AM500 spectrometer operating at 500, 76.75, and 125.72 MHz, respectively. The (indenyl)Rh(diene) complexes (~100 mg) were dissolved in CD_2Cl_2, and the solutions were filtered, degassed, and cooled to −80 °C at which temperature several drops of trifluoroacetic acid were added. The initially yellow solutions became dark amber or red on protonation. To obtain the ^2H NMR spectra, the solvent used was CH_2Cl_2.

Bis(ethylene)(η^5-indenyl)rhodium(I) (**7a**) was synthesized by using the method described by Green et al.[8] Protonation of **7a** was followed by ^1H and ^{13}C NMR spectroscopy which showed the formation of bis(ethylene)(η^6-indene)rhodium(I) trifluoroacetate and, subsequently, of indene itself. The ^1H and ^{13}C NMR data are collected in Table I. Protonation of bis(ethylene)(η^5-1-methylindenyl)rhodium(I) (**7b**), prepared as described elsewhere,[12] yielded as the major product 1-methylindene which exhibited ^1H NMR peaks (in trifluoroacetic acid solution) at δ 7.50 (d, 7.4 Hz) [H-4], 7.39 (d, 7.4 Hz) [H-7], 7.35 (t, 7.4 Hz) [H-6], 7.24 (t, 7.4 Hz) [H-5], 6.27 (m) [H-2], 3.37 (d, 1.3 Hz) [H-3], and 2.12 (d, 1.3 Hz) [Me]; weaker resonances at δ 7.56 (d) [H-4], 7.32 (d) [H-7], 7.11 (t) [H-6], 7.05 (t) [H-5], 6.70 (d) [H-2], 3.43 (d) [H-3], 2.98 (d) [H-3′], and 2.10 (s) [Me] can be attributed to the η^6-complex **8b**. At −90 °C, the ratio of complex to free methylindene was

higher, but there was no evidence of a metal hydride intermediate.

(1,2:5,6-η^4-Cyclooctatetraene)(η^5-indenyl)rhodium(I) (**15**), synthesized as described previously,[8] was protonated at −80 °C, and the NMR spectra were recorded over the temperature range −80 to +30 °C. At no stage was there a peak observable at low frequency (high field) attributable to a rhodium–hydride intermediate. The ^1H and ^{13}C NMR data are collected in Table II.

Electrophile- and Nucleophile-Induced Transformations of μ-Ketene Ligands on Triosmium Clusters

Sherri L. Bassner, Eric D. Morrison, and Gregory L. Geoffroy*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802
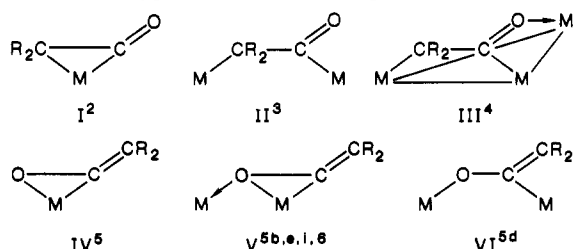
Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, Delaware 19716

The reaction of [PPN][$Os_3(CO)_{10}$(μ-I)(μ-CH_2CO)] (**2**, PPN = ($Ph_3P)_2N$) with various electrophilic and nucleophilic reagents is reported. Cluster **2** reacts with MeOH and MeLi to give the enolate clusters [PPN][$Os_3(CO)_{11}$($CH_2C\{O\}R$)] (R = OMe (**4**), Me (**6**)). These belong to a relatively rare class of terminal alkyl clusters, and **4** is one of the few to be structurally characterized: $P2_1/c$, a = 19.875 (4) Å, b = 15.056 (4) Å, c = 19.118 (6) Å, β = 115.27 (2)°, V = 5173 (3) Å^3, Z = 4, R = 0.042, R_w = 0.051 for 4982 reflections with $F_o > 4\sigma(F_o)$. The enolate ligand is bound to a single Os atom in an equatorial position and points away from the Os_3 triangle. Electrophilic $CH_3OSO_2CF_3$ alkylates the ketene oxygen in **2** to give the fluxional σ,π-vinyl cluster $Os_3(CO)_{10}$(μ-I)(μ-C(OCH$_3$)CH$_2$) (**7**). A similar reaction of **2** with $HOSO_2CF_3$ gives the acetyl cluster $Os_3(CO)_{10}$(μ-I)(μ-O=CCH$_3$) (**5**). This product is proposed to form via initial protonation of the ketene oxygen to yield a hydroxyvinyl ligand which tautomerizes to the acetyl ligand. Cluster **2** also reacts at the ketene oxygen with the Lewis acid BF_3·Et_2O to give an unstable adduct which rapidly protonates to yield **5**. Both complex **2** and the neutral ketene cluster $Os_3(CO)_{12}$(μ-CH_2CO) react with amines to yield free amides, although the reactions are highly sensitive to the steric bulk of the amines. The reactivity of **2** is discussed in terms of the contributions of oxycarbene and oxyvinyl resonance forms.

Introduction

A number of organometallic complexes have been prepared which contain ketene and substituted ketene ligands.[1] These have a variety of different ketene coordination modes with those illustrated in I–VI being most common.[1-7] Type I is an η^2-(C,C) ligand bound to a single

metal center typically found for low-valent middle to late transition metals. In type II, a μ_2,η^2-(C,C) ligand bridges

(1) For a review on the chemistry of transition-metal ketene complexes, see: Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.* 1987, 27, 0000.

(2) (a) Bodnar, T. W.; Cutler, A. R. *J. Am. Chem. Soc.* 1983, *105*, 5926. (b) Miyashita, A.; Shitara, H.; Nohira, H. *J. Chem. Soc., Chem. Commun.* 1985, 850. (c) Miyashita, A.; Grubbs, R. H. *Tetrahedron Lett.* 1981, *22*, 1255. (d) Miyashita, A.; Shitara, H.; Nohira, H. *Organometallics* 1985, *4*, 1463. (e) Herrmann, W. A.; Plank, J. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 525. (f) Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Weidenhammer, K. *J. Am. Chem. Soc.* 1979, *101*, 3133. (g) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* 1974, *13*, 335. (h) Redhouse, A. D.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* 1976, *15*, 615. (i) Hoberg, H.; Korff, J. *J. Organomet. Chem.* 1978, *152*, 255. (j) Schorpp, K.; Beck, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1973, *28B*, 738. (k) Herrmann, W. A.; Plank, J.; Kriechbaum, G. W.; Ziegler, J. L.; Pfisterer, H.; Atwood, J. L.; Rogers, R. D. *J. Organomet. Chem.* 1984, *264*, 327. (l) Bodnar, T. W.; Crawford, E. J.; Cutler, A. R. *Organometallics* 1986, *5*, 947. (m) Cutler, A.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* 1974, *77*, 381. (n) Roper, W. R.; Wright, A. H., unpublished results cited in: Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* 1986, *25*, 121. (o) Herrmann, W. A.; Weichmann, J.; Balbach, B.; Ziegler, M. L. *J. Organomet. Chem.* 1982, *231*, C69.
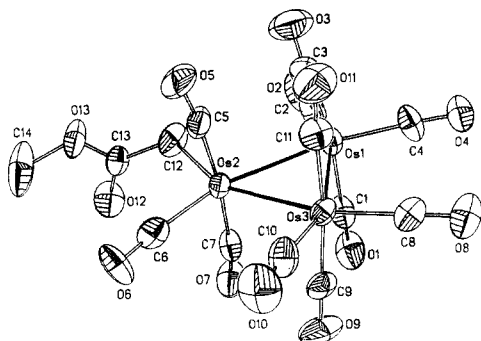
Figure 1. An ORTEP drawing of [PPN][Os₃(CO)₁₁(CH₂C{O}OCH₃)] (4). Thermal ellipsoids are drawn at the 40% probability level. The major orientation (72%) of the disordered –CH₂C(O)OCH₃ and C(6)–O(6) groups is shown (see text).

adjacent metals in binuclear and cluster compounds. In type III the carbonyl oxygen also interacts with a third metal atom. Early transition metals generally give η^2-(C,O) ketene complexes with this ligand bound to a single metal as in IV or to two metals as in V and VI. There also exist a few other ketene complexes that do not fit any of these simple classifications.[7] Synthetic methods for ketene complexes vary,[1] but the most useful have involved carbonylation of carbene ligands,[2a–f,3,4,5a,h] addition of free ketenes to unsaturated complexes,[2h–j,5f,6a,b] and deprotonation of acyl ligands.[5b–e,6d]

While the synthesis and structural characterization of ketene complexes are under active investigation, relatively little is known about the reactivity of this ligand and how the coordination mode influences its chemistry.[1,7b] Co-

ordinated ketene ligands could prove useful in organic synthesis[8] as well as in modeling important chain growth steps for oxygenate production on metal surfaces.[9] We have undertaken such a reactivity study of the coordinated ketene ligands of type II found in the cluster compounds Os₃(CO)₁₂(μ-CH₂CO) (1)[3a,b] and [PPN][Os₃(CO)₁₀(μ-I)(μ-CH₂CO)] (2) (PPN⁺ = (Ph₃P)₂N⁺).[3c,d] The neutral cluster
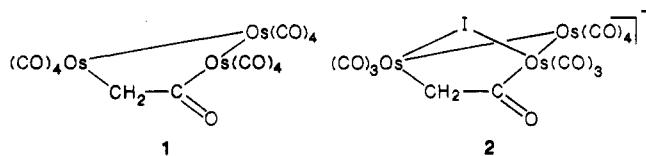
1 was earlier reported to react with MeOH, H₂O, and H₂ to give methyl acetate, acetic acid, and acetaldehyde, respectively.[3b] Herein we extend the reactivity of 1 with various amines and alcohols, probing the steric environment around the ketene ligand. Also reported are reactions of the anionic μ-ketene cluster 2 with alcohols, MeLi, MeOSO₂CF₃, CF₃SO₃H, BF₃·Et₂O, and amines in which the ketene ligand is converted into alkyl, vinyl, and acyl ligands and free amides. In addition, the crystal structure of the enolate complex [PPN][Os₃(CO)₁₁{CH₂C(O)OCH₃}] is described. This is one of the few alkyl-substituted clusters to have been structurally characterized.[10] A preliminary report of part of this work has been published.[11]

Results

The ketene cluster 2 rapidly and quantitatively forms when the methylene cluster 3 is exposed to a CO atmosphere (eq 1).[3c,d] However, this reaction immediately
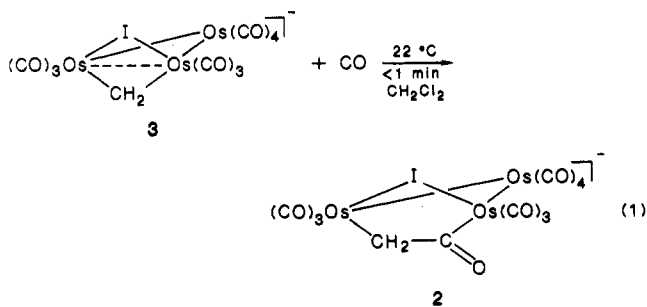
reverses when the CO atmosphere is removed. Therefore, all experiments with 2 described herein were conducted by forming the cluster in situ from 3 and with all solutions maintained under CO atmospheres during reaction.

Reaction of 2 with CH₃OH and NaOMe To Give the Anionic Enolate Cluster [Os₃(CO)₁₁{CH₂C(O)OCH₃}]⁻ (4). Although the neutral ketene cluster 1 reacts rapidly and quantitatively with CH₃OH to give methyl acetate,[3b] the reaction of anionic 2 with methanol requires ~4 h to go to completion, and the major product is the anionic enolate cluster 4 (eq 2). Also formed in this reaction are small amounts of Os₃(CO)₁₂ along with

(3) (a) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 4104. (b) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 4783. (c) Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 254. (d) Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 3541. (e) Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679. (f) Roper, M.; Strutz, H.; Keim, W. *J. Organomet. Chem.* **1981**, *219*, C5. (g) Weinstock, I.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1986**, *108*, 8298. (h) Schulze, W.; Hartl, H.; Seppelt, K. *J. Organomet. Chem.* **1987**, *319*, 77. (i) Akita, M.; Kondoh, A.; Moro-Aka, Y. *J. Chem. Soc., Chem. Commun.* **1986**, *1296*. (j) Doherty, N. M.; Filders, M. J.; Forrow, N. J.; Knox, S. A. R.; MacPherson, K. A.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 1335. (k) Masters, A. P.; Sorensen, J. S.; Ziegler, T. *J. Org. Chem.* **1986**, *51*, 3558.

(4) Holmgren, J. S.; Shapley, J. R.; Wilson, S. R.; Pennington, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 508.

(5) (a) Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178. (b) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499. (c) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068. (d) Ho, S. C. H.; Straus, D. A.; Armantrout, J.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2210. (e) Waymouth, R. M.; Santarsiero, B. D.; Coots, R. J.; Bronikowski, M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 1427. (f) Gambarotta, S.; Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 1173. (g) Casey, C. P.; O'Conner, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 2919. (h) Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 3172. (i) Hong, P.-B.; Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1821. (j) Meinhart, J. O.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 3318. (k) Rusik, C. A.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 4652.

(6) (a) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1978**, *100*, 1921. (b) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1979**, *17*, 2995. (c) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, *462*. (d) Waymouth, R. M.; Sanatarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 4050. (e) Young, S. J.; Hope, H.; Schore, N. E. *Organometallics* **1984**, *3*, 1585. (f) Choukroun, R.; Dahan, F.; Gervais, D. *J. Organomet. Chem.* **1984**, *266*, C33. (g) Engelhardt, L. M.; Jacobsen, G. E.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1984**, 220.

(7) (a) Herrmann, W. A.; Gimeno, J.; Weichman, J.; Zeigler, M. L.; Balbach, B. *J. Organomet. Chem.* **1981**, *213*, C26. (b) Bkouche-Waksman, I.; Ricci, J. S.; Koetzle, T. F.; Weichman, J.; Herrmann, W. A. *Inorg. Chem.* **1985**, *24*, 1492.

(8) (a) Miyashita, A.; Kihara, T.; Nomura, K.; Nohira, H. *Chem. Lett.* **1986**, 1607. (b) Mitsudo, T.; Kadokura, M.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1539.

(9) See, for example: (a) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (b) Bell, A. T. *Catal. Rev.* **1981**, *23*, 203. (c) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (d) Pettit, R.; Brady, R. C., III *J. Am. Chem. Soc.* **1980**, *102*, 6181. (e) Pettit, R.; Brady, R. C. III *Ibid.* **1981**, *103*, 1287.

(10) (a) Zuffa, J. L.; Gladfelter, W. L.; *J. Am. Chem. Soc.* **1986**, *108*, 4669. (b) Saito, T.; Nishida, M.; Yamagata, T.; Yuriko, Y.; Yamaguchi, Y. *Inorg. Chem.* **1986**, *25*, 1111.

(11) Bassner, S. L.; Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 5358.

2

4 (35%)
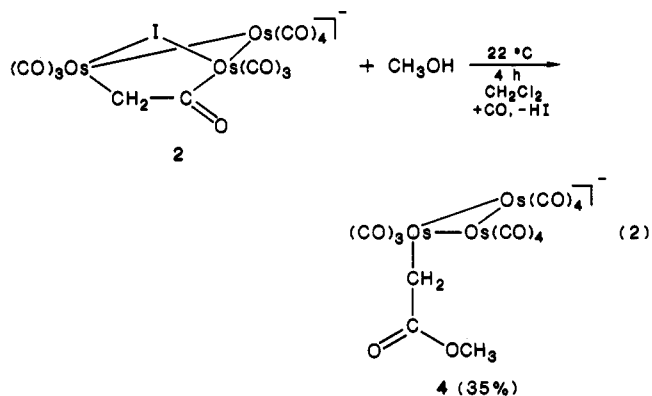
$Os_3(CO)_{10}(\mu\text{-}O\text{==}CCH_3)$ (5), which derives from protonation of 2 (see below). Note that conversion of 2 into 4 releases a proton which can subsequently react with 2 to give 5. Also, in the 2 → 4 conversion a CO ligand is taken up from the CO atmosphere that the reaction is necessarily conducted under (see above). Cluster 4 also forms when 2 is allowed to react with $NaOCH_3$.

Cluster 4 has been spectroscopically as well as structurally characterized (see below). An ORTEP drawing is shown in Figure 1, and the spectroscopic data are consistent with the determined structure. 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.[12a] The δ 2.31 ¹H NMR resonance for the methylene protons is in the range found for mononuclear metal enolates,[12b] but downfield from the normal metal alkyl region (δ -1.0 → δ +0.5). Interestingly, the ¹³C NMR spectrum of 4 shows only one broad peak at δ 185.5 assignable to the metal carbonyls, implying the existence of a fluxional process which rapidly equilibrates the CO ligands. This resonance broadened upon cooling, but even at -80 °C the individual carbonyl resonances were not resolved.

Reaction of 2 with MeLi To Give the Enolate Cluster [Os₃(CO)₁₁{CH₂C(O)CH₃}]⁻ (6). The anionic ketene cluster 2 reacts with CH_3Li to give cluster 6 (eq 3) analogous to 4. Cluster 6 was isolated as an orange oil and
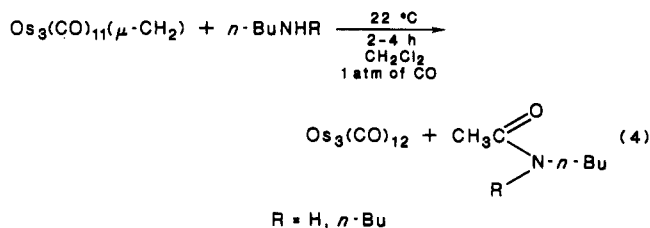

2

(3)

6
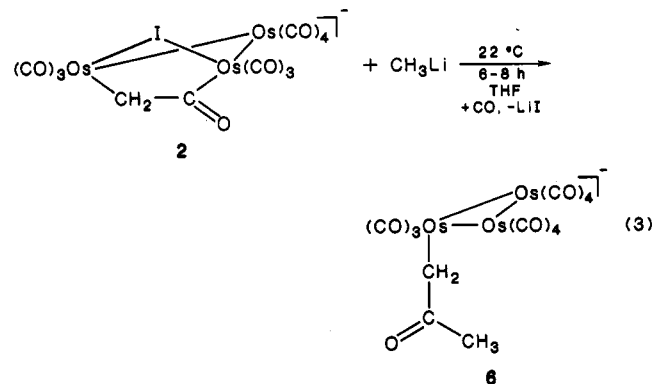
has been spectroscopically characterized. Its IR spectrum in the terminal carbonyl region is similar to that of structurally characterized 4, implying similar structures for the two compounds. The alkyl ligand in 6 is formally the enolate of acetone, and it shows a ketonic ν_{CO} stretch

---

(12) (a) Free Li⁺ enolates generally show ν_{CO} bands in the 1550–1600 cm⁻¹ region. See: Jackman, L. M.; Lange, B. C. *Tetrahedron* 1977, *33*, 2737. (b) Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* 1985, *107*, 3724.

---

at 1676 cm⁻¹, 39 cm⁻¹ lower in energy than that of free acetone. The ¹H NMR spectrum of 6 shows resonances for the enolate ligand at δ 2.53 (2 H, CH_2) and 2.27 (3 H, CH_3).

Further Reactions of Clusters 1 and 2 with Nucleophiles. Neither the neutral ketene cluster 1 nor the anionic ketene cluster 2 showed any reactivity with *t*-BuOH or KO-*t*-Bu, although such reactions could have given free *tert*-butyl acetate or enolate clusters analogous to 4 and 6. The decrease in reactivity in moving from CH_3OH to *t*-BuOH is presumably a consequence of increased steric interactions of the latter with the clusters.

However, both clusters 1 and 2 react with amines. These reactions typically were conducted by placing the free amine and either 3 or the neutral methylene cluster Os₃-(CO)₁₁(μ-CH₂) into a Schlenk flask and then admitting CO to form the ketene clusters 2 and 1, respectively. Control reactions showed no detectable reaction of the starting methylene clusters with the amines after several hours. The neutral ketene cluster 1, which forms over a 2–4-h period, reacts with *n*-Bu₂NH and *n*-BuNH₂ to form Os₃-(CO)₁₂ and the corresponding free amides during this time period (eq 4). IR monitoring of the reactions showed

$$Os_3(CO)_{11}(\mu\text{-}CH_2) + n\text{-}BuNHR \xrightarrow[\substack{2\text{-}4 \text{ h} \\ CH_2Cl_2 \\ 1 \text{ atm of CO}}]{22 \text{ °C}}$$

R = H, *n*-Bu

progressive loss of IR vibrations of the starting methylene cluster and the simultaneous growth of the IR bands of Os₃(CO)₁₂ over the course of ~4 h. The IR bands of the ketene cluster 1 were never observed, implying either that the amines react with cluster 1 as it forms or that they intercept an intermediate in the Os₃(CO)₁₁(μ-CH₂) to Os₃(CO)₁₂(μ-CH₂CO) conversion. That the latter is likely correct was indicated by the very slow (4 days) reaction observed when free amine was added to solutions of *preformed* 1. These observations are consistent with the formation of a coordinatively unsaturated and highly reactive ketene cluster enroute to fully saturated 1, as previously proposed for the reaction of Os₃(CO)₁₁(μ-CH₂) with CH_3OH/CO.[3b] A similarly coordinatively unsaturated reactive intermediate was invoked to explain the reactivity of [CpRu(CO)₂](μ-CH₂CO) with methanol.[3e]

Anionic ketene cluster 2 also reacts with *n*-Bu₂NH and *n*-BuNH₂, but much more slowly than does 1. The reaction of 2 with *n*-Bu₂NH gives Os₃(CO)₁₂ and CH₃C(O)N-*n*-Bu₂ in near quatitative yield, although the reaction takes 5 h to reach completion. Reaction of 2 with *n*-BuNH₂ requires over 12 h for completion and gives the corresponding amide in 72% yield. Ketene clusters 1 and 2 showed similar slow reactions with *t*-BuNH₂ to give ~50% and ~35% yields of the free amide CH₃C(O)NH-*t*-Bu after 3 days. Previous studies have shown that the anionic ketene cluster 2, when maintained under a CO atmosphere as in these experiments, slowly loses I⁻ over a 24-h period and adds CO to form the neutral ketene cluster 1.[3d] Given the time scale of the above reactions of 2 with amines, it is possible that cluster 2 may be unreactive with these amines and that reaction only occurs when cluster 1 is formed from 2.

Alkylation of 2 To Form the Fluxional σ,π-Vinyl Cluster Os₃(CO)₁₀(μ-I)(μ-C(OCH₃)=CH₂) (7). Electrophilic $CH_3OSO_2CF_3$ adds to the ketene carbonyl oxygen of 2 to form the σ,π-vinyl cluster 7 (eq 5). An X-ray

2

7 (71%)

2

5 (70%)
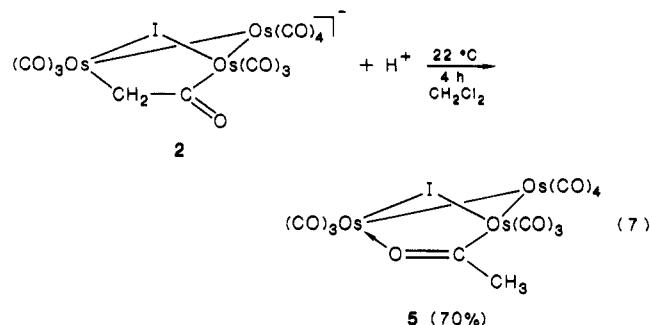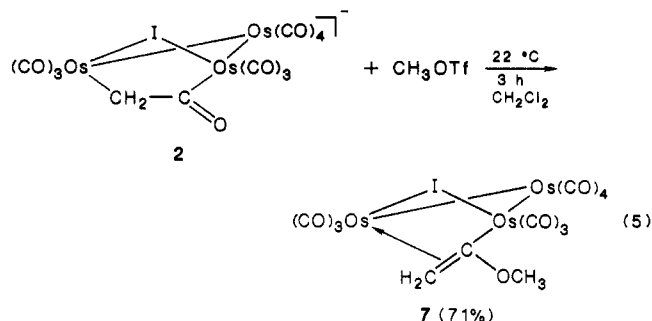
diffraction study on a disordered crystal of **7** showed the assigned structure to be correct,[13] but a satisfactory refinement was not possible (see Figure 1S, supplementary material). Spectroscopic data of **7** are consistent with those of the assigned structure. Its ¹H NMR spectrum shows the expected methoxy resonance at δ 3.85 (s, 3 H) and resonances due to the inequivalent methylene protons at δ 5.10 (d, 1 H, J_{HH} = 4.92 Hz) and 5.06 (d, 1 H). The -80 °C ¹³C NMR spectrum of **7** shows ten separate resonances attributable to the ten inequivalent carbonyl ligands of **7** as well as resonances at δ 199.4 (C(OCH₃)CH₂) and 35.9 (C(OCH₃)CH_2) due to the vinyl ligand. These compare well to resonances found in other σ,π-vinyl compounds.[14]

When the mixture is warmed to room temperature, the carbonyl ¹³C NMR spectrum of **7** broadens, coalesces, and then sharpens into six resonances, although no change is seen in the vinyl ligand resonances. We attribute these spectral changes to a fluxional process in which the σ,π-vinyl ligand exchanges its coordiantion environment in a "windshield wiper" motion similar to that seen in other σ,π-vinyl compounds (eq 6).[14] This fluxional process
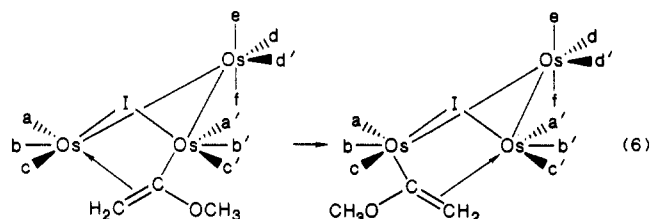

creates an effective mirror plane in the averaged structure with the pairs of carbonyls (a,a'), (b,b'), (c,c'), and (d,d') appearing equivalent at room temperature.

Protonation of 2 To Give the μ-Acetyl Cluster Os₃(CO)₁₀(μ-I)(μ-O═CCH₃) (5). Protonation of the anionic ketene cluster **2** with a slight excess of CF₃SO₃H gave the previously characterized μ-acetyl cluster **5**,[15] (eq 7). The immediate dark orange to light orange color change

followed by slow formation of the yellow color of **5** indicated the presence of an intermediate species in this transformation. The ¹H NMR spectrum recorded immediately following addition of CF₃SO₃H to **2** showed two doublets at δ 5.24 and 4.78 with J_{HH} = 6.3 Hz which are attributed to this intermediate complex. These decayed over ~45 min as the δ 2.58 resonance of **5** correspondingly increased in intensity. The IR spectrum of this intermediate is similar to that of the σ,π-vinyl cluster **7**, implying that this species is a hydroxyvinyl structure formed by initial protonation of the ketene oxygen.

Reaction of 2 with BF₃·Et₂O. Addition of a stoichiometric amount of BF₃·Et₂O to a CDCl₃ solution of **2** gave immediate reaction as indicated by IR and ¹H NMR analysis. The ketene IR stretch of **2** immediately disappeared upon BF₃ addition, and a new species formed which has a terminal ν_{CO} pattern similar to that of the σ,π-vinyl cluster **7** (see Experimental Section). Likewise, rapid disappearance of the ¹H NMR resonances of **2** occurred upon BF₃ addition, and a new pair of doublets appeared at δ 5.2 and 5.0 (J_{HH} = 7.3 Hz), in 60% integrated yield, along with several unidentified resonances. The position of these new resonances are similar to that of **7** (δ 5.10, 5.06 (J_{HH} = 5 Hz)) and along with the IR results imply the formation of a BF₃ adduct **8** similar in structure to **7** (eq 8). Species **8**, however, proved impossible to isolate; ¹H

2

8
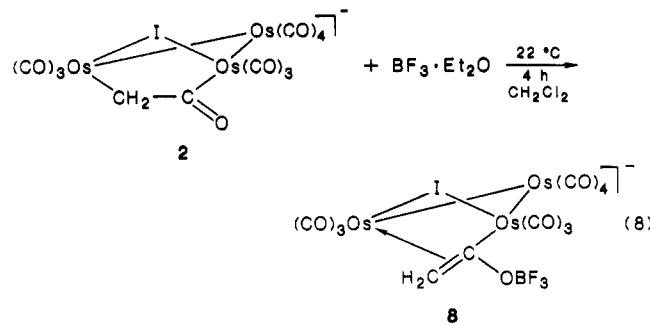
NMR monitoring showed conversion of **8** to the μ-acetyl complex **5** in 83% yield over a 24-h period. This conversion presumably occurs through scavenging of a proton from adventitous H₂O.

Crystal and Molecular Structure of [PPN][Os₃(CO)₁₁{CH₂C(O)OCH₃}] (4). Crystallographic data for **4** are given in Table I–III, and the labeling scheme used is indicated in Figure 1. The structure is disordered with the -CH₂C(O)CH₃ and C(6)O(6) groups doubly positioned in a 72/28% occupancy across a pseudo-mirror plane perpendicular to the equatorial plane (see Experimental Section for details). The three Os atoms form a triangular cluster with all Os–Os distances within normal bonding values.[16] All carbonyl ligands are terminal, and the -CH₂C(O)OCH₃ ligand is bonded to only one Os atom in

(13) Partial crystallographic characterization of **7** confirms the structure assigned by spectroscopic methods. Severe and ultimately unmodelable disorder prevented satisfactory completion of the refinement. Three crystallographically independent molecules were found: molecule A (Figure 1s in supplementary material) was ordered and confirmatory; molecule B was doubly disordered (the Os atoms formed an axially-elongated "Star-of-David" pattern with superimposed carbonyl oxygen atoms; and molecule C could only be partially resolved, but presented a heavy-atom pattern suggesting quadruple disorder. Triclinic, $P\bar{1}$ (not proved), a = 8.999(3), b = 15.413(4), c = 19.373(6)Å, α = 79.10(2), β = 78.57(3), γ = 76.65(2)°, V = 2533(1)Å³, Z = 6. At temination of refinement with only the Os and I atoms of molecule A anisotropic: R_F = 7.1%, R_{wF} = 8.0%, GOF = 1.97, highest peak (final difference map) = 2.1eÅ⁻³, lowest trough, -1.8eÅ⁻³.

(14) (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.; Boureard, P.; Sayer, B. G.; Peng, S.; McGlinchey, M. J.; Marinetti, A.; Saillard, J.; Naceur, J. B.; Mentzen, B.; Jaouen, G. *Organometallics* **1985**, *4*, 1123 and references cited therein.

(15) (a) Jensen, C. M.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 5926. (b) Morrison, E. D.; Bassner, S. L.; Geoffroy, G. L. *Organometallics* **1986**, *6*, 408.

(16) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878. Average Os-Os distance = 2.8771 (27) Å in Os₃(CO)₁₂.

**Table I. Crystallographic Data for
[PPN][Os₃(CO)₁₁(CH₂C{O}OCH₃)] (4)**

formula	$Os_3C_{50}H_{35}NO_{13}P_2$
cryst system	monoclinic
space group	$P2_1/c$
cryst size	0.24 × 0.24 × 0.38
cryst color	orange yellow
a, Å	19.875 (4)
b, Å	15.056 (4)
c, Å	19.118 (6)
β, Å	115.27 (2)
V, Å³	5173 (3)
Z	4
D(calcd), g cm⁻³	1.913
μ, cm⁻¹	74.8
max/min transm	0.417/0.314
diffractometer	Nicolet R3
radiatn	Mo Kα (λ = 0.710 73 Å)
monochromator	graphite crystal
temp, °C	23
scan technique	ω, full profile
scan speed, deg min⁻¹	variable 5–20
2θ scan limits, deg	$4 \leq 2\theta \leq 45$
octants collected	$\pm h, +k, +l$
data collected	7447
unique data	6759
R(int), %	2.01
unique data with $F_o \geq 4\sigma(F_o)$	4982
data/parameters	8.8
std reflctns	3 std/97 reflctns (<2% decay)
g^a	0.001
R_F, R_{wF}, GOF^a	0.042, 0.051, 1.067
Δ/σ, final cycle	0.068
highest peak, final diff map, e Å⁻³	1.05 (1.06 Å from Os(2))

$^a w^{-1} = \sigma^2(F_o) + |g|(F_o)^2$; $R_F = \sum[|F_o| - |F_c|]/\sum|F_o|$; $R_{wF} = [\sum w^{1/2}(|F_o| - |F_c|)]/\sum w^{1/2}|F_o|$.

an equatorial position. This ligand points away from the Os₃ triangle and clearly shows no interaction with the rest of the cluster. Bond distances and angles within this ligand are unexceptional, and no interionic contacts are noteworthy. The only other structurally characterized carbonyl cluster with a terminally bound alkyl ligand is the recently prepared [PPN][HOs₃(NCO)(CO)₉{CHCH₂C(O)OC(O)}] (9) with a succinoyl anhydride ligand.[10a] The Os(2)–C(12) distance of 2.15 (1) Å in 4 compares well with the Os–C-(alkyl) distances of 2.200 (6) Å in 9 and 2.16 (2) and 2.20 (2) Å in *cis*-Os(CH₂C₆F₅)₂(CO)₄.[17]
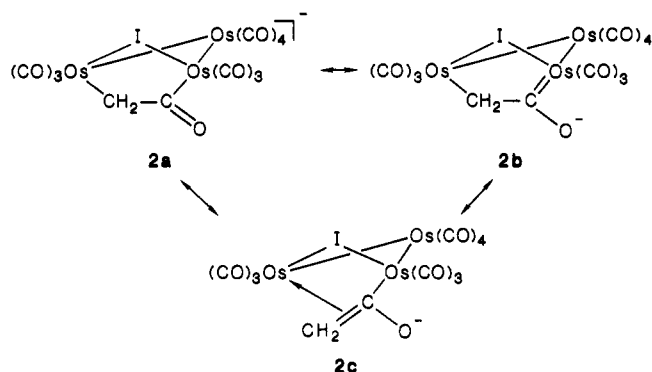
Discussion

It is apparent from the reactions described above that the μ-ketene ligand in 2 is a reactive moiety and readily transforms into vinyl, acyl, and enolate ligands upon treatment with appropriate nucleophiles and electrophiles. The observed reactivity pattern shows that nucleophiles attack the ketene carbonyl carbon of 2 whereas electrophiles add to the carbonyl oxygen. The enolate clusters

2
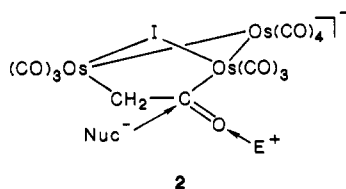
4 and 6 and the free amides CH₃C(O)N-*n*-Bu₂ and CH₃C-(O)NH-*n*-Bu appear to derive by simple nucleophilic addition of OMe⁻, Me⁻, and amines to the ketene carbonyl,

much like nucleophilic addition to free ketenes,[18] organic carbonyls, and metal acyl complexes.[19]

The reactions of 2 with electrophiles imply that important contributing resonance forms for 2 are the oxycarbene (2b) and oxyvinyl (2c) structures. The oxy-

carbene resonance form is known to be important for anionic metal *acyl* complexes and contributes to the ease with which these are alkylated at the carbonyl oxygen by R⁺ reagents to yield metal carbenes.[19] The conversion of 2 into the observed methoxyvinyl complex 7 occurs by similar addition of CH₃⁺ to the carbonyl oxygen, eq 5, and spectroscopic data indicate that BF₃ also adds to the ketene carbonyl oxygen. Although the crystal structure of 2 has not been determined, the relatively low energy of the ν_{CO} stretch of the ketene carbonyl of 2 at 1551 cm⁻¹ implies the importance of resonance forms 2b and 2c. This vibration is substantially lower in energy than the 1684 and 1676 cm⁻¹ "organic" carbonyl ν_{CO} bands in the enolate ligands in 4 and 6 as well as the 1622 and 1574 cm⁻¹ vibrations of the ketene carbonyl in the neutral μ-ketene complexes Cp(CO)₂Ru(μ-CH₂CO)RuCp(CO)₂[3e] and 1.[3b]

The most reasonable path for the proton-induced conversion of 2 into the μ-acetyl complex 5 involves addition of H⁺ to the ketene carbonyl oxygen to produce a hydroxyvinyl complex 10 followed by tautomerization of 10 to 5 (eq 9). The latter is, of course, similar to organic

(9)
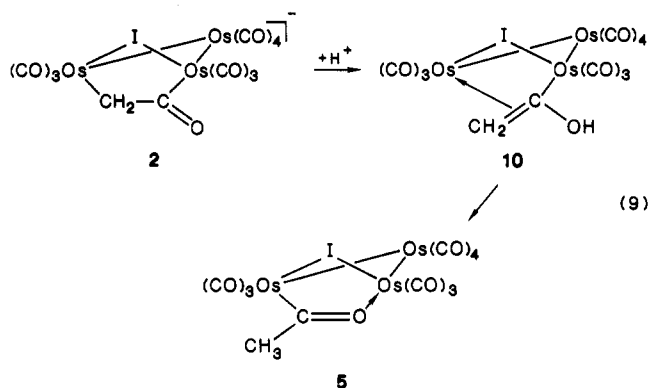
keto–enol tautomerization. Infrared and ¹H NMR spectra clearly show the presence of an intermediate in the 2 → 5 conversion which we assign to 10. The IR spectrum of this intermediate is similar to that of 7, and its ¹H NMR spectrum shows two nonequivalent methylene protons, consistent with structure 10.

It is interesting to compare the reactions of the ketene clusters 1 and 2 with methanol. Neutral cluster 1 reacts with CH₃OH to give acetic acid and Os₃(CO)₁₂.[3b] In con-

(17) Aleksandrov, G. G.; Sol'nikov, G. P.; Krickaja, I. I.; Struchov, J. T. *Koord. Khim.* **1980**, *6*, 629.

(18) Brady, W. T. In *The Chemistry of Ketenes, Allenes, and Related Compounds*; Wiley: New York, 1980.

(19) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, 1985.

Table II. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for [PPN][Os₃(CO)₁₁(CH₂C{O}OCH₃)] (4)

	x	y	z	U^d		x	y	z	U^d
Os(1)	1635 (1)	7246 (1)	2031 (1)	53 (1)	C(21)	4020 (4)	2609 (6)	910 (4)	67 (6)
Os(2)	1979 (1)	7261 (1)	3663 (1)	46 (1)	C(22)	4367	2667	414	84 (8)
Os(3)	636 (1)	8098 (1)	2575 (1)	48 (1)	C(23)	5141	2635	712	78 (8)
P(1)	3982 (2)	2470 (2)	2330 (2)	40 (1)	C(24)	5568	2546	1507	70 (7)
P(2)	2306 (2)	2472 (2)	1684 (2)	45 (1)	C(25)	4220	2487	2003	56 (6)
N(1)	3131 (5)	2303 (7)	1797 (6)	54 (4)	C(26)	4446	2519	1705	44 (5)
O(1)	2456 (5)	9028 (7)	2213 (5)	95 (5)	C(31)	4448 (4)	4233 (5)	2633 (4)	62 (6)
O(2)	3002 (6)	6357 (10)	2007 (7)	143 (8)	C(32)	4559	5024	3047	94 (10)
O(3)	1019 (8)	5390 (7)	2090 (7)	132 (8)	C(33)	4429	5059	3708	90 (9)
O(4)	601 (6)	7523 (7)	332 (5)	97 (5)	C(34)	4187	4302	3955	80 (7)
O(5)	1052 (6)	5650 (7)	3708 (6)	106 (6)	C(35)	4076	3510	3540	60 (6)
O(6)	2104 (9)	7797 (11)	5242 (7)	114 (9)	C(36)	4206	3476	2880	42 (5)
O(6')	3404 (25)	6145 (33)	4239 (26)	132 (17)[b]	C(41)	5070 (4)	1650 (5)	3633 (4)	58 (6)
O(7)	3095 (5)	8764 (7)	3951 (5)	96 (5)	C(42)	5370	929	4128	80 (7)
O(8)	-457 (5)	8802 (7)	1004 (5)	96 (5)	C(43)	4977	132	3991	87 (9)
O(9)	1598 (6)	9812 (6)	3069 (7)	109 (6)	C(44)	4285	55	3356	77 (8)
O(10)	-51 (6)	8628 (9)	3671 (6)	116 (7)	C(45)	3985	776	2864	53 (6)
O(11)	-265 (5)	6367 (7)	2226 (7)	113 (6)	C(46)	4378	1573	3001	41 (5)
O(12)	3859 (7)	6897 (10)	5176 (8)	93 (7)	C(51)	2369 (4)	4112 (7)	1090 (6)	97 (9)
O(12')	3314 (21)	7737 (25)	5692 (21)	97 (12)[b]	C(52)	2083	4838	598	129 (12)
O(13)	3109 (7)	5825 (9)	5272 (7)	87 (7)	C(53)	1342	4839	53	123 (13)
O(13')	2751 (19)	6495 (25)	5626 (20)	87 (11)[b]	C(54)	886	4114	0	133 (11)
C(1)	2139 (7)	8375 (10)	2165 (7)	69 (6)	C(5)	1171	338	492	82 (7)
C(2)	2495 (7)	6688 (11)	2027 (7)	84 (7)	C(56)	1913	3387	1037	53 (5)
C(3)	1226 (8)	6104 (10)	2094 (8)	81 (8)	C(61)	2010 (5)	3476 (5)	2760 (5)	88 (9)
C(4)	993 (7)	7400 (11)	972 (7)	75 (7)	C(62)	1951	3587	3457	108 (10)
C(5)	1345 (7)	6284 (9)	3647 (7)	65 (6)	C(63)	2092	2873	3965	99 (10)
C(6)	2039 (7)	7565 (9)	4678 (8)	67 (7)	C(64)	2292	2049	3778	82 (8)
C(7)	2633 (7)	8221 (9)	3792 (7)	62 (6)	C(65)	2351	1939	3082	67 (6)
C(8)	-37 (7)	8530 (9)	1609 (7)	63 (6)	C(66)	2210	2652	2573	50 (5)
C(9)	1266 (7)	9153 (8)	2876 (8)	68 (6)	C(71)	1127 (4)	1317 (5)	1341 (4)	59 (6)
C(10)	221 (7)	8412 (10)	3270 77)	75 (7)	C(72)	722	547	1021	73 (7)
C(11)	100 (7)	7016 (9)	2381 (8)	68 (7)	C(73)	972	-49	626	74 (6)
C(12)	2903 (6)	6361 (10)	4036 (7)	74 (7)	C(74)	1628	125	550	68 (7)
C(13)	3358 (9)	6363 (13)	4856 (10)	59 (8)	C(75)	2033	895	870	53 (6)
C(13')	2702 (27)	7308 (33)	5353 (28)	71 (14)[b]	C(76)	1782	1491	1266	47 (5)
C(14)	3476 (9)	5974 (14)	6100 (8)	145 (11)					

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Isotropic U.

Table III. Selected Bond Distances and Angles for [PPN][Os₃(CO)₁₁(CH₂C{O}OCH₃)]

Bond Distances (Å)

Os(1)-Os(2)	2.895 (1)	Os(3)-C(8)	1.87 (1)
Os(1)-Os(3)	2.905 (1)	Os(3)-C(9)	1.95 (1)
Os(2)-Os(3)	2.880 (1)	Os(3)-C(10)	1.90 (2)
Os(1)-C(1)	1.93 (1)	Os(3)-C(11)	1.89 (1)
Os(1)-C(2)	1.91 (1)	C(12)-C(13)	1.44 (2)
Os(1)-C(3)	1.93 (1)	C(13)-O(12)	1.22 (2)
Os(1)-C(4)	1.89 (1)	C(13)-O(13)	1.37 (3)
Os(2)-C(5)	1.93 (1)	O(13)-C(14)[a]	1.45 (2)
Os(2)-C(6)[a]	1.95 (2)	P(1)-N(1)	1.578 (8)
Os(2)-C(7)	1.89 (1)	P(2)-N(1)	1.581 (11)
Os(2)-C(12)[a]	2.15 (1)	C-O(carbonyl)[b]	1.15 (2)

Bond Angles (deg)

Os(1)-Os(2)-Os(3)	60.4 (0)	C(5)-Os(2)-C(7)[a]	173.9 (5)
Os(2)-Os(3)-Os(1)	60.1 (0)	C(5)-Os(2)-C(6)[a]	87.5 (6)
Os(3)-Os(1)-Os(2)	59.6 (0)	C(5)-Os(2)-C(12)[a]	89.1 (5)
Os-C-O(av)	174 (2)	C(7)-Os(2)-C(6)[a]	86.7 (6)
Os(1)-Os(2)-C(6)[a]	164.1 (4)	C(7)-Os(2)-C(12)[a]	89.8 (5)
Os(3)-Os(2)-C(6)[a]	105.1 (4)	C(6)-Os(2)-C(12)[a]	97.9 (5)
Os(1)-Os(2)-C(12)[a]	97.4 (4)	P(1)-N(1)-P(2)	145.7 (8)

[a] This value may be affected by disorder (see text). [b] The average value which does not include C(6)-O(6), 1.09 (2) Å, and C-(12)-O(6)', 0.96 (5)Å; both values are affected by the disorder in the structure.

trast, the anionic ketene cluster 2 reacts slowly with CH₃OH to form the alkyl cluster 4. Presumably neutral 1 initially reacts with CH₃OH to give a similar alkyl cluster, but the alkyl ligand must be quickly removed by protonation by the H⁺ released in the CH₃OH addition. The alkyl ligand in 4 is presumably retained because the released H⁺ is taken up by the iodide ligand of 2 to form HI

which should not be extensively dissociated in the organic solvents used in these reactions.

Steric considerations appear to be important in determining the reactivity of the μ-ketene ligands in these clusters. Recall that in the presence of carbon monoxide Os₃(CO)₁₁(μ-CH₂) reacts rapidly with n-Bu₂NH and n-BuNH₂ but only slowly with the more hindered t-BuNH₂. No reaction was observed with highly hindered t-BuOH and KO-t-Bu. Likewise, the anionic ketene cluster 2 reacts rapidly with MeOH, slowly with the more nucleophilic but sterically demanding amines, and not at all with t-BuOH and KOt-Bu.

The results reported herein allow a different interpretation of the course of a previously described reaction in which the μ-methylene dimer Fe₂(μ-CH₂)(CO)₈ (11), gave alkyl acetates and acetic acid upon reaction with alcohols and H₂O.[3f,20] These observations were explained by invoking initial addition of alcohol or H₂O to a coordinated CO to give an alkoxycarbonyl or hydroxycarbonyl ligand followed by coupling with the methylene ligand and protonation to give the observed products (eq 10). Our results, as well as those of others,[2a,b,3b,e,f] which show that alcohols add to coordinated ketenes to give alkyl acetates, combined with the known propensity of 11 to form a μ-ketene complex,[3f] indicate that this reaction may proceed via initial formation of a coordinated ketene ligand which is then attacked by methanol to directly give the observed acetates (eq 11).

(20) (a) Hackenbruch, J.; Keim, W.; Roper, M.; Strutz, H. *J. Mol. Catal.* **1984**, *26*, 129. (b) Summer, C. E., Jr.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350.

R = H, Me, Et
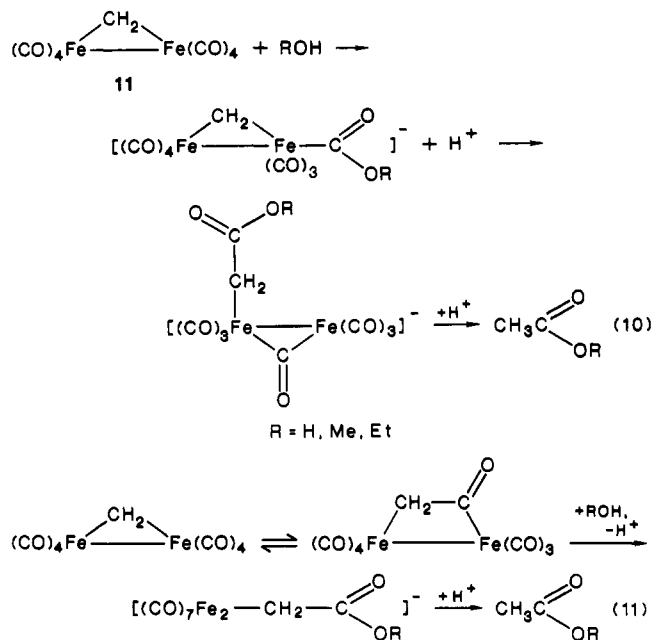
Experimental Section

The complexes $Os_3(CO)_{11}(\mu\text{-}CH_2)$ and $[PPN][Os_3(CO)_{10}(\mu\text{-}I)(\mu\text{-}CH_2)]$ were prepared according to literature methods.[21] Solvents were dried by standard methods, and all reactions were conducted under a prepurified N_2 atmosphere with use of standard Schlenk techniques.[22] All other chemicals were used as received. IR spectra were recorded on an IBM FTIR-32 spectrometer operated in the absorbance mode. NMR spectra were recorded on a Bruker WP 200 FT NMR spectrometer with $Cr(acac)_3$ (1.0 mol %) added to all ^{13}C NMR samples as a shiftless relaxation agent.[22] Field-desorption (FD) mass spectra were obtained by G. Steinmetz and R. J. Hale at the Tennessee Eastman Company, Kingsport, TN. Electron-impact (EI) mass spectra were recorded on an AEI-MS9 mass spectrometer. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY.

In Situ Generation of $[PPN][Os_3(CO)_{10}(\mu\text{-}I)(\mu\text{-}CH_2CO)]$ (2). In a typical procedure, the salt $[PPN][Os_3(CO)_{10}(\mu\text{-}I)(\mu\text{-}CH_2)]$ (3) was placed in a 50-mL three-necked round-bottom flask fitted with a gas adapter and a rubber septum. The flask was evacuated, back-filled with CO three times, and left under a CO atmosphere. Dry, degassed solvent (THF or CH_2Cl_2, 10 mL) was then added by syringe, and the ketene cluster 2 formed instantaneously and quantitatively.[3d]

Reaction of 2 with MeOH To Form $[PPN][Os_3(CO)_{11}\{C\text{-}H_2C(O)OCH_3\}]$ (4). Freshly distilled MeOH (200 μL, 4.93 mmol) was added via syringe to a CH_2Cl_2 solution of 2, generated as above from 3 (110 mg, 0.072 mmol), and the mixture was stirred under static CO atmosphere for 4 h. After a gradual color change from dark orange to light orange, the solvent was removed under vacuum to leave an orange oil. Trituration with pentane yielded a light yellow solid which upon extraction with dry ether gave an orange oil and a yellow solid. Recrystallization of the oil from ether/hexane gave orange crystals of 4 in 35% yield (37.2 mg, 0.025 mmol). 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. IR (CH_2Cl_2): 2070 (w), 2029 (m), 2012 (m), 1993 (vs), 1964 (w), 1684 (w, br) cm⁻¹. ¹H NMR (20 °C, CDCl₃): δ 2.31 (s, 2 H, CH_2C(O)OCH₃), 3.61 (s, 3 H, CH₂C(O)-OCH_3). $^{13}C\{^1H\}$ NMR (20 °C, CDCl₃): δ −20.66 (s, CH_2C(O)CH₃), 50.07 (s, CH₂C(O)OCH_3), 184.76 (s, CH₂C(O)OCH₃), 185.57 (br, M–CO's).

Reaction of 2 with NaOMe To Form 4. NaOMe (20 mg, 0.37 mmol) was dissolved in ~2 mL of distilled MeOH, and 200 μL

of this solution was added via syringe to a THF solution of 2 generated from 3 (112 mg, 0.073 mmol) as described above. The mixture was stirred under 1 atm of CO overnight. Workup as in the above reaction with MeOH gave the same product 4 in 37% (40.2 mg, 0.027 mmol) isolated yield.

Reaction of 2 with MeLi To Form $[PPN][Os_3(CO)_{11}\{C\text{-}H_2C(O)CH_3\}]$ (6). MeLi (48.8 μL of a 1.2 M solution in ether) was added via syringe to a THF solution of 2 generated from 3 (88.7 mg, 0.058 mmol) as described above. The mixture was stirred under 1 atm of CO overnight, and workup as in the above reaction with MeOH yielded an orange viscous oil (57.4 mg) which failed to crystallize upon trituration with pentane or attempted recrystallization from various solvents. IR (CH_2Cl_2): 2068 (w), 2029 (m), 2014 (m), 1995 (s), 1821 (w, br), 1676 (w, br) cm⁻¹. ¹H NMR (CDCl₃): δ 2.27 (s, 3 H, CH₂C(O)CH_3), 2.53 (s, 2 H, CH_2C(O)CH₃).

Reaction of 2 with Amines. $n\text{-}Bu_2NH$ (8.6 μL, 0.051 mmol) was added via syringe to a CH_2Cl_2 solution of 2 prepared from 3 (79.5 mg, 0.052 mmol) as above under a CO atmosphere. Over a 5-h period the IR bands of 2 decreased as bands due to $Os_3(CO)_{12}$ and $CH_3C(O)N\text{-}n\text{-}Bu_2$ (ν_{CO} = 1634 cm⁻¹) grew in, with no other products detected.

Cluster 2 reacted similarly with $n\text{-}BuNH_2$, dried over 4-Å molecular seives, to yield $Os_3(CO)_{12}$ and $CH_3C(O)NH\text{-}n\text{-}Bu$. ¹H NMR monitoring of the reaction of 2 in CDCl₃ with 1 equiv of $n\text{-}BuNH_2$ showed the formation of the amide in 72% integrated yield.

Reaction of 1 with $n\text{-}Bu_2NH$ To Form $CH_3C(O)N\text{-}n\text{-}Bu_2$. $Os_3(CO)_{11}(\mu\text{-}CH_2)$ (60.3 mg, 0.068 mmol) was dissolved in 20 mL of dry CH_2Cl_2 followed by syringe addition of $(n\text{-}Bu)_2NH$ (11.4 μL, 0.068 mmol). No detectable reaction occurred over the course of 1 h after which the solution was saturated with CO to form the ketene cluster 1. IR spectral monitoring showed the formation of Os_3CO_{12} and $CH_3C(O)N(n\text{-}Bu)_2$ over the course of ~12 h. Similarly, reaction of 1 with $n\text{-}BuNH_2$ gave formation of $Os_3(CO)_{12}$ and $CH_3C(O)NH\text{-}n\text{-}Bu$.

Reaction of 2 with $CH_3OSO_2CF_3$ To Form $Os_3(CO)_{10}(\mu\text{-}I)(\mu\text{-}C\{OCH_3\}CH_2)$ (7). Methyl triflate (5.5 μL, 0.048 mmol) was added via syringe to a CH_2Cl_2 solution of 2 generated from 3 (67.3 mg, 0.044 mmol) as described above. The reaction was stirred overnight during which time the color changed from orange to light orange-yellow. Removal of solvent under vacuum gave an orange-yellow residue which was redissolved in CH_2Cl_2. Chromatography on SiO_2 in air with 30% CH_2Cl_2/pentane as eluent gave a single yellow band of 3 from which microcrystalline $3\cdot C_5H_{12}$ was isolated in 71% yield (32.3 mg, 0.031 mmol). 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. IR (pentane): 2105 (w), 2054 (m), 2020 (s), 2014 (sh), 2001 (sh), 1995 (m), 1979 (w) cm⁻¹. ¹H NMR (CDCl₃): δ 5.10 (d, 1 H, J_{H-H} = 4.92 Hz, C(OCH₃)CH_2), 5.06 (d, 1 H, C-(OCH₃)CH_2), 3.85 (s, 3 H, C(OCH_3)CH₂). MS (EI) (^{190}Os): m/e 1034 (M⁺). $^{13}C\{^1H\}$ NMR (CDCl₃, 22 °C): δ 199.4 (s, 1 C, C-(OCH₃)CH₂), 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, 1 C, C(OCH₃)CH₂ J_{C-H} = 153 Hz). $^{13}C\{^1H\}$ NMR (CD₂Cl₂, −80 °C, terminal CO only): δ 179.5 (s, 1 C, CO), 179.1 (s, 1 C, CO), 178.6 (s, 1 C, CO), 178.2 (s, 1 C, CO), 176.2 (s, 1 C, CO), 175.2 (s, 1 C, CO), 174.8 (s, 1 C, CO), 173.9 (s, 1 C, CO), 164.8 (s, 1 C, CO), 164.7 (s, 1 C, CO).

Protonation of 2 To Give $Os_3(CO)_{10}(\mu\text{-}O=CCH_3)(\mu\text{-}I)$ (5). A CH_2Cl_2 solution of 2, generated from 3 (81.0 mg, 0.053 mmol), was acidified with 1.0 mL of a 0.055 M solution of CF_3SO_3H in CH_2Cl_2. The orange solution immediately turned a cloudy, lighter orange and showed ν_{CO} bands at 2114 (w), 2105 (w), 2064 (vs), 2055 (sh), 2029 (sh), 2018 (s), and 1999 (sh) cm⁻¹. Within 2 h the solution had turned yellow, and the solvent was then removed under vacuum. The resulting yellow oil was chromatographed on a silica TLC plate using 10% CH_2Cl_2 in hexane as eluant to give one yellow band which upon extraction gave the known compound 5[15] in 70% yield (38.0 mg, 0.037 mmol).

Reaction of 2 with $BF_3\cdot Et_2O$. The methylene cluster 3 (39.8 mg, 0.026 mmol) was dissolved in dry CDCl₃. The solution was filtered into a 5-mm NMR tube, capped with a septum, and saturated with CO to form the ketene cluster 2, as evidenced by its characteristic ¹H NMR spectrum. $BF_3\cdot Et_2O$ (3.2 μL, 0.026 mmol) was syringed into the tube and an NMR spectrum immediately recorded. The resonances of 2 were replaced by a pair

(21) (a) Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1985**, *5*, 1413. (b) Steinmetz, G. R.; Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 2559.

(22) Shriver, D. F. *The Manipulation of Air Sensitive Compounds*; McGraw-Hill: New York, 1969.

(23) Gansow, O. A.; Burke, A. R.; La Mar, G. N. *J. Chem. Soc., Chem. Commun.* **1972**, 456.

of doublets at δ 5.2 and 5.0 (J_{HH} = 7.3 Hz) in 60% yield, along with several unidentified species. After 24 h, the doublets at δ 5.2 and 5.0 were replaced by the characteristic resonance of the μ-acetyl cluster 5 (83% yield) at δ 2.58.[15] IR monitoring of the reaction of 2 with $BF_3 \cdot Et_2O$ showed immediate loss of the ketene ν_{CO} stretch and the formation of a new species with ν_{CO} (CH_2Cl_2) bands at 2107 (w), 2066 (s), 2033 (w), 2018 (s), and 1999 (w) cm^{-1}.

Crystal and Molecular Structure of [PPN][Os₃(CO)₁₁(C-H₂C{O}OCH₃)] (4). A crystal of 4 was cleaved from a much larger and well-formed specimen and was mounted with epoxy cement on a glass fiber. The crystal, data collection, and refinement parameters are contained in Table I. Unit-cell parameters were obtained from the least-squares fit of the angular settings of 25 reflections (22 ° ≤ 2θ ≤ 29°) which contained Friedel related reflections to check optical and diffractometer alignment. The intensity data were processed with a profile-fitting routine to improve the accuracy in the measurement of weak reflections and corrected for a 2% linear decay, Lp effects, and absorption (empirical, six-parameter ellipsoid model, 252 data).

The structure was solved by direct methods and completed by a series of difference Fourier syntheses. The equatorial plane of Os(2) is disordered about an approximate, perpendicular mirror plane containing the axial carbonyl groups (5 and 7), C(14), and the midpoint of the Os(1)–Os(3) bond. The methylene carbon atom of the –CH₂C(O)OCH₃ group, C(12), and the carbon atom of the carbonyl group, C(6), are superimposed, as are the terminal methyl groups, C(14), of the two acetate orientations. These atoms were refined at full occupancy. The atoms O(6), O(12), O(13), and C(13) were paired with their primed counterparts, and their occupancies were collectively refined; the sum of the primed and unprimed sets was constrained to unit occupancy. The unprimed set occupancy is 72 (1)%; this is the set shown in Figure 1.

The six phenyl rings of the PPN⁺ ion were constrained to rigid, planar hexagons (d(C–C) = 1.395 Å) with calculated hydrogen atom contributions. No hydrogen atom contributions were included for the minor orientation of the disordered CH₂C(O)OCH₃ group but were for the major one. All non-hydrogen atoms (except for the 28%—occupied primed atoms) were refined with anisotropic temperature factors.

All programs and sources of the scattering factors are included in the P3 and SHELXTL (version 5.1) program libraries distributed by the Nicolet Corp., Madison, WI. Atomic coordinates are given in Table II and selected bond distances and angles in Table III. Tables of structure factors, complete bond lengths and angles, and anisotropic temperature factors were previously supplied as supplementary material to ref 11.

Kinetics, Stereochemistry, and Mechanism of the Interconversions of Cobaltaoxanorbornadiene and Cobaltacyclopentene Complexes

Alan M. Stolzenberg* and Maryrose Scozzafava

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254

Received April 14, 1987

The metallaoxanorbornadiene complexes 1-(cyclopentadienyl)-1-cobalta-5,7-dicarbomethoxy-3-methoxy-2-oxa-6-R-norbornadiene (**1a**, R = phenyl; **1b**, R = carbomethoxy) reacted with P(C₆H₅)₃, P(OCH₃)₃, (CH₃)₃CNC, P(n-C₄H₉)₃, and n-C₃H₇NH₂ to afford the ligand-substituted cobaltacyclopentene complexes **2–6**, respectively. No evidence was seen for activation of the coordinated ester group in 1. The equilibrium positions for the interconversion of cobaltacyclopentene/cobaltaoxanorbornadiene complexes were determined as a function of temperature. Thermodynamic data established that the formation of 1 was driven entirely by entropy. Kinetic measurements showed the reaction of 1 and ligand to be first order in both 1 and the ligand. Activation parameters for the reaction of 1 with P(C₆H₅)₃ and (CH₃)₃CNC were consistent with an associative mechanism in which the entering ligand displaced the coordinated ester group. Ligands attacked from the face of the metallacycle opposite the coordinated ester group. Isomeric complexes with ligand on the same face as the coordinated ester group were obtained in low yield as kinetic products of preparative scale reactions when the concentration of ligand was high and the steric bulk of the ligand was low. These complexes were observed only when intermolecular trapping of a coordinatively unsaturated cobaltacyclopentene intermediate became competitive with intramolecular trapping by the ester group. The results establish that cobaltaoxanorbornadiene complexes are the kinetically important intermediates in the reactions of cobaltacyclopentenes.

During an investigation in our laboratories of the reactivity of metallacyclopent-2-ene complexes, we discovered a novel class of [2.2.1]-cobaltacyclic complexes, 1, which we refer to as cobaltaoxanorbornadienes.[1] These complexes formally result from ligand substitution reactions in which the carbonyl oxygen of a metallacycle β-ester substituent displaces triphenylphosphine from the metal center of a cobaltacyclopent-2-ene complex, 2 (eq 1). The only precedent for substitution of an ester group for a phosphine ligand is found in the formation of (η^5-C₅H₅)-Ru[C(CO₂CH₃)CHC(OCH₃)O][P(C₆H₅)₃] from (η^5-C₅H₅)-Ru[η^1-C(CO₂CH₃)CH(CO₂CH₃)][P(C₆H₅)₃]₂.[2] Reactions

(1) Stolzenberg, A. M.; Scozzafava, M.; Foxman, B. M. *Organometallics* 1987, *6*, 769.

(2) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1974, 106.