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Synthesis of Vicinal and Geminal Bis(μ-acyl) Derivatives:[1] *vic*- and *gem*-$Os_3\{\mu\text{-}O{=}CR\}_2(CO)_{10}$ and *vic*-$Ru_2\{\mu\text{-}O{=}CMe\}_2(CO)_6$

C. M. Jensen, Y. J. Chen, and H. D. Kaesz*

Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024

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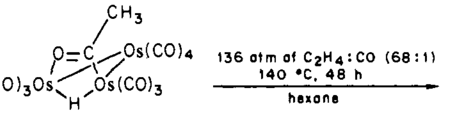
Earlier the reaction of ethylene with $Ru_3\{\mu\text{-}H,\mu\text{-}O{=}CMe\}(CO)_{10}$ at 25° and 3 atm of pressure was observed to form *gem*-$Ru\{\mu\text{-}O{=}CMe\}\{\mu\text{-}O{=}CEt\}(CO)_{10}$.[2] We have now examined the same reaction for $Os_3\{\mu\text{-}H,\mu\text{-}O{=}CMe\}(CO)_{10}$, finding it to require more forcing conditions (eq 1); the triosmium framework remains intact, and both geminal and vicinal isomers[1] are obtained (46% yield).[3]



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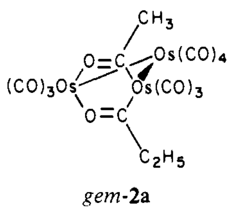
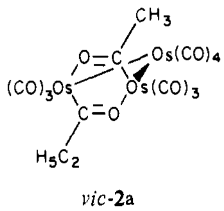
$$\textit{gem}\text{-}\mathbf{2a} \overset{3:1}{\rightleftharpoons} \textit{vic}\text{-}\mathbf{2a} \quad (1)$$



gem-**2a**

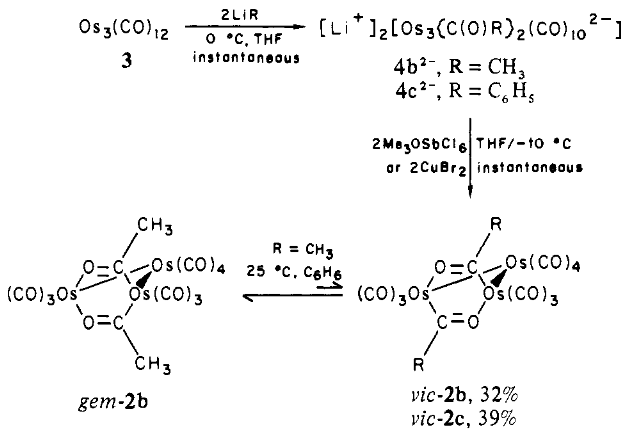


vic-**2a**

The carbonyl IR absorptions of the mixture of the isomers of **2a**[3] consist of a pattern of bands whose maxima come very close to those of a product observed in the sequence of reactions shown in Scheme I. Dianions $[Os_3\{C(O)R\}_2(CO)_{10}^{2-}]$ (**4b**$^{2-}$ or **4c**$^{2-}$)[4] are obtained instantaneously by treatment of $Os_3(CO)_{12}$ (**3**) at 0 °C with 2 equiv of LiR (R = CH_3 or C_6H_5) in dry, freshly distilled tetrahydrofuran (THF).

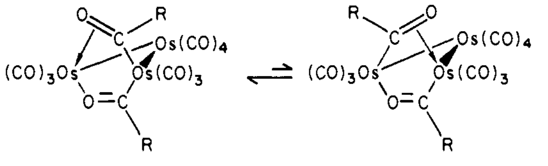
Treatment of the dianions with 2 equiv of $[(CH_3)_3O][Sb(Cl)_6]$ leads to their oxidation[5] to bis(acyl) derivatives; the oxidation can also be accomplished with $CuBr_2$. Performing the oxidations at −10 °C leads exclusively to the vicinal bis(acyl) isomers $Os_3\{1,2\text{-}\mu\text{-}O{=}CR\}\{2,1\text{-}\mu\text{-}O{=}CR\}(CO)_{10}$, (*vic*-**2b** or -**2c**);[6] solvent is removed at −10 °C, and the product is extracted into benzene and purified by chromatography on silica gel, eluting with petroleum ether.[7]

Scheme I



The vicinal bis(acyl) derivatives are stable in the solid or in a nonpolar solvent such as petroleum ether. In benzene solution, *vic*-**2b** equilibrates without decomposition to a mixture of 3.3:1 *gem*-**2b**:*vic*-**2b** in 16 h 25 °C (see lower part of Scheme I). In $CHCl_3$, *vic*-**2b** isomerizes within 1 h at 25 °C to a solution containing the limiting ratio 2.4:1 gem:vic. Pure *gem*-**2b**[9] can be selectively crystallized out of this mixture by slow evaporation of the solvent.

These isomerizations provide the first example of acyl group migration.[10] These most likely proceed through the μ(σ/π)-bonded acyl intermediates A and B. Bridging (σ/π)acyl groups are isostructural with bridging σ/π vinyl groups that are known to isomerize rapidly on the NMR time scale.[11]



By techniques similar to those of Scheme I, we have been able to synthesize the *vic*-bis(acyl)diruthenium complex, **7**[12] (eq 2 and 3).

We arrive at three important conclusions through this work.

(1) Vicinal bis(acyl) derivatives are the kinetic products of the low-temperature alkylation/oxidation route in both the triruthenium and the triosmium systems; the triosmium cluster complexes do *not* dissociate, by contrast to the ready formation of bis(acyl)diruthenium complexes.

(2) Isomerization of the bis(acyl) triosmium complexes at the temperature of their reaction with ethylene provides an *equilibrium* mixture of products; the geminal isomer predominates. This *masks*

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(1) For bridging acyl groups: geminal = $M\{1,2\text{-}\mu\text{-}O{=}CR\}_2M$; vicinal = $M\{1,2\text{-}\mu\text{-}O{=}CR\}\{2,1\text{-}\mu\text{-}O{=}CR\}M$. Structure assignments are derived from ^{13}C NMR.[6,9]

(2) Kampe, C. E.; Boag, N. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 2896–2897.

(3) Carbonyl IR absorptions of the mixture consists of a superposition of the spectra of two isomers, as indicated below. IR ν_{CO}, petroleum ether, cm^{-1}: 2102 w, 2068 s, 2046 m, 2015 s, 2003 s, 1996 m, 1987 m, 1981 m, 1975 m, 1516 w (μ-acyl).

(4) (a) For **4b**$^{-2}$. IR ν_{CO}, THF, cm^{-1}: 2057 vw, 2018 vw, 1987 sh, 1960 vs, 1921 m, 1910 sh, 1542 w, (acyl). ^1H NMR, THF-d_8, δ relative to Me_4Si: 2.38 (s), $C(O)(CH_3)$. $\{^1H\}^{13}C$ NMR, THF-d_8 with $Cr(acac)_3$, δ relative to Me_4Si: 246.3, $C(O)CH_3$; 193.5, 10 CO (fluxional); 56.9 $C(O)CH_3$.

(5) (a) Fischer, E. O.; Kiener, V.; Bunbury, D. S. P.; Frank, E.; Lindley, P. F.; Mills, O. S. *J. Chem. Soc., Chem. Commun.* **1968**, 1378–1380. (b) Fischer, E. O.; Kiener, V. *J. Organomet. Chem.* **1970**, *23*, 215–223.

(6) (a For *vic*-**2b**. Pale yellow crystals, mp 102–104 °C dec. IR ν_{CO}, petroleum ether, cm^{-1}: 2101 w, 2071 s, 2047 m, 2017 s, 2004 w, 1997 w, 1982 m, 1515 vw (μ-acyl); ^1H NMR δ relative to Me_4Si, C_6D_6: 2.22 (s). $\{^1H\}^{13}C$ NMR, C_6D_6 ($Cr(acac)_3$ added), all resonances of approximately equal intensity, δ relative to Me_4Si: 288.6, $\mu\text{-}O{=}CCH_3$; 187.5, 186.0, 180.7, 176.2, 172.7, *CO*; 52.4, $\mu\text{-}O{=}CCH_3$. For the vicinal bis(acyl) derivative we expect five pairs of equivalent carbonyl groups as observed; see also ^{13}C NMR data for *vic*-**2c** below.

(7) Upon column chromatography, $Os_3\{\mu\text{-}Cl\}_2(CO)_{10}$[8] and $Os_3\{\mu\text{-}Cl,\mu\text{-}O{=}Cr\}(CO)_{10}$ (**5**) are obtained in minor (2%) yields when the oxidation is performed with Me_3OSbCl_6.

(8) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1970**, 897–891.

(9) (a) For *gem*-**2b**. Pale yellow crystals, mp 127–130 °C. IR ν_{CO}, petroleum ether, cm^{-1}: 2101 w, 2068 s, 2047 m, 2016 s, 2004 m, 1988 m, 1975 m, 1520 vw (μ-acyl). ^1H NMR C_6D_6, δ relative to Me_4Si: 2.23 (s). $\{^1H\}^{13}C$ NMR, C_6D_6 ($Cr(acac)_3$ added) δ relative to Me_4Si (approximate relative intensity): 285.7 (2), $\mu\text{-}O{=}CCH_3$; 186.7 (2), 183.7 (2), 180.1 (2), 177.6 (1), 174.7 (1), 173.6 (2), *CO*; 55.1, $\mu\text{-}O{=}CCH_3$. For the geminal bis(acyl) derivative we expect three pairs of equivalent and four unique carbonyl groups. This fits the observed ^{13}C NMR spectrum 2:2:2:1:1:2 with two unique carbonyls being accidently degenerate. Mass spectrum: parent ion *m/e* 936 (^{190}Os). (b) The same ratio of vic:gem is obtained by allowing pure gem to stand in benzene solution for 16 h.

(10) Acyl migration through an intermediate containing the $\mu\text{-}C(R)O^-$ group was discussed and considered unlikely for rearrangement in dinuclear Mn–Re anions: Casey, C. P.; Cyr, C. R.; Anderson, R. L.; Marten, D. F. *J. Am. Chem. Soc.* **1975**, *104*, 4679–4680.

(11) Clauss, A. D.; Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *Inorg. Chem.* **1981**, *20*, 1528–1533.

(12) **7** is unstable to chromatography on silica gel; it was recrystallized three times from Et_2O to remove an impurity showing an absorption at 2128 cm^{-1} (in Et_2O). For **7**. IR ν_{CO}, Et_2O, cm^{-1}: 2062 vs, 2007 m, 2001 m, 1550 w (acyl). ^1H NMR, $CDCl_3$, δ relative to Me_4S: 2.97 (s), $\mu\text{-}O{=}CH_3$. $\{^1H\}^{13}C$ NMR, C_6D_6 ($Cr(acac)_3$ added), δ relative to Me_4Si (all resonances of approximately equal intensity): 274.8, $\mu\text{-}O{=}CCH_3$: 193.5, 190.6, 189.8, *CO*; 48.7, $\mu\text{-}O{=}CCH_3$.

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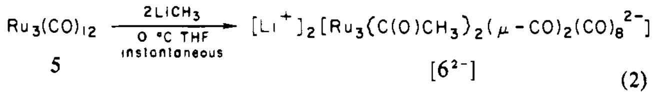
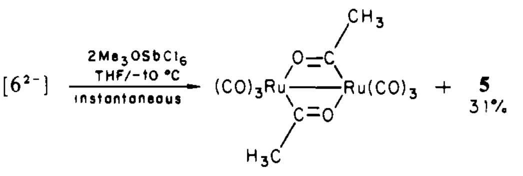


$$\underset{5}{Ru_3(CO)_{12}} \xrightarrow[\text{0 °C THF, instantaneous}]{2LiCH_3} \underset{[6^{2-}]}{[Li^+]_2[Ru_3(C(O)CH_3)_2(\mu\text{-}CO)_2(CO)_8{}^{2-}]} \quad (2)$$



(3)

7, 58%

what the kinetic product may be in the reaction of ethylene with hydrido–triosmium complexes.

(3) Bis(acyl)diruthenium complexes do *not* isomerize.[13] The *kinetic* product of each chemical path in which they are formed is thus *frozen*. The *gem*-bis(acyl)diruthenium complex isolated earlier in the reaction of ethylene with hydrido–acyl–triruthenium complexes can now be identified conclusively as the *kinetic* product.

Acknowledgment. This work was supported by National Science foundation Grant CHE 79-08406.

Supplementary Material Available: Synthetic details and spectroscopic data for $Os_3\{1,2\text{-}\mu\text{-}O{=}CPh\}\{2,1\text{-}\mu\text{-}O{=}CPh\}(CO)_{10}$ (*vic*-**2c**) and $Os_3\{\mu\text{-}Cl,\mu\text{-}O{=}CR\}(CO)_{10}$ (**5**) (R = Me or Ph) (2 pages). Ordering information is given on any current masthead page.

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(13) A possible basis for nontautomerism of the bis(acyl)diruthenium complexes may derive from the short Ru–Ru distance of 2.686 (1) Å as determined for the geminal derivative: Kampe, C. E.; Boag, N. M.; Kaesz, H. D. *J. Mol. Catal.* **1983**, *21*, 297–312. This separation is significantly shorter than Ru–Ru separations in trimeric complexes for which we may take $Ru_3\{\mu\text{-}H,\mu\text{-}O{=}CNMe_2\}(CO)_{10}$ as an example: Szostak, R.; Strouse, C. E.; Kaesz, H. D. *J. Organomet. Chem.* **1980**, *191*, 243–248. In this trimeric complex, the Ru–Ru separations are bridged, 2.8755 (15) Å and unbridged, 2.8319 (15) and 2.8577 (15) Å. Factors operating to shorten the bond in the bis(acyl)diruthenium complexes may lock the acyl groups into the σ,σ-bonded form.

Ab Initio SCF-MO Study of (α-Lithiomethylene)phosphorane

Robert S. McDowell[1] and Andrew Streitwieser, Jr.*

Department of Chemistry, University of California
Berkeley, California 94720

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In a recent communication, Corey and Kang[2] announced the synthesis and chemistry of (α-lithiomethylene)triphenylphosphorane, which was shown to react as an ylide equivalent in good yield with epoxides and hindered ketones, compounds that are inert to normal Wittig conditions.[3] While alternative methods for increasing ylide reactivity are being explored,[4] α-lithiation promises to become an important means of activating alkylidene ylides, thereby greatly extending their synthetic utility. We report here ab initio SCF-MO studies of (α-lithiomethylene)phosphorane, a prototypical lithiated ylide, and its corresponding free anion.

The geometries of (α-lithiomethylene)phosphorane and the methinylphosphoranyl anion were optimized at the 3-21G+(*)[5] level, by the gradient technique available in a modified version[6] of GAUSSIAN80.[7] Although no symmetry was assumed in the optimizations, both species had global minima possessing C_s symmetry. The results are shown in Table I.

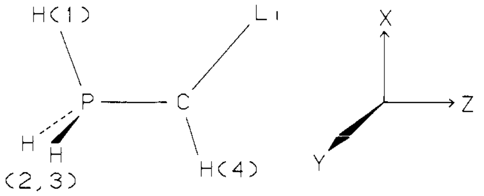
Table I. 3-21G+(*) Optimized Geometries of H_3PCHLi and H_3PCH^-

	H_3-PCHLi	H_3-PCH^-		H_3-PCHLi	H_3-PCH^-
Bond Lengths, Å			Bond Angles, Deg		
P–C	1.67	1.64	H(4)–C–P	114.0	119.9
P–H(1)	1.40	1.40	Li–C–P	131.2	
P–H(2,3)	1.42	1.46	H(1)–P–C	112.9	111.3
C–H(4)	1.09	1.09	H(2)–P–H(3)	95.4	91.3
C–Li	1.92		H(2)–P–H(3)[a]	34.0	28.6

[a] Dihedral angle, with *YZ* plane.

Integrated spatial electron population analysis was used to determine the charge distributions in the two systems.[8] Division of a molecule into fragments demarked by saddle points in the projected electron-density surface yields, upon integration, the spatial electron populations of the fragments.[9] Such populations provide quantitative measures of the effective charges on reactive sites in a molecule. Using the optimized geometries in Table I, we calculated SCF wave functions at the 3-21G+*[5] level for both compounds, and the resulting electron-density surfaces were partitioned as described above. The lithiated ylide has a lithium population of 2.20 electrons and a –CH fragment population of 8.78 electrons. By comparison, the –CH fragment population of the free anion is 8.82 electrons and corresponds essentially to a methinyl dianion bonded to a phosphonium cation. That is, the lithiated species shows a large degree of charge transfer from lithium to carbon and the reactive methinyl group bears essentially the same charge in the lithiated ylide as in the anion. This simple ion pair picture is also supported by the striking similarity in the geometries of the lithiated ylide and its free anion that suggests a cation located at the electrostatic minimum with respect to interaction with the anion. In common with most organolithium compounds, this species is expected to exist as aggregates in solution.[10] We have found the degrees of charge transfer in methyllithium oligomers to be essentially the same as in the monomeric salt;[11] thus the electronic structures of (α-lithiomethylene)phosphorane aggregates in solution are expected to be closely similar to that of the monomer calculated here.

We conclude that (α-lithiomethylene)phosphorane is best described as a contact ion pair whose chemistry is largely that of the corresponding free anion. α-Lithiation increases the inherent nucleophilicity of the alkylidene ylide, but the concomitant



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[1] Eastman Kodak Graduate Fellow.

[2] Corey, E. J.; Kang, J. *J. Am. Chem. Soc.* **1982**, *104*, 4724.

[3] (a) McMurray, J. E.; Choy, W. *Tetrahedron Lett.* **1980**, *21*, 2477. (b) Sowerby, R. L; Coates, R. M. *J. Am. Soc.* **1972**, *94*, 4758. (c) McMurray, J. E. *Ibid.* **1968**, *90*, 6821.

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(7) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406.

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