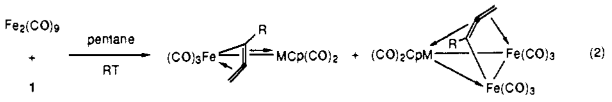
of step 1 to reactions of **1** with group VIII metal carbonyls has afforded allenyl-bridged heteronuclear compounds. Accordingly, stirring (24 h) equimolar quantities of $Fe_2(CO)_9$ and **1** as a room-temperature pentane suspension, followed by chromatography of the reaction mixture on Florisil, provides **2** and **3** (eq 2).[6] The reaction occurs with cleavage of the $M-CH_2$ bond in **1** and concomitant rehybridization of the propargyl carbon ($sp^3 \rightarrow sp^2$). Refluxing (18 h) $Fe_3(CO)_{12}$ and **1** in benzene gives the reverse product distribution of **2** and **3**.



major

minor

2
M = Mo; R = Me (**2a**), Ph (**2b**)
M = W; R = Me (**2c**), Ph (**2d**), *p*-MeC_6H_4 (**2e**)

3
M = Mo; R = Me (**3a**), Ph (**3b**)
M = W; R = Me (**3c**), Ph (**3d**), *p*-MeC_6H_4 (**3e**)

The structures of **2e** and **3d** were unambiguously confirmed by X-ray crystallography (Figures 1 and 2).[7] On the basis of the normal bond lengths of the bridging carbons (C_6-C_7 = 1.390 (9) Å, C_7-C_8 = 1.375 (8) Å) and the sp^2 hybridization at C_6 ($J_{^{13}C-^1H}$ = 164 Hz), **2e** is best formulated as a rare example of a heterobinuclear μ-η^2,η^3-allenyl compound.[3] The angle about the central allenyl carbon ($C_6-C_7-C_8$ = 128.9 (6)°) is even more acute than that observed in the structurally similar $(Mo(CO)_2Cp')_2(\mu$-η^2,η^3-$HC{=}C{=}CH_2)^+$ ($Cp' = C_5H_4Me$)[8] and may reflect the contribution of resonance stabilization from other structures.

Compounds **3** represent the first examples of heterotrinuclear μ_3-η^1,η^2,η^2-allenyl complexes.[9] The allenyl ligand in **3d** has similar bond distances (C_9-C_{10} = 1.371 (5) Å, $C_{10}-C_{11}$ = 1.385 (6) Å) to those in **2e**; however, the angle about the central allene carbon atom is less strained ($C_9-C_{10}-C_{11}$ = 144.3 (3)°) owing to the μ_3 coordination. A dative bond is shown between Fe and W to satisfy the $18e^-$ requirement at each metal.

Complexes **2** afford no detectable **3** when heated or irradiated alone in solution. However, conversion of **2** to **3** by reaction with $Fe_2(CO)_9$ in pentane or by photolysis with $Fe(CO)_5$ does occur but only in minor yields (<20%). Moreover, only **2** is isolated (up to 95%) when a 1:2 molar ratio of $Fe_2(CO)_9$ and **1** is employed. We suggest that these reactions may occur via transition-metal-assisted electrophilic attack on the alkyne moiety of **1** by a coordinatively unsaturated $Fe(CO)_x$ (x = 3 or 4) fragment in a manner similar to that proposed for reactions of **1** with organic electrophiles.[10]

When $Ru_3(CO)_{12}$ and **1** are reacted under similar conditions to those used in the reaction of $Fe_3(CO)_{12}$, the Ru analogue of **3d**, **4a**,[11] is formed along with a minor amount of $Ru_2Cp_2(CO)_4$. No heterobinuclear allenyl species was isolated. The crystal structure of **4a**[7] confirms the allenyl coordination ($C_9-C_{10}-C_{11}$ = 138 (2)°; C_9-C_{10} = 1.40 (2) Å, $C_{10}-C_{11}$ = 1.37 (2) Å). Interestingly, the configurations of the tungsten atoms in **4a** and **3d** differ. In **3d** C_4 and C_8 are nearly eclipsed ($C_8-W-Fe_2-C_4$ = −15.3°), whereas in **4a** they are trans to each other ($C_8-W-Ru_2-C_4$ = −179.1°).

We are currently investigating the generality of this methodology, including extensions to reactions of mononuclear metal-η^1-allenyl complexes with metal carbonyls.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation (through Grant CHE-8420806 to A.W.) and Ministero Pubblica Istruzione (Rome). High field NMR and mass spectra were obtained at The Ohio State University Chemical Instrument Center (funded in part by National Science Foundation Grant 79-10019)).

Supplementary Material Available: Spectroscopic and analytical data for metal–allenyl complexes **2** and **3** (except **2d** and **3d**) and details of the structure determinations of **2e**, **3d**, and **4a** as listed in ref 7 (24 pages). Ordering information is given on any current masthead page.

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(5) Wido, T. G.; Young, G. H.; Wojcicki, A.; Calligaris, M.; Nardin, G. *Organometallics* **1988**, *7*, 452.

(6) E.g., reaction mixture of $Fe_2(CO)_9$ and **1d** was eluted with 2% ether in pentane to give **2d** (58%) as an orange solid upon concentration: IR (C_6H_{12}) ν_{CO} 2046 m, 2036 s, 1993 vs, 1973 s, 1960 vs, 1946 m cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 213.30 (W–CO, $J_{^{183}W-^{13}C}$ = 166 Hz), 211.67 (Fe–CO), 210.63 (W–CO, $J_{^{183}W-^{13}C}$ = 173 Hz), 111.76 (=C=, $J_{^{183}W-^{13}C}$ = 34 Hz), 80.50 (=CPh), 70.53 ($=CH_2$); ^1H NMR ($CDCl_3$) δ 5.39, 3.99 (2 d, J = 0.7 Hz, $=CH_2$); mass spectrum (^{184}W) m/z (rel intensity) 560 (M^+, 5.53) followed by five successive peaks due to CO loss ($M^+ - 4CO$, 100). Anal. Calcd for $C_{19}H_{12}FeO_5W$: C, 40.75; H, 2.16. Found: C, 41.04; H, 1.99. Elution with ether gave **3d** (5.3%) as purple plates upon recrystallization from 1:1 CH_2Cl_2/pentane: IR (C_6H_{12}) ν_{CO} 2052 s, 2020 vs, 1996 s, 1984 m, 1963 m, 1951 w cm^{-1}; ^{13}C NMR ($CDCl_3$) 223.93, 221.10 (W–CO), 211.53 (Fe–CO), 155.86 (=C=), 27.80 ($=CH_2$); ^1H NMR ($CDCl_3$) δ 3.44, 2.86 (2d, J = 1.1 Hz, $=CH_2$); mass spectrum (^{184}W) m/z (rel intensity) 700 (M^+, 0.89) followed by eight successive peaks due to CO loss ($M^+ - 4CO$, 100). Anal. Calcd for $C_{22}H_{12}Fe_2O_8W$: C, 37.75; H, 1.73. Found: C, 37.22; H, 1.51.

(7) Details of the structure determination, including crystal data, data collection and refinement, positional parameters and their standard deviations, temperature factor expressions (B's), and selected bond distances and angles are available in Supplementary Material.

(8) Meyer, A.; McCabe, D. J.; Curtis, M. D. *Organometallics* **1987**, *6*, 1491.

(9) Homotrinuclear μ_3-η^3-allenyl compounds, all possessing bridging ligands, have been reported: (a) Gervasio, G.; Osella, D.; Valle, M. *Inorg. Chem.* **1976**, *15*, 1221. (b) Nucciarone, D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1984**, *3*, 177.

(10) Wojcicki, A. In *Fundamental Research in Organometallic Chemistry*; Tsutsui, M., Ishii, Y., Huang, Y., Eds.; Van Nostrand-Reinhold: New York, 1982; pp 569–597.

(11) **4a** was isolated (21%) as orange needles by recrystallization from 1:1 $CHCl_3$/pentane: IR (C_6H_{12}) ν_{CO} 2067 s, 2032 s, 1998 m, 1981 m, 1967 m cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 225.25, 222.28 (W–CO), 201.79, 198.74, 196.06, 195.13, 192.67 (Ru–CO), 161.59 (=C=, $J_{^{183}W-^{13}C}$ = 45 Hz), 114.09 (=CPh), 26.99 ($=CH_2$); mass spectrum (^{184}W) m/z (rel intensity) 790 (M^+, 0.5) followed by eight successive peaks due to loss of CO ($M^+ - 3CO$, 100). Anal. Calcd for $C_{22}H_{12}O_8Ru_2W$: C, 33.43; H, 1.53. Found: C, 33.45; H, 1.46.

$RhCl(PPh_3)_3$-Catalyzed Hydrosilation of Organoiron Acyl Complexes

Edward J. Crawford, Paul K. Hanna, and Alan R. Cutler*

Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York 12180

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Two general procedures currently are available for reducing acyl ligands on organotransition-metal complexes.[1,2] (1) Carbocationic activation of acyl $L_xM-C(O)R$ and hydride transfer from a borohydride affords α-alkoxyalkyl compounds $L_xM-CH(OR')R$,[3] and (2) borane (BH_3) typically reduces acyl complexes to saturated alkyl compounds L_xM-CH_2R.[4] The established

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(1) Cutler, A. R.; Hanna, P. K.; Vites, J. C. *Chem. Rev.* **1988**, *88*, 1363.

(2) Intermolecular reduction of electron-deficient η^2-acyl complexes [e.g., $Cp_2Zr(X)(COR)$] by metal hydrides,[2a] *i*-Bu_2AlH, aluminum alkyls AlR_3,[2b] zirconocene alkyl complexes,[2c] and Lewis bases[2d] has been documented. (a) Marsella, J. A.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Inorg. Chim. Acta* **1985**, *96*, 161. Gell, K. I.; Posin, P.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846. Erker, G.; Kropp, K. *Chem. Ber.* **1982**, *115*, 2437. Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. Katahira, D. A.; Moloy, K. G.; Marks, T. J. *Organometallics* **1982**, *1*, 1723. (b) Waymouth, R. M.; Grubbs, R. H. *Organometallics* **1988**, *7*, 1631. (c) Martin, B. D.; Matchett, S. A.; Norton, J. R.; Anderson, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 7952. Matchett, S. A.; Norton, J. R.; Anderson, O. P. *Organometallics* **1988**, *7*, 2228. (d) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J.; Arif, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 149 and references cited.

(3) (a) Green, M. L. H.; Mitchard, L.; Swanwick, M. *J. Chem. Soc.* **1971**, 794. (b) Davison, A.; Reger, D. *J. Am. Chem. Soc.* **1972**, *94*, 9237. (c) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258; **1981**, *103*, 979. (d) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31. (e) α-Alkoxyalkyl complexes are useful precursors to transition-metal–carbene complexes: Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411.

(4) (a) Van Doorn, J. A.; Masters, C.; Volger, H. C. *J. Organomet. Chem.* **1976**, *105*, 245. (b) α-Hydroxyalkyl complexes sometimes form: Vaughn, G. D.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1462. Vaughn, G. D.; Gladysz, J. A. *Ibid.* **1986**, *108*, 1473.

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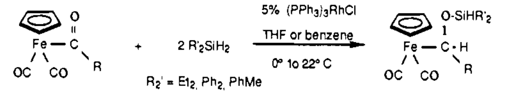
Table I. $(PPh_3)_3RhCl$-Catalyzed Hydrosilation of Organoiron Acyl Complexes

acyl complex[a]	% of reaction[b]	product	% isolated yield	^1H NMR (C_6D_6) δ Fe-CH
Fp–C(O)CH_3 (**1a**)	100 (10 min)	Fp–CH($OSiHEt_2$)CH_3 (**1b**)	83[c]	5.68 (q, J = 5.9 Hz)
Fp–C(O)CH_2CH_3 (**2a**)	68 (1.0 h)	Fp–CH($OSiHEt_2$)CH_2CH_3 (**2b**)	59[c]	5.43 (dd, J = 3.3, 8.4)
Fp–C(O)CH$(CH_3)_2$ (**3a**)	50 (14 h)[d]	Fp–CH($OSiHEt_2$)CH$(CH_3)_2$ (**3b**)	43[e]	5.41 (d, J = 5.1)
Fp–C(O)$CH_2CH_2CH_3$ (**4a**)	55 (1.0 h)	Fp–CH($OSiHEt_2$)$CH_2CH_2CH_3$ (**4b**)	45[c]	5.57 (dd, J = 2.4, 9.1)
Fp–C(O)CH_2CH$(CH_3)_2$ (**5a**)	30 (4.5 h)[d]	Fp–CH($OSiHEt_2$)CH_2CH$(CH_3)_2$ (**5b**)	21[e]	5.73 (dd, J = 2.1, 9.5)
(C_5Me_5)$(CO)_2$Fe–C(O)CH_3 (**6a**)	100 (0.25 h)	(C_5Me_5)$(CO)_2$Fe–CH($OSiHEt_2$)CH_3 (**6b**)	88[c]	5.19 (q, J = 6.0)
(C_9H_7)$(CO)_2$Fe–C(O)CH_3 (**7a**)	100 (0.75 h)	(C_9H_7)$(CO)_2$Fe–CH($OSiHEt_2$)CH_3 (**7b**)	91[c]	5.14 (q, J = 5.8)
Fp–C(O)Ph (**8a**)	60 (1.0 h)[d]	Fp–CH($OSiHEt_2$)Ph (**8b**)	51[e]	6.62 (s)
Fp–C(O)CH_3 (**1a**)	60 (0.5 h)[f]	Fp–CH($OSiHPh_2$)CH_3 (**9b**)	46[e]	5.91 (q, J = 6.0)
Fp–C(O)CH_3 (**1a**)	100 (0.25 h)[g]	Fp–CH(OSiHMePh)CH_3 (**10b**)	59[e]	5.50 (q, J = 6.0)
Cp[P$(OMe)_3$](CO)Fe–C(O)CH_3 (**11a**)	100 (0.50 h)	Cp[P$(OMe)_3$](CO)Fe–CH($OSiHEt_2$)CH_3 (**11b**)		5.35 (dq, J_{PH} = J_{CH} = 6.2)

[a] Fp = (η^5-C_5H_5)Fe$(CO)_2$, C_9H_7 = η^5-indenyl. [b] Reaction conditions: 5% (mol) $(PPh_3)_3RhCl$, 2.0 mol equiv Et_2SiH_2 in benzene or THF at 0 °C, and 0.67 M in iron acyl. Extent of reaction is ascertained by IR spectral monitoring. [c] IR, ^1H, and ^{13}C NMR spectral assignments and results of acceptable elemental analysis are in Table II (supplementary material). [d] 10% $(PPh_3)_3RhCl$ is used. [e] Yield is ascertained by ^1H NMR spectroscopy using Cp_2Fe or C_6Me_6 as an internal standard, since the product retains small amounts of unidentified polysilane residues. IR, ^1H, and ^{13}C NMR spectral assignments are recorded in Table II. [f] Identical reaction conditions, but Ph_2SiH_2 is used. [g] Identical reaction conditions, but $PhMeSiH_2$ is used; product obtained as a 1:1 mixture of diastereomers.

Rh(I)-catalyzed hydrosilation of organic ketones to give siloxyethers[5-7] offers precedent for similar reduction of acyl complexes to their α-siloxyalkyl compounds L_xM–CH($OSiR_3'$)R. In the absence of catalyst, hydrosilanes react only with the more labile acyl compounds [e.g., $(CO)_4Co$–C(O)R[9] and $(CO)_5Mn$–C(O)R[10,11]] by apparent oxidative addition and reductive elimination steps that initially remove the acyl group as aldehyde. We now report that $(PPh_3)_3RhCl$[12] efficiently catalyzes the homogeneous hydrosilation of non-labile organoiron acyl complexes Cp$(CO)_2$Fe–COR with dihydrosilanes to produce stable α-siloxyalkyl derivatives (eq 1).



(1)

Fp(acetyl) (**1a**) immediately reacts with diethylsilane (2 equiv) in benzene or THF solution (0 °C) in the presence of 5 mol % $(PPh_3)_3RhCl$. The reaction is over within ten minutes as judged by IR spectral monitoring. Evaporating solvent and excess silane and then passing pentane extracts of the reaction mixture through a short silica gel column[13] affords analytically pure FpCH($OSiHEt_2$)CH_3 (**1b**) as a yellow-brown oil (83%). With lower catalyst concentrations (e.g., 1 mol %) or less dihydrosilane (1 equiv), reaction rates greatly diminish and the reactions do not go to completion.[14] We do not detect Fp(ethyl), Fp(vinyl), or Fp(α-siloxyvinyl)[15] in these reactions.

Iron acyl complexes listed in Table I likewise undergo $(PPh_3)_3RhCl$-catalyzed hydrosilation at the acyl ligand. Fp(propanoyl) (**2a**), Fp(n-butanoyl) (**4a**), and the (η^5-C_5Me_5)- and (η^5-indenyl)Fe$(CO)_2$ acetyl compounds (**6a** and **7a**) add Et_2SiH_2 under comparable conditions. Both acetyl compounds **6a** and **7a**, nearly as reactive as $FpCOCH_3$, give their siloxyethyl complexes **6b** and **7b** in high yields, whereas the straight-chain Fp(acyls) **2a** and **4a**, less reactive than $FpCOCH_3$, provide their α-siloxyalkyls **2b** and **4b** (also fully characterized) in moderate yields. Branched-chain Fp(i-butanoyl) (**3a**) and Fp(i-pentanoyl) (**5a**) and Fp(benzoyl) (**8a**) do not react in benzene or THF solution with 2–4 equiv of Et_2SiH_2 and 5% $(PPh_3)_3RhCl$ (0° to 22 °C), although sluggish reactions ensue with higher catalyst concentrations (10%). From these reactions, we isolated in low yields the α-siloxyalkyl

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(5) (a) Ojima, I.; Kogure, T.; Nihonyanagi, M.; Nagai, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3506. Ojima, I.; Nihonyanagi, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1972**, 938. Ojima, I.; Nihonyanagi, M.; Kogure, M.; Kumagai, M.; Horiuchi, S.; Nakatsugawa, K. *J. Organomet. Chem.* **1975**, *94*, 449. (b) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1975**, *85*, 19. (c) Semmelhack, M. F.; Misra, R. N. *J. Org. Chem.* **1982**, *47*, 2469. (d) Peyronel, J.-F.; Fiaud, J.-C.; Kagan, H. B. *J. Chem. Res. (M)* **1980**, 4057.

(6) Reviews: (a) Ojima, I.; Hirai, K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 103. (b) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 45. (c) Brunner, H. *Top. Stereochem.* **1988**, *18*, 129; *Synthesis* **1988**, 645. (d) Chaloner, P. A. *Handbook of Coordination Catalysis in Organic Chemistry*, Butterworths: Boston, 1986; Chapter 7.2. (e) Dickson, R. S. *Homogeneous Catalysis with Compounds of Rhodium and Iridium*; D. Reidel Publishing Co.: Boston, 1985; Chapter 3.11.

(7) (α-Siloxyalkyl)rhodium(III) hydride complexes $(PPh_3)_2$Cl(H)Rh–$CR_2(OSiR'_3)$ are proposed intermediates in these catalytic systems.[8] Cobalt[9] and manganese[10] carbonyl trialkylsilyl compounds $(CO)_xM$–SiR'_3 (x = 4, 5) also incorporate aldehydes and generate unstable α-siloxyalkyl complexes $(CO)_xM$–CH(R)($OSiR'_3$).

(8) (a) Ojima, I.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Sato, T. *J. Organomet. Chem.* **1976**, *122*, 83. Ojima, I.; Kogure, T.; Kumagai, M. *J. Org. Chem.* **1977**, *42*, 1671. Ojima, I.; Kogure, T. *Organometallics* **1982**, *1*, 1390. (b) Hayashi, T.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1976**, *113*, 127. (c) Corriu, R. J. P.; Moreau, J. J. E. *Nouv. J. Chim.* **1977**, *1*, 71. (d) Peyronel, J. F.; Kagan, H. B. *Nouv. J. Chim.* **1978**, *2*, 211. Kagan, H. B.; Peyronel, J. F.; Yamagishi, T. In *Adv. Chem. Ser. No. 173*; King, R. B., Ed.; American Chemical Society: Washington, D.C., 1979; p 50. (e) Kolb, I.; Hetflejs *Collect. Czech. Chem. Commun.* **1980**, *45*, 2224.

(9) (a) Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837. Chatani, N.; Fujii, S.; Yamasaki, Y.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1986**, *108*, 7361. (b) Kovacs, I.; Sisak, A.; Ungvary, F.; Marko, L. *Organometallics* **1988**, *7*, 1025.

(10) (a) Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 147. Gladysz, J. A. *Acc. Chem. Res.* **1984**, *17*, 326. Johnson, D. L.; Gladysz, J. A. *Inorg. Chem.* **1981**, *20*, 2508. (b) Several α-siloxyalkyl manganese and rhenium complexes, including $(CO)_5Mn$–CH_2OSiMe_3 and $(CO)_5M$–CH($OSiMe_3$)Ph, have been characterized. Selover, J. C.; Vaughn, G. D.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1455. Brinkman, K. C.; Vaughn, G. D.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1056. Reference 4b.

(11) Wegman, R. W. *Organometallics* **1986**, *5*, 707.

(12) Jardine, J. F. *Prog. Inorg. Chem.* **1981**, *28*, 63.

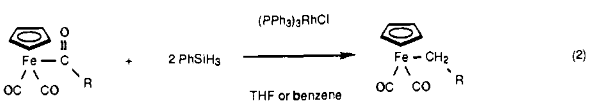
(13) Merck silica gel (60–200 mesh) was used: 1.5 g in a 1.2 × 7.0 cm column suffices for reactions using 0.1–0.3 g of $FpCOCH_3$. Attempted chromatography using longer columns, "flash"-grade silica gel (even at −40 °C), or neutral or basic alumina (activity 3) inevitably decomposes Fp(α-siloxyalkyl) complexes. FpCH($OSiHEt_2$)CH_3 (**1b**) also can be purified by distillation at 70 °C (10^{-3} mm). IR (CH_2Cl_2) 2004, 1943 cm^{-1} (CO), 2095 (w) (SiH); ^1H NMR ($CDCl_3$) δ 5.66 (q, J = 6.1 Hz, FeCH), 4.77 (s, Cp), 4.44 (quint, J = 2.2, SiH), 1.72 (d, J = 6.1, FeCHCH_3), 1.00 (t, J = 7.8, $SiCH_2CH_3$), 0.97 (t, J = 7.8, $SiCH_2CH_3$), 0.65 (m, 4 H, $SiCH_2CH_3$); $\{^1H\}^{13}C$ NMR ($CDCl_3$) δ 217.4 and 216.8 (CO), 86.2 (Cp), 70.4 (FeCH), 35.2 (FeCHCH_3), 6.8 ($SiCH_2CH_3$), 5.5 ($SiCH_2CH_3$), 5.2 ($SiCH_2CH_3$). Anal. Calcd for $C_{13}H_{20}O_3FeSi$: C, 50.63; H, 6.54. Found: C, 50.32; H, 6.77.

(14) Catalyst deactivation could result from it decarbonylating FpCOR to give FpR and $(PPh_3)_2$(CO)RhCl, which does not function as a hydrosilation catalyst. Alexander, J. J.; Wojcicki, A. *Inorg. Chem.* **1973**, *12*, 74. Kuhlmann, E. J.; Alexander, J. J. *J. Organomet. Chem.* **1979**, *174*, 81; *Inorg. Chim. Acta* **1979**, *34*, 197.

(15) (a) Analogous η^1-(α-alkoxyvinyl ether) compounds Cp(L)(CO)Fe–C(OR')=CH_2: (L = CO) Casey, C. P.; Tukada, H.; Miles, W. H. *Organometallics* **1982**, *1*, 1083. (L = PPh_3) Reference 3b. (b) Siloxyvinyl ethers are encountered as byproducts during Rh(I)-catalyzed hydrosilation of ketones, e.g., PhC($OSiR'_3$)=CH_2 from PhC(O)CH_3. Benes, J.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1976**, *41*, 2264. Matsumoto, H.; Hoshino, Y.; Nagai, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1279. Payne, N. C.; Stephan, D. W. *Inorg. Chem.* **1982**, *21*, 182. Lappert, M. F.; Maskell, R. K. *J. Organomet. Chem.* **1984**, *264*, 217. Brunner, H.; Becker, R.; Riepl, G. *Organometallics* **1984**, *3*, 1354. Brunner, H.; Kurzinger, A. *J. Organomet. Chem.* **1988**, *346*, 413. (c) Rh(I)- or Ru(II)-catalyzed homogeneous hydrosilation of organic aldehydes and ketones RC(O)CH_2R' produces neither fully reduced hydrocarbons RCH_2CH_2R' nor vinyl compounds RCH=CHR'.[5,6]

complexes **3b**, **5b**, and **8b**, which are contaminated only by small amounts of silane residues.[16]

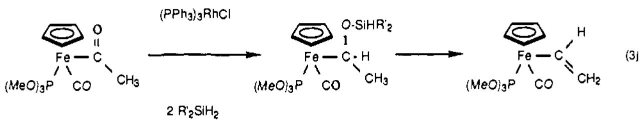
Iron α-diethylsiloxyalkyl complexes **1b–8b**, all yellow-brown oils, also are stable as dichloromethane, benzene, or THF solutions. Their ^{1}H NMR spectra are especially diagnostic, with a Si–H quintet invariably appearing at δ (C_6D_6) 4.4–4.8. The α-methine hydrogen on straight-chain α-siloxyalkyls **2b** and **4b** and on **5b** (Table I) appears as a doublet of doublets due to vicinal coupling with diastereotopic β-methylene hydrogens. Other indications of the chiral centers on **1b–8b** include the presence of diastereotopic Si–ethyl groups (^{1}H and ^{13}C NMR spectroscopy) and diastereotopic carbonyls (^{13}C NMR).



1a R = CH_3
8a R = Ph

Other hydrosilanes have been surveyed for their reactivity in the catalytic hydrosilation of iron acyls. Monohydrosilane Et_3SiH in the presence of $(PPh_3)_3RhCl$ (5 mol %) does not consume $FpCOCH_3$ (**1a**) (10 h, 22 °C) in benzene or THF solutions. Dihydrosilanes Ph_2SiH_2 and $PhMeSiH_2$, reacting analogous to Et_2SiH_2, quantitatively provide their stable α-siloxyethyl Fp complexes **9b** and **10b**, as determined by IR and ^{1}H NMR spectral monitoring.[18] The phenyl-containing dihydrosilanes proved less useful, however, as the isolated products **9b** and **10b** inevitably retained higher boiling disilanes and other silane residues.[16] Trihydrosilane $PhSiH_3$ reacting differently reduces Fp(acetyl) (**1a**) and Fp(benzoyl) (**8a**) in the presence of $(PPh_3)_3RhCl$ catalyst to their alkyl complexes (eq 2).[15c] Isolated yields after column chromatography of Fp(ethyl) (45%) and Fp(benzyl) (70%) are independent of the amount of $PhSiH_3$ used (2–4 mol equiv).

Hydrosilation of trimethyl phosphite substituted acetyl compounds **11a** (eq 3) is complicated by subsequent degradation of siloxyethyl **11b** to its vinyl complex **12**. ^{1}H NMR spectral monitoring of the diphenyl- and diethylsilane reactions with **11a** [1.7–5.0% $(PPh_3)_3RhCl$ and 1.0–2.0 equiv of silane in C_6D_6] clearly indicates that **11b** is the kinetic product. Workup of these reactions and removal of the catalyst (silica gel chromatography) affords product mixtures that range from 1:1 **11b** and **12** to exclusively vinyl complex **12**. In the absence of rhodium catalyst and dihydrosilane, **11b** does not transform to **12**.



11a **11b** **12**

Rh(I)-catalyzed hydrosilation of organoiron acyl complexes with dihydrosilanes occurs under mild conditions at the acyl ligand and produces stable α-siloxyalkyl complexes. Studies in progress are probing the role of Rh(III) hydrosilane adducts in converting iron α-siloxyalkyl complexes to their fully reduced alkyl or vinyl derivatives, surveying potential catalytic systems for hydrosilating a variety of acyl complexes, and extending these hydrosilation reactions to controlling the stereochemistry at the emerging chiral center.

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Supplementary Material Available: Table II containing ^{1}H and ^{13}C NMR and IR spectral assignments for **1b–11b** and **12** and microanalytical data (7 pages). Ordering information is given on any current masthead page.

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[16] In competing side reactions, $(PPh_3)_3RhCl$ efficiently catalyzes both silane redistribution and dehydrogenative coupling of dihydrosilanes to disilanes and oligomeric Si–Si bonded species.[17] Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590.

[17] (a) Yamamoto, K.; Okinoshima, H.; Kumada, M. *J. Organomet. Chem.* **1971**, *27*, C31; **1970**, *23*, C7. (b) Ojima, I.; Inaba, S.-I.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1973**, *55*, C7. (c) Lappert, M. F.; Maskell, R. K. *J. Organomet. Chem.* **1984**, *264*, 217. (d) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 6531. (e) Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381. Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059; *J. Organomet. Chem.* **1985**, *279*, C11; *Can. J. Chem.* **1986**, *64*, 1677. (f) Corey, J. Y.; Chang, L. S.; Corey, E. R. *Organometallics* **1987**, *6*, 1595. (g) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068. (h) Wang, W.-D.; Hommeltoft, S. I.; Eisenberg, R. *Organometallics* **1988**, *7*, 2417.

[18] No reaction occurs between $FpCOCH_3$ in benzene or THF and the dihydrosilanes Ph_2SiH_2 and Et_2SiH_2 in the absence of $(PPh_3)_3RhCl$ catalyst. M. Akita and co-workers (Tokyo Institute of Technology) also have detected **9b** during $(PPh_3)_3RhCl$-catalyzed hydrosilation of FpC(O)CH_3 (**1a**), personal communication.

Ion Conductance along Lipid Monolayers

F. M. Menger,* S. D. Richardson, and G. R. Bromley

Department of Chemistry, Emory University
Atlanta, Georgia 30322

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We report here studies of ion conduction in lipid monolayers at water/air interfaces. Motivation for the work relates in part to the Nobel Prize-winning "chemiosmotic hypothesis" of Peter Mitchell:[1] Proton movement across a membrane creates a potential that drives ATP production. In 1983, Haines[2] proposed that this chemiosmotic flux is coupled to proton translocation *along* the membrane surface. More recently, Prats et al.[3] claimed, on the basis of fluorescent probe data, that protons do indeed diffuse rapidly among lipid headgroups. Gutman et al.,[4] however, strongly denied this assertion, citing evidence derived from a laser-excited proton emitter trapped near a membrane surface. Owing to the obvious importance of lateral ion movement along membranes and to the debate over its efficiency, we felt a direct measurement with electrodes (and requiring no incorporated probe) would be useful.

Lateral ion movement among lipids can in principle be investigated via their monomolecular films (assemblies that are structurally similar to membrane leaflets). Yet to our knowledge, only one published paper has appeared in which conductance of lipid films at various film pressures has been measured directly. Thus, Morgan et al.[5] reported enhanced conductance when a phospholipid monolayer was compressed above a critical packing density (Figure 1). In sharp contrast, we have observed a conductance *decrease* (Figure 2) upon compression of a distearoylphosphatidylcholine (DSPC) film. Details of this surprising result, possible sources of discrepancy with past work, and the mechanism of the interfacial conductance comprise the present communication.

It must be revealed forthwith that severe reproducibility problems were encountered when we (like Morgan et al.[5]) measured conductance with a dc electrical field. Thus, a dc voltage was applied to two bright Pt electrodes immersed in the subphase between the barriers of a film balance.[6] Ultimately we abandoned the dc approach because plots of conductance vs area were acceptably capricious despite a host of precautions and instrumental refinements: (a) A nitrogen atmosphere and Ascarite were used to protect the system from its extreme sensitivity to CO_2.[7] (b) An automatic dipping control was installed to achieve a repro-

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[1] Mitchell, P. *Nature* **1961**, *191*, 144.

[2] Haines, T. H. *Proc. Natl. Acad. Sci. U.S.A* **1983**, *80*, 160.

[3] Prats, M.; Tocanne, J. F.; Teissie, J. *Eur. J. Biochem.* **1985**, *149*, 663. Prats, M.; Tocanne, J. F.; Teissie, J. *J. Membr. Biol.* **1987**, *99*, 225.

[4] Gutman, M.; Nachliel, E.; Moshiach, S. *Biochemistry* **1989**, *28*, 2936.

[5] Morgan, H.; Taylor, D. M.; Oliveira, O. N., Jr. *Chem. Phys. Lett.* **1988**, *150*, 311.

[6] Menger, F. M.; Wood, M. G., Jr.; Richardson, S.; Zhou, Q.; Elrington, A. R.; Sherrod, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 6797. This article describes full experimental details on the precautions required in the use of a film balance (cleanliness, high water purity, etc.).

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