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Conversion of the μ-Ketene Ligand in $[PPN][Os_3(CO)_{10}(\mu\text{-}I)(\mu\text{-}CH_2CO)]$ into Enolate, Acyl, and Vinyl Ligands

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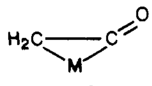
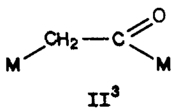
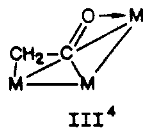
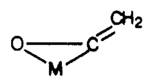
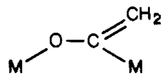
Free ketene is a valuable organic synthetic reagent, but its utility is somewhat limited by its high reactivity and tendency to dimerize to yield diketene.[1] The ketene *ligand* is obviously stabilized by metal coordination in a variety of bonding modes, I–VI,[2-6] but it is not yet known how coordination influences the chemistry of this important molecule. We have studied the reactivity of the coordinated ketene ligand of type II found in the anionic cluster compound $[PPN][Os_3(CO)_{10}(\mu\text{-}I)(\mu\text{-}CH_2CO)]$ (**1**) ($PPN^+ = (Ph_3P)_2N^+$)[3b] and herein show that this ligand is readily converted into η^1-enolate ligands upon reaction with simple nucleophiles and into vinyl and acetyl ligands upon reaction with electrophiles.

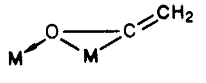

I[2]


II[3]

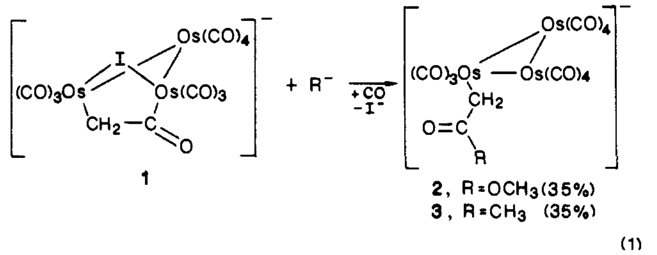

III[4]


IV[5a-c]


V[5c]


VI[5a,d]

Cluster **1** slowly reacts with CH_3OH solvent (22 °C, 4 h) to form the cluster enolate **2**,[7] eq 1. In this reaction a CO ligand is added and the iodide is lost, presumably as HI.[8] The same product **2** also rapidly forms when **1** is allowed to react with $NaOCH_3$ in CH_3OH/CH_2Cl_2 solution. Cluster **2** has been spectroscopically[7] as well as structurally characterized, Figure 1.[9] The latter shows the η^1-enolate ligand to occupy an equatorial position on a single Os atom. However, the equatorial plane of Os(2) is disordered about an approximate mirror plane containing the axial CO's 5 and 7, C(14), and the midpoint of the Os(1)–Os(3) bond. Thus the methylene carbon of the $CH_2C(O)OCH_3$ ligand, C(12), and the carbon of the carbonyl group, C(6), are superimposed as are the terminal CH_3 groups, C(14), of the two acetate orientations.



1

2, R = OCH_3 (35%)
3, R = CH_3 (35%)

(1)

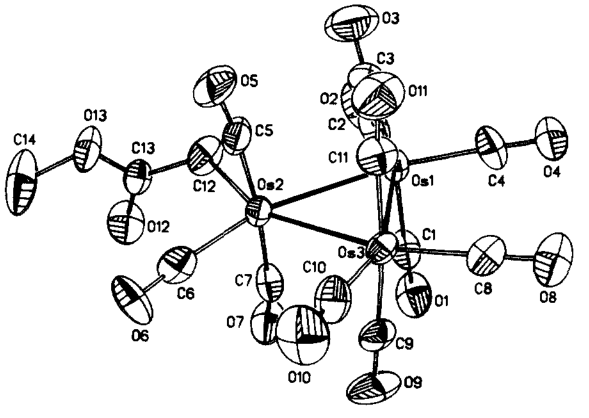


Figure 1. ORTEP drawing of $[PPN][Os_3(CO)_{11}(CH_2C\{O\}OCH_3)]$ (**2**). Thermal ellipsoids are drawn at the 40% probability level. The major orientation (72%) of the disordered $CH_2C(O)OCH_3$ and C(6)–O(6) groups is shown.[9] Important bond lengths (Å) and angles (deg): Os(1)–Os(2), 2.895 (1); Os(1)–Os(3), 2.905 (1); Os(2)–Os(3), 2.880 (1); Os(2)–C(12), 2.145 (13); Os(2)–C(6), 1.947 (16); O(13)–C(13), 1.367 (26); O(12)–C(13), 1.222 (21); O(13)–C(14), 1.449 (19); C(12)–C(13), 1.437 (19); Os(1)–Os(2)–Os(3), 60.4 (1); Os(1)–Os(2)–C(12), 97.4 (4); C(6)–Os(2)–C(12), 97.9 (5); Os(2)–C(12)–C(13), 114.4 (12); C(13)–O(13)–C(14), 113.9 (13); O(12)–C(13)–O(13), 121.2 (16); O(12)–C(13)–C(12), 123.2 (18); O(13)–C(13)–C(12), 114.7 (13).

Clusters with η^1-alkyl ligands of any type are surprisingly rare,[10,11] and **2** is only the second to be structurally characterized.[10] The alkyl ligand in **2** is formally the enolate of methyl acetate, and this formalism is reflected in its spectroscopic data. The ester ν(CO) stretch at 1684 cm^{-1} is 51 cm^{-1} lower in energy than that of free methyl acetate at 1735 cm^{-1}, implying significant delocalization of electron density onto the ligand carbonyl.[12] The δ 2.31 ^{1}H NMR resonance for the methylene protons is in the range found for mononuclear metal enolates[13] but downfield from the normal metal alkyl region (δ −1.0 → 0.5).

A similar reaction of **1** occurs with CH_3Li in THF solution to yield the cluster enolate of acetone **3**,[14] eq 1. The terminal carbonyl region IR spectrum of **3** is similar to that of structurally characterized **2**, and the ketonic ν(CO) stretch of **3** at 1676 cm^{-1} lies 34 cm^{-1} lower in energy than that of free acetone at 1713 cm^{-1}, consistent with the enolate formalism.

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(6) A number of compounds containing substituted ketene ligands (e.g., $Ph_2C{=}C{=}O$) are also known with structures similar to I–V. For example, see: Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Weidenhammer, K. *J. Am. Chem. Soc.* **1979**, *101*, 3133.

(7) **2**: IR (CH_2Cl_2) 2070 (w), 2029 (m), 2012 (m), 1993 (vs), 1964 (w), 1684 (w br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 2 H, CH_2), 3.61 (s, 3 H, OCH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ −20.66 (s, 1 C, CH_2), 50.07 (s, 1 C, OCH_3), 184.76 (s, C=O), 185.57 (br, M–CO). Anal. Calcd for $C_{50}H_{35}NO_{13}Os_3P_2$: C, 40.30; H, 2.35. Found: C, 39.57; H, 2.20.

(8) Since cluster **1** rapidly loses CO to form $[PPN][Os_3(CO)_{10}(\mu\text{-}I)(\mu\text{-}CH_2)]$, all reactions of **1** were carried out under 1 atm of CO.[3b]

(9) $P2_1/c$, a = 19.875 (4) Å, b = 15.056 (4) Å, c = 19.118 (6) Å, β = 115.27 (2)°, V = 5173.4 (4) Å^3, Z = 4, R_F = 0.042, R_{wF} = 0.051 for 4982 reflections with $F_0 \geq 4\sigma(F_0)$. Atoms C(12), C(6), and C(14) were refined at full occupancy. Atoms O(6), O(12), O(13), and C(13) were paired with their primed counterparts and their occupancies were collectively refined with the sum of the primed and unprimed sets constrained to unit occupancy. The unprimed set occupancy is 72 (1)%.

(10) Zuffa, J. L.; Gladfelter, W. L. *J. Am. Chem. Soc.*, in press. Gladfelter, W. L., private communication.

(11) Morrison, E. D.; Bassner, S. L.; Geoffroy, G. L. *Organometallics* **1986**, *5*, 408.

(12) Free Li^+ enolates generally show ν(CO) bands in the 1550–1600-cm^{-1} region; see: Jackman, L. M.; Large, B. C. *Tetrahedron* **1977**, *33*, 2737.

(13) Doney, J. J.; Bergman, R. G.; Heathcock, C. H., *J. Am. Chem. Soc.* **1985**, *107*, 3724.

(14) **3**: IR (CH_2Cl_2) 2068 (w), 2029 (m), 2014 (m), 1995 (s), 1821 (w br), 1676 (w br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.53 (2 H, CH_2), 2.27 (3 H, CH_3).

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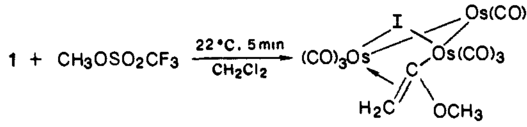
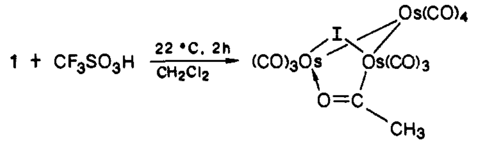
Reaction of **1** with *electrophiles* follows a different course. Addition of $CH_3OSO_2CF_3$ to **1** gives alkylation of the ketene carbonyl oxygen to form the σ,π-vinyl cluster **4**,[15] eq 2. An X-ray diffraction study on a disordered crystal of **4** showed the assigned structure to be correct, but a satisfactory refinement was not obtained.[16] The ^1H NMR spectrum of **4** shows the expected methoxy and methylene protons at δ 3.85 (s, 3 H) and δ 5.10 (d, 1 H, J_{HH} = 4.92 Hz), 5.06 (d, 1 H), respectively. The −80 °C ^{13}C NMR spectrum of **4** shows separate resonances attributed to the 10 inequivalent carbonyl ligands in the assigned structure, but upon warming, these broaden, coalesce, and then sharpen into six resonances at 25 °C. We attribute this to a fluxional process in which the σ,π-vinyl ligand exchanges between the front two osmium atoms in a "windshield wiper" motion similar to that seen in other σ,π-vinyl compounds.[17]



4 (70%)

(2)

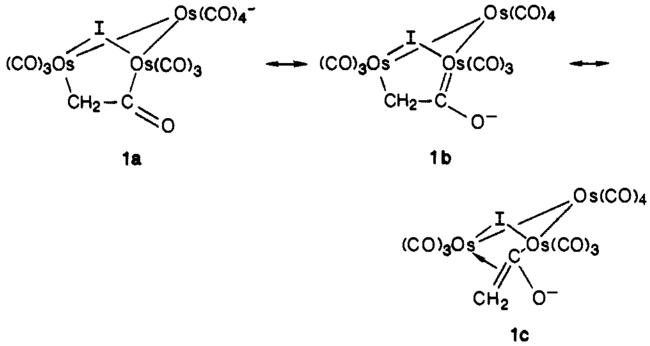
Addition of acid to **1** converts the ketene ligand into a μ-acetyl ligand in the known cluster **5**,[11,18] eq 3. This reaction proceeds through the formation of an intermediate species, indicated by the immediate dark to light-orange color change followed by slow formation of the yellow color of **5**. The intermediate has an IR spectrum[19] similar to that of the σ,π-vinyl cluster **4**, and we suggest a similar structure in which protonation initially occurs on the ketene oxygen to give a hydroxyvinyl ligand which subsequently tautomerizes to the acetyl form in **5**.



5 (72%)

(3)

The reactions of **1** with the *nucleophiles* CH_3^- and CH_3O^- to give the cluster enolates **2** and **3** are similar to established reactions of nucleophiles with free ketenes,[1] organic carbonyls,[20] and metal acyl complexes.[21] The reactions of **1** with the *electrophiles* H^+ and CH_3^+ imply that important contributing resonance forms for **1** are the oxycarbene (**1b**) and oxyvinyl (**1c**) structures drawn below. Oxycarbene resonance forms are known to be important for anionic metal acyl complexes and contribute to the ease with which these are alkylated at the carbonyl oxygen to yield metal carbenes.[21] Oxyvinyl structures such as **1c** have not been previously considered. The facile alkylation and apparent protonation of the ketene oxygen in the **1** → **5** and **1** → **6** transformations indicate the importance of resonance forms **1b**/**1c** as does the unusually low ketene ν(CO) band of **1** at 1551 cm^{-1}.[3b]



These and other studies[2-5] indicate that coordinated ketene ligands have a rich derivative chemistry and may prove to be of synthetic utility if it can be shown that coordinated ketene ligands undergo organic reactions different from those of free ketene. Our further studies in this area will emphasize the reactions of **1** and related type II ketene complexes with more sophisticated organic nucleophiles and electrophiles so as to begin to define the synthetic utility of these ligands.

Acknowledgment. We thank the Department of Energy, Office of Basic Energy Sciences, for support of this research and the National Science Foundation for contributing funds toward the purchase of the X-ray diffractometer at the University of Delaware.

Supplementary Material Available: Tables of atomic positional parameters, bond lengths and angles, anisotropic temperature factors, and hydrogen coordinates for **2**; crystallographic details and an ORTEP drawing of molecule A of **4** (8 pages). Ordering information is given on any current masthead page.

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[15] **4**: IR (pentane) 2105 (w), 2068 (s), 2054 (m), 2020 (s), 2014 (sh), 2001 (sh), 1995 (m), 1979 (w) cm^{-1}; MS (EI) (^{190}Os), *m/z* 1034 M^+, plus fragments corresponding to loss of 10 CO's and CH_3; ^{13}C NMR ($CDCl_3$, 22 °C) (22 °C) δ 199.4 (s, 1 C, *C*(OCH_3)CH_2), 179.0 (s 2 C, CO), 178.4 (s, 1 C, CO), 178.3 (s, 1 C, CO), 175.0 (s, 2 C, CO), 174.4 (s, 2 C, CO), 164.6 (s, 2 C, CO), 35.9 (t, C(OCH_3)CH_2, J_{CH} = 153 Hz); (CD_2Cl_2, −80 °C, metal carbonyls) δ 179.5, 179.1, 178.6, 178.2, 176.2, 175.2, 174.8, 173.9, 164.8, 164.7. Anal. Calcd for $C_{13}H_5O_{11}IOs_3{\cdot}C_5H_{12}$: C, 19.53; H, 1.54. Found: C, 19.30; H, 1.58.

[16] See supplementary material.

[17] (a) Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *94*, C43. (b) Lee, K. W.; Brown, T. L. *Organometallics* **1985**, *4*, 1030 and references cited therein. (c) Mlekuz, M.; Bougeard, P.; Sayer, B. G.; Peng, S.; McGlinchey, M. J.; Marinetti, A.; Saillard, J.; Naceur, J. B.; Mentzeen, B.; Jaouen, G. *Organometallics* **1985**, *4*, 1123 and references cited therein. (d) Aime, S.; Gobetto, R.; Osella, D.; Milone, L.; Rosenberg, E.; Anslyn, E. V. *Inorg. Chim. Acta* **1986**, *111*, 95.

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[19] ν(CO) (CH_2Cl_2): 2114 (w), 2105 (w), 2064 (vs), 2055 (sh), 2029 (sh), 2018 (s), 1999 (sh) cm^{-1}.

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Transfer of Perfluoroalkyl Groups between Metals: Preparation of the Anionic Perfluoroalkyl Metal Complex $Ag[CF(CF_3)_2]_2^-$

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Despite the large number of transition-metal organofluorine compounds and the importance of fluorocarbons as specialty chemicals, little is known about the fundamental chemical reactivity of metal-bonded fluorocarbons.[1] We have initiated a systematic exploration of the reaction chemistry of metal-bonded fluorocarbons. We quickly discovered an exception to the common belief that transition-metal-mediated transformations of fluorocarbons are prevented by the low lability of metal-bonded perfluoroalkyl groups. The silver perfluoroalkyl $(CF_3)_2CFAg(CH_3CN)$ is heterolytically labile, existing in dynamic equilibrium in solution with solvated Ag^+ and the new anionic perfluoroalkyl metal complex $Ag[CF(CF_3)_2]_2^-$. Equilibrium 1 demonstrates the facile transfer of perfluoroalkyl groups between metals in solution and provides a synthetic route to the first isolable anionic perfluoroalkyl metal complex.

$$2(CF_3)_2CFAg(CH_3CN) \overset{K_{eq}}{\rightleftharpoons} Ag^+ + Ag[CF(CF_3)_2]_2^- \quad (1)$$

The perfluoroalkyl complex $(CF_3)_2CFAg(CH_3CN)$ is prepared by reaction of AgF with $CF_3CF{=}CF_2$ in acetonitrile.[2] The ^{19}F

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