1.2U$ for attached carbon). No significant peaks were observed on the final difference map (highest peak = 0.883 e \AA^{-3}).

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(13) CH_3COOH was identified by its IR spectrum and titration with NaOH; $\text{CH}_3\text{CO}_2\text{CH}_3$ was identified by a combination of IR and ^1H NMR spectroscopy and by its gas chromatography retention time.

protons implies that the puckered Os_3C_2 ring must be quite flexible since these two hydrogens are clearly nonequivalent in the solid-state structure.

Interestingly, the ketene moiety of the trimetallacyclopentanone ring retains ketene-like reactivity with nucleophiles. For example, **4** reacts rapidly with both H_2O and CH_3OH to yield $\text{CH}_3\text{CO}_2\text{H}$ and $\text{CH}_3\text{CO}_2\text{CH}_3$, respectively, along with $\text{Os}_3(\text{CO})_{12}$.¹³ These reactions are most easily conducted by forming $\text{Os}_3(\text{CO})_{12}(\eta^2\text{-}(\text{C},\text{C})\mu\text{-CH}_2\text{CO})$ in situ. Thus, $\text{Os}_3(\text{CO})_{11}(\mu\text{-CH}_2)$ does not react with H_2O (nor CH_3OH), but when placed in THF solution with ~ 10 equiv of H_2O under a CO atmosphere, it is completely consumed within ~ 12 h to give $\text{Os}_3(\text{CO})_{12}$ and acetic acid in quantitative yield, the latter determined by subsequent titration with standardized NaOH. Such reaction with traces of water, and probably with other nucleophiles as well, likely accounts for the slow solution decomposition of **4** noted above.

A labeling experiment shows that the ketene carbonyl derives from one of the initial $\text{Os}_3(\text{CO})_{11}(\mu\text{-CH}_2)$ carbonyl ligands and not from the added CO. When a sample of $\text{Os}_3(\text{CO})_{11}(\mu\text{-CH}_2)$ that was 25% ^{13}C enriched in all carbons (prepared from 25% ^{13}C -enriched $\text{Os}_3(\text{CO})_{12}$ ^{7a}) was allowed to react with 90% ^{13}C -enriched CO in methanol solution, the ^{13}C NMR spectrum of the methyl acetate produced showed the acetate methyl and carbonyl resonances to be of equal intensity. Thus both of these carbons must come from the initial $\text{Os}_3(\text{CO})_{11}(\mu\text{-CH}_2)$, which in turn implies a preequilibrium between $\text{Os}_3(\text{CO})_{11}(\mu\text{-CH}_2)$ and a coordinatively unsaturated ketene complex that subsequently adds two CO's to give **4**.

Formation of the ketene complex **4** from the methylene complex **3** is reversible, although the instability of **4** precludes quantitative recovery of **3**. Thus, when a CDCl_3 solution of **4** is heated to 60–64 °C for 30 min under reduced pressure, the methylene proton resonances of **3** appear and grow in to $\sim 10\%$ of their expected intensity on the basis of the amount of **4** consumed. This observation is in accord with Arce and Deeming's^{7c} recent preparation of **3** from the reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ with ketene, a synthesis that perhaps proceeds through the intermediacy of **4**, although this species was not detected in their reaction.

The ease with which the bridging methylene complex **3** reacts with CO to form the new carbon-carbon bond in the ketene complex **4** suggests that such a reaction may be important in the formation of carbon-carbon bonds on metal surfaces during heterogeneous catalysis of CO reduction. Further explorations of the chemistry of **4** and other insertion reactions of **3** are in progress.

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Supplementary Material Available: Tables of positional and thermal parameters, bond lengths, bond angles, and structure factors for **4** (21 pages). Ordering information is given on any current masthead page.

Studies Concerning the Mechanism of Electrophilic Substitution Reactions of Mitomycin C

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Mitomycin C (**1**) has found widespread use for the treatment of various neoplasms.² Suggestions have been made that **1**

functions as a bioreductive alkylating agent.³ Recently Moore outlined a detailed mechanism for the cross-linking of DNA by **1**^{3d} (Scheme I). Intermediate **3** has been advanced as the biologically active form of **1** that leads to difunctional binding of the genetic material. Evidence in favor of this scenario has been presented by Tomasz and Lipman.⁴ These investigators demonstrated that treatment of **1** under reductive conditions (catalytic and enzymatic) near neutral pH in the absence of strong nucleophiles led to the formation of 2,7-diaminomitosene (**6a**) along with other mitomycin-based products. Compound **6a** has been proposed to arise from **3** through an internal reduction-oxidation process⁴ (Scheme II).

In this communication, we report direct evidence for the origin of **6a**. The stereochemical features of this substitution reaction are also addressed. A similar issue corresponding to nucleophilic substitution at carbon 1 has been the subject of intensive investigation.⁵⁻¹²

Two likely mechanisms exist for the formation of **6a**, and these are outlined as follows (Scheme II): (1) pathway *a* is that proposed by Tomasz and Lipman⁴ and involves tautomerization of the quinone methide **3**; (2) pathway *b* would proceed by direct reduction of the aziridine moiety in **2** followed by reoxidation of this species during workup. Such a pathway is preceded since aziridines readily undergo hydrogenolysis under mild conditions to give acyclic amines.¹³ Moreover, in 2-phenylaziridines cleavage occurs selectively between the nitrogen and the phenyl-substituted carbon atom.¹⁴

To test the viability of the second pathway, compound **1** was treated with PtO_2 and D_2 gas under conditions (Na_2HPO_4 , H_2O , pH 5.1) identical with those previously described.⁴ Isolation of **6a** by liquid chromatography gave a product whose spectral properties showed no deuterium incorporation at carbon 1. This result excludes the direct reduction pathway *b* for the formation of **6a**.

Information in support of the first mechanism and the stereochemical mode of proton addition at carbon 1 was attained by conducting the experiment with PtO_2 and H_2 gas in $\text{Na}_2\text{DP-O}_4\text{-D}_2\text{O}$ (pD 5.1¹⁵). Under these conditions, the extent of

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