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Transformation of Manganese Acyls $(CO)_5MnC(O)CH_2R$ (R = H, CH_3, OCH_3) into Their Siloxyvinyl Derivatives $(CO)_5MnC(OSiEt_3){=}CHR$ with Triethylsilane. An Approach to Double Carbonylation of Manganese Alkyl Complexes $(CO)_5MnCH_2R$

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Treatment of the manganese acyl complexes $(CO)_5MnC(O)CH_2R$ [R = H (**1a**), CH_3 (**1b**), OCH_3 (**1c**)] with triethylsilane gave stable α-triethylsiloxyvinyl compounds (*Z*)-$(CO)_5MnC(OSiEt_3){=}CHR$ (**3a**−**c**). Carbonylation of **3a** and **3b**, followed by protonolysis of the resulting $(CO)_5MnC(O)C(OSiEt_3){=}CHR$ [R = H (**5a**), CH_3 (**5b**)] provided their α-ketoacyl derivatives $(CO)_5MnC(O)C(O)CH_2R$ (**6a** and **6b**), which represents a net double carbonylation of their alkyl precursors $(CO)_5MnCH_2R$.

Introduction

In a recent communication,[1] Murai and co-workers documented the reductive oligomerization of carbon monoxide involving Rh(I)-catalyzed reactions with hydrosilanes. The presence of the C2 and C3 kinetic products, (*Z*)-1,2-bis(siloxy)ethenes and (*Z*)-1,2,3-tris(siloxy)propenes, was accounted for by the intermediacy of a hypothesized Rh(I) (*E*)-1,2-bis(siloxy)vinyl intermediate, Scheme 1. Addition of hydrosilane to this intermediate before or after carbonylation presumably yields the observed C2 and C3 products. It is this carbonylation of an α-siloxyvinyl complex and subsequent potential ligand reactions that relate to our ongoing studies on the hydrosilation and carbonylation of labile manganese acyl complexes.[2]

Treatment of the manganese acetyl $(CO)_5MnC(O)CH_3$ (**1a**) with 1−2 equiv of a monohydrosilane affords mixtures of α-siloxyethyl $(CO)_5MnCH(OSiR_3)CH_3$ (**2**) and α-siloxyvinyl $(CO)_5MnC(OSiR_3){=}CH_2$ (**3**) complexes. The choice of hydrosilane appears to be the most important consideration in controlling relative proportions of **2** and **3**, which vary from 14/1 with $PhMe_2SiH$ to 1/2 with Et_3SiH.[2a] Their formation was accounted for by an autocatalysis pathway, Scheme 2, in which silane-induced degradation of initially formed **2** or of the starting **1a**[3b] provides the coordinatively unsaturated $(CO)_4MnSiR_3$[3] as the active catalyst for combining substrate **1a** and R_3SiH.[2a]

According to this autocatalysis pathway, the active catalyst $(CO)_4MnSiR_3$ binds **1a** as bimetallic *μ*-acetyl, which rearranges to the unsaturated *μ*-siloxyethylidene **4**, the key catalysis intermediate. Silane addition followed by reductive elimination affords **2**, whereas *β*-deinsertion produces **3**. Both reactions ultimately regenerate the active catalyst, which evidently is unstable and is replenished continuously through the silane-induced decomposition of **2**. It is the *β*-deinsertion step, however, that distinguishes this pathway. Assigning this *β*-elimination step to **4** nicely accounts for generating the α-siloxyvinyl complex **3**, as opposed to forming either (undetected) $CH_3CH_2OSiR_3$ or $CH_2{=}CH(OSiEt_3)$ byproducts from an unsaturated $(CO)_4MnCH(OSiR_3)CH_3$.[2a]

We now report the carbonylation chemistry of the manganese α-triethylsiloxyvinyl complexes **3a**−**3c** (Scheme 3). These were obtained via the triethylsilane reactions with manganese acetyl (**1a**), propionyl (**1b**), and methoxyacetyl (**1c**) compounds, $(CO)_5MnC(O)CH_2R$ (R = H, CH_3, and OCH_3). Subsequent carbonylation of **3a** and **3b** followed by protonolysis of the triethylsiloxy groups then provided the manganese-2-ketoacyl complexes **6a** and **6b**. These overall ligand transformations represent a "double-carbonylation" sequence[4] that converts manganese methyl and ethyl compounds $(CO)_5MnCH_2R$ (precursors to **1a** and **1b**) to their 2-ketoacyl derivatives.

Experimental Section

Synthetic manipulations were performed using a combination of standard Schlenk line, glovebox, and vacuum line procedures.[5] Infrared spectra of benzene solutions were recorded on a Perkin-Elmer FT spectrophotometer, model no. 1600, over the carbonyl *ν*(CO) frequency range (2200−1600

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[1] Chatani, N.; Shinohara, M.; Ikeda, S.-I.; Murai, S. *J. Am. Chem. Soc.* **1997**, *119*, 4303.

[2] (a) Gregg, B. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1996**, *118*, 10069. (b) Hanna, P. K.; Gregg, B. T.; Tarazano, D. L.; Pinkes, J. R.; Cutler, A. R. In *Homogeneous Transition Metal Catalyzed Reactions*; Advances in Chemistry Series No. 230; Moser, W. R., Slocum, D. W., Eds.; American Chemical Society: Washington, DC, 1992; p 491. (c) Gregg, B. T.; Hanna, P. K.; Crawford, E. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1991**, *113*, 384. (d) Mao, Z.; Gregg, B. T.; Cutler, A. R. *Organometallics* **1998**, *17*, 1993.

[3] (a) Gregg, B. T.; Cutler, A. R. *Organometallics* **1993**, *12*, 2006. (b) In the presence of excess $PhMe_2SiH$, this active catalyst intermediate affords a detectable "resting-state" complex $(CO)_4MnH(SiMe_2Ph)_2$: Xu, C.; Tetrick, S. M.; Punia, S.; Cutler, A. R. *J. Am. Chem. Soc.*, submitted for publication.

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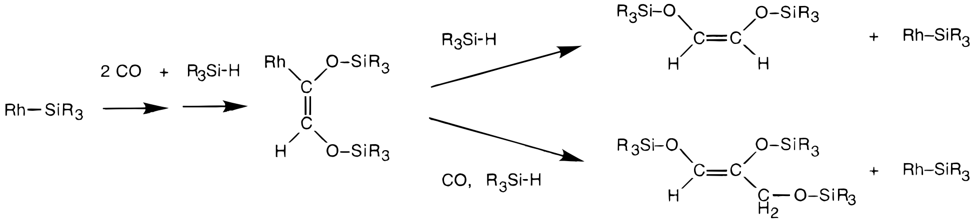
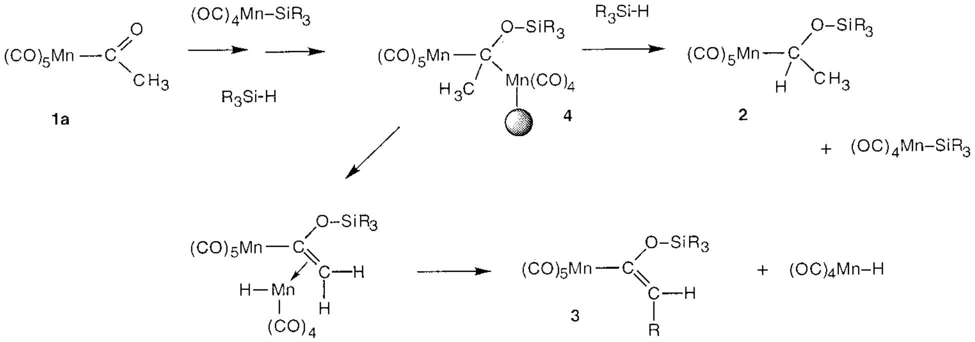
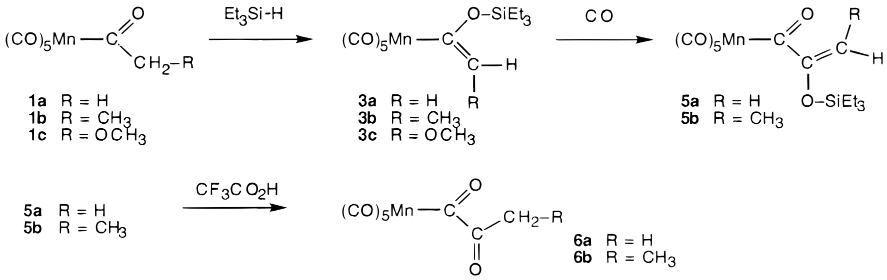
Scheme 1



Scheme 2



Scheme 3



cm^{-1}). NMR spectral data were obtained in C_6D_6 and were reported as δ values relative to residual C_6H_6 (^1H: 7.15 ppm), C_6D_6 (^{13}C: 128.00 ppm), and external $SiMe_4$ (^{29}Si: 0 ppm) using Varian model XL-200 and IBM-WP100 spectrometers. Combustion microanalyses were done by Quantitative Technologies, Bound Brook, NJ.

Organic and inorganic reagents were obtained commercially and used as received; silanes and C_6D_6 were stored in a glovebox under nitrogen. THF and benzene were distilled from sodium benzophenone ketyl. Manganese acyl complexes $(CO)_5MnC(O)CH_3$ (**1a**),[6] $(CO)_5MnC(O)CH_2CH_3$ (**1b**),[7] and $(CO)_5MnC(O)CH_2OCH_3$ (**1c**)[8] were prepared by treating $Mn(CO)_5K$ in THF with the appropriate acyl halide.[9]

Triethylsilane was dried over freshly activated 4 Å molecular sieves and fractionally distilled. Only the fraction that was collected over the boiling point range 107−108 °C was used; its NMR spectral data, ^1H δ 3.87 (sept, $J = 3.1$ Hz, SiH), 0.97 (t, $J = 6.8$, $SiCH_2CH_3$), 0.54 (m, $SiCH_2CH_3$); $^{13}C\{^1H\}$ 8.3 ($SiCH_2CH_3$), 2.9 ($SiCH_2CH_3$); $^{29}Si\{^1H\}$ δ 0.42, are consistent with the absence of the disiloxane Et_6Si_2O, $^{13}C\{^1H\}$ δ 7.0 ($SiCH_2CH_3$), 6.8 ($SiCH_2CH_3$); $^{29}Si\{^1H\}$ δ 9.29, or detectable concentrations of other triethylsilyl derivatives.

Preparation of $(CO)_5MnC(OSiEt_3){=}CH_2$ (3a). A benzene solution (6.0 g) containing $(CO)_5MnC(O)CH_3$ (**1a**) (4.00 g, 16.8 mmol) and triethylsilane (2.93 g, 25.2 mmol) turned from pale yellow to dark orange within 30 min, commensurate with slow, steady gas evolution. After 4 h, the solution was added to a 2 × 5 cm column of activity 3 alumina (neutral)−hexane and eluted with hexane (30 mL). This left a brown layer at the top of the column and removed an orange band, which was evaporated to a mixture of orange solid and oil. The orange residue was extracted with hexane (3 × 4 mL), leaving most of the solid, and the supernatant liquid was transferred to a centrifuge tube. It then was cooled to −78 °C for 5 min and centrifuged to separate additional orange solid. The centrifugate was transferred and evaporated, yielding 3.82 g of spectroscopically pure **3a**[2a] (64%) as an orange oil: IR (C_6D_6) ν(CO) 2086 (w), 2045 (vs), 2017 (s sh) cm^{-1}; ^1H NMR (C_6D_6) δ 5.08 (d, $J = 1.4$ Hz, E-CHH), 4.29 (d, $J = 1.4$, Z-CHH), 1.02 (m, $SiCH_2CH_3$), 0.71 (q, $J = 7.9$, $SiCH_2CH_3$); ^{13}C NMR δ 210.9 (br, CO), 174.1 (COSi), 108.6 (CH_2), 6.9 ($SiCH_2CH_3$), 5.6 ($SiCH_2CH_3$). The combined orange solids, 1.09 g after brief drying, contained primarily $Mn_2(CO)_{10}$ (IR spectroscopy).

Carbonylation of $(CO)_5MnC(OSiEt_3){=}CH_2$ (3a). An orange acetonitrile solution (50 mL) containing **3a** (3.80 g, 10.78 mmol) was added to the glass insert of a Parr Minireactor. This was set up in the Parr pressure reactor, which was fitted with an overhead mechanical stirrer, and the apparatus was pressurized to 1000 psig CO. Three cycles of pressurization−depressurization (to 1 atm) were carried out before the apparatus was left at 1000 psig CO for 3 days. The pressure then was vented, and the remaining pale yellow solution was evaporated to a light yellow oil. This was chromatographed on a 2.5 × 5 cm column of silica gel in hexane, from which a pale yellow band was eluted with additional hexane (30 mL). Removal of solvent left a yellow oil (3.52 g) that was identified spectroscopically as $(CO)_5MnC$-

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[6] Lukehart, C. M.; Torrence, G. P.; Zeile, J. V.; Dombek, B. D.; Angelici, R. J. *Inorg. Synth.* **1990**, *28*, 199.

[7] Coffield, T. H.; Kozikowski, J.; Closson, R. D. *J. Org. Chem.* **1957**, *22*, 598.

[8] Cawse, J. N.; Fiato, R. A.; Pruett, R. L. *J. Organomet. Chem.* **1979**, *172*, 405.

[9] Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553.

$(O)C(OSiEt_3){=}CH_2$ (**5a**) (86% yield): IR (C_6D_6) ν(CO) 2115 (w), 2046 (vs), 2017 (vs br) cm^{-1}, ν(C=O) 1634 cm^{-1}; ^1H NMR (C_6D_6) δ 4.67 (d, $J = 1.5$ Hz, *Z*-C*H*H), 3.78 (d, $J = 1.5$, *E*-CH*H*), 0.91 (m, $SiCH_2CH_3$), 0.68 (m, $SiCH_2CH_3$); ^{13}C NMR δ 250.5 (Mn*C*=O), 209.8 (*C*O), 159.6 (*C*OSi), 87.1 (CH_2), 6.6 ($SiCH_2CH_3$), 4.6 ($SiCH_2CH_3$).

^1H NMR spectra of the product before and after chromatography were consistent with the presence of ≤2% of starting **3a**, although **5a** slowly decarbonylated in solution to regenerate **3a**. For example, a concentrated sample of **5a** in C_6D_6 after a ^{13}C NMR spectral run (3 h) had transformed to **3a** (30%).

Protonolysis of $(CO)_5MnC(O)C(OSiEt_3){=}CH_2$ (5a). Trifluoroacetic acid (0.5 mL, 6.94 mmol) was added dropwise to a light yellow benzene solution (15 mL) of **5a** (861 mg, 2.26 mmol). This immediately produced a dark red solution, which was evaporated (10^{-1} mm), and the resulting red oil was chromatographed on silica gel−hexane (1 × 10 cm column). A pale yellow band that was eluted with hexane (25 mL) contained $Mn_2(CO)_{10}$ and unidentified organic residues. Continued elution with 1/1 hexane−dichloromethane (25 mL) removed a light red band, which after removal of solvent left spectroscopically pure $(CO)_5MnC(O)C(O)CH_3$ (**6a**)[10] as a pink powder, 0.52 g (86% yield). Its IR and ^1H NMR spectral data and its mp of 73−76 °C (previously reported 76−77 °C) are in agreement with Casey's data:[10] IR (C_6D_6) ν(CO) 2118 (w), 2059 (sh), 2023 (vs) cm^{-1}, ν(C=O) 1716 (w), 1640 (m), 1599 (w) cm^{-1}; IR (C_6H_{12}) ν(CO) 2118 (w), 2048 (w, sh), 2026 (vs), 2010 (vs), 1989 (w, sh), ν(C=O) 1720 (w), 1642 (m), 1602 (w) cm^{-1}; ^1H NMR (C_6D_6) δ 1.64 (s, CH_3); ^{13}C NMR δ 261.6 (Mn*C*=O), 209.5 (Mn*C*OCOCH$_3$), 194.2 (MnCO*C*OCH$_3$), 20.5 (CH_3).

Preparation of (*Z*)-$(CO)_5MnC(OSiEt_3){=}CH(CH_3)$ (3b). To a 5 mL vial in the glovebox was added $(CO)_5MnC(O)CH_2CH_3$ (**1b**) (1.00 g, 3.97 mmol), benzene (1.60 g), and $HSiEt_3$ (692 mg, 5.95 mmol). After the light orange solution had turned dark brown (5 h), it was chromatographed on a 2 × 10 cm column of activity 3 alumina with benzene. The orange band that eluted with benzene was evaporated to an orange oily solid. This was extracted with hexane (2 × 5 mL), and the supernatant solution was separated from the $Mn_2(CO)_{10}$ residue and transferred to a centrifuge tube. Cooling the yellow solution (−78 °C) for 5 min afforded additional orange solid, which was collected and identified as $Mn_2(CO)_{10}$. The centrifugate was transferred and evaporated to a light yellow oil (822 mg) that was identified as **3b** (56%): IR (C_6D_6) ν(CO) 2114 (w), 2054 (w), 2015 (vs), 1990 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 5.70 (q, $J = 6.7$ Hz, *E*-C*H*), 1.66 (d, $J = 6.7$, CH_3), 1.00 (m, $SiCH_2CH_3$), 0.65 (m, $SiCH_2CH_3$); ^{13}C NMR δ 210.5 (*C*O), 163.4 (*C*OSi), 116.4 (*C*H), 16.3 (CH_3), 6.9 ($SiCH_2CH_3$), 6.8 ($SiCH_2CH_3$), 5.8 ($SiCH_2CH_3$). Anal. Calcd for $C_{14}H_{19}O_6SiMn$: C, 45.78; H, 5.21. Observed: C, 45.53; H, 4.89.

Carbonylation of (*Z*)-$(CO)_5MnC(OSiEt_3){=}CH(CH_3)$ (3b). An orange acetonitrile solution (20 mL) containing **3b** (460 mg, 1.26 mmol) was pressurized to 1010 psig with CO. After 3 days, the pressure was released, and the resulting light yellow solution was evaporated and chromatographed with hexane on a 2.5 × 5 cm column of flash-grade silica gel. The pale yellow band that was eluted with hexane provided $Mn_2(CO)_{10}$ plus unidentified organic residues. Continued elution of the column with 1/1 hexane−dichloromethane cleanly removed a second yellow band that yielded (*E*)-$(CO)_5MnC(O)C(OSiEt_3){=}CH(CH_3)$ (**5b**) as a yellow oil (406 mg, 80%).

The manganese (α-triethylsiloxy)crotonyl complex **5b** also was synthesized by hydrosilation of manganese propionyl **1b** and then carbonylation of the unpurified **3b**. A benzene solution (10 g) of **1b** (1.50 g, 5.90 mmol) was treated with 1.52 equiv of $HSiEt_3$ (1.04 g, 8.98 mmol) for 5 h. The solution, which had changed from light orange to dark brown, was chromatographed on silica gel−hexane (2.5 × 10 cm column). The orange eluate was concentrated to an orange residue that was dissolved in 20 mL of acetonitrile, and this solution was treated with carbon monoxide (1015 psig) for 3 days. The resulting yellow solution was chromatographed on silica gel with 1/1 hexane−dichloromethane in order to provide **5b** as a yellow oil (1.061 g, 46% overall yield): IR (C_6D_6) ν(CO) 2113 (w), 2046 (sh), 2021 (vs), 2009 (vs), 1999 (sh) cm^{-1}, ν(C=O) 1630 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 4.40 (q, $J = 7.2$ Hz, *Z*-C*H*), 1.65 (d, $J = 7.2$, CH_3), 0.94 (m, $SiCH_2CH_3$), 0.66 (m, $SiCH_2CH_3$); ^{13}C NMR δ 251.6(Mn*C*=O), 209.8 (*C*O), 156.8 (*C*OSi), 97.5 (*C*H), 11.3 (CH_3), 6.9 ($SiCH_2CH_3$), 6.6 ($SiCH_2CH_3$), 5.9 ($SiCH_2CH_3$), 5.1 ($SiCH_2CH_3$).

Protonolysis of (*E*)-$(CO)_5MnC(O)C(OSiEt_3){=}CH(CH_3)$ (5b). A light orange benzene solution (10 mL) of **5b** (630 mg, 1.60 mmol) was treated with trifluoroacetic acid (0.50 mL, 6.94 mmol). The resulting dark red solution was evaporated to a red oil that was chromatographed on a 1 × 10 cm column of silica gel in hexane. A red band was eluted by 1/1 hexane−dichloromethane, which upon evaporation left analytically pure $(CO)_5MnC(O)C(O)CH_2CH_3$ (**6b**) as a pale red powder (412 mg, 89% yield), mp 58−60 °C: IR (C_6D_6) ν(CO) 2118 (m), 2022 (vs) cm^{-1}, ν(C=O) 1714 (w), 1624 (m, br) cm^{-1}; IR (C_6H_{12}) ν(CO) 2118 (w), 2025 (vs), 2009 (vs), 1989 (w, sh) cm^{-1}, ν(C=O) 1717 (w), 1630 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 2.09 (q, $J = 7.2$ Hz, CH_2), 0.79 (t, $J = 7.2$, CH_3); ^{13}C NMR δ 261.3 (Mn*C*=O), 209.0 (Mn*C*OCOCH$_3$), 196.7 (MnCO*C*OCH$_2$), 27.2 (CH_2), 7.1 (CH_3). Anal. Calcd for $C_9H_5O_7Mn$: C, 38.60; H, 1.80. Found: C, 38.31; H, 1.68.

Preparation of (*Z*)-$(CO)_5MnC(OSiEt_3){=}CH(OCH_3)$ (3c). A dark orange C_6D_6 solution (600 mg) containing triethylsilane (174 mg, 1.49 mmol) and $(CO)_5MnC(O)CH_2OCH_3$ (**1c**) (200 mg, 0.74 mmol) was transferred to a 5 mm NMR tube. Gas evolution was evident as the solution turned dark brown over 4 h and over 90% of the **1c** transformed to **3c** (^1H NMR spectral monitoring). The brown solution was chromatographed on a 1 × 10 cm column of silica gel (40 μm, flash grade)−hexane, and the resulting orange hexane eluate (25 mL) was evaporated to an orange oily solid. The combined hexane extracts (3 × 1.5 mL) were cooled to −78 °C, centrifuged, and separated from additional orange solid ($Mn_2(CO)_{10}$). Removal of solvent from the centrifugate left 230 mg of an orange oil that was identified by ^1H and ^{13}C NMR spectroscopy as **3c** (81% yield), although the residual $Mn_2(CO)_{10}$ that was evident by its IR spectrum (<5%) was not eliminated after extensive pumping at 10^{-3} mm. IR (C_6D_6) ν(CO): 2116 (w), 2045 (w), 2018 (vs), 1989 (m) cm^{-1}. ^1H NMR (C_6D_6): δ 6.68 (s, =C*H*), 3.18 (s, OCH_3), 1.03 (m, $SiCH_2CH_3$), 0.73 (m, $SiCH_2CH_3$). ^{13}C NMR δ 210.4 (*C*O), 150.1 (*C*OSi), 143.1 (=*C*H), 58.7 (O*C*H$_3$), 7.0 ($SiCH_2CH_3$), 5.8 ($SiCH_2CH_3$). Anal. Calcd for $C_{14}H_{19}O_7SiMn$: C, 43.98; H, 5.01. Observed: C, 43.37; H, 4.78.

Results and Discussion

Hydrosilation of the Manganese Acyl Complexes $(CO)_5MnC(O)CH_2R$, R = H (1a), CH_3 (1b), and OCH_3 (1c), with Triethylsilane. Treatment of the manganese acyl complexes **1a**−**1c** with 1.5−2.0 equiv of $HSiEt_3$ in benzene solutions for 4−5 h provided the α-triethylsiloxyvinyl complexes **3a**−**3c** in 56−76% isolated yields (eq 1). The reaction conditions chosen optimized the conversion of the parent manganese acetyl **1a** plus triethylsilane to its α-(triethylsiloxy)vinyl derivative **3a**.[2a] Although the α-(triethylsiloxy)ethyl byproduct $(CO)_5MnCH(OSiEt_3)CH_3$ (**2a**) and **3a** independently form, **3a**/**2a** = 2 (Scheme 2), any residual Et_3SiH over the 1 equiv required for forming these products selectively degraded **2a**. From previous attempts to isolate **2a**, we also know that any surviving **2a** would not survive the chromatographic workup on alumina. These

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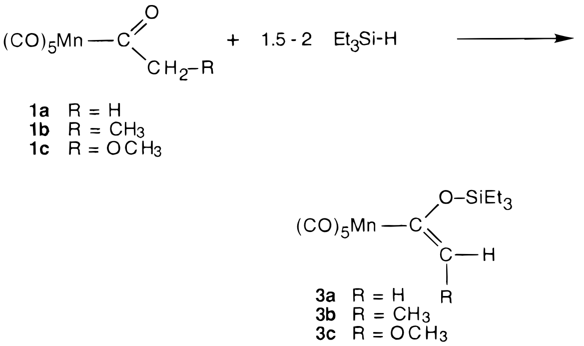
[10] Casey, C. P.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 1166.

degradation routes presumably were the source of the $Mn_2(CO)_{10}$ that made the isolation of pure **3a** so tedious.



1a R = H
1b R = CH3
1c R = OCH3

3a R = H
3b R = CH3
3c R = OCH3

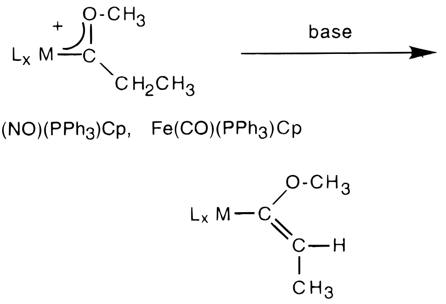
(**1**)

The parent $(CO)_5MnC(OSiEt_3){=}CH_2$ (**3a**) previously had been fully characterized.[2a] Its ^1H NMR spectrum, for example, shows two diagnostic vinylic doublets at δ 5.08 and 4.29 with a small geminal coupling ($^2J = 1.4$ Hz). IR spectra in benzene exhibit the expected three-band pattern for terminal carbonyl $\nu(CO)$ bands between 2120 and 1980 cm^{-1} (with relative intensities weak–medium–very strong/broad) that typify the $(CO)_5MnR$ system with C_{4v} local symmetry.[11]

Triethylsilane also transformed the manganese propionyl **1b** and methoxyacetyl **1c** complexes to the stable (*Z*)-1-(pentacarbonyl)manganese-1-triethylsiloxypropenyl (**3b**) and (*Z*)-1-(pentacarbonyl)manganese-1-triethylsiloxy-2-methoxyvinyl (**3c**) compounds, respectively (eq 1). Under these conditions, we did not detect their potential α-siloxyalkyl byproducts $(CO)_5MnCH(OSiEt_3)CH_2R$ ($R = CH_3$, OCH_3), but they could have formed and then degraded under the reaction conditions. Indeed, considerable amounts of $Mn_2(CO)_{10}$ were present that complicated the purification of **3b** and **3c**.

Complexes **3b** and **3c** were characterized by ^1H, ^{13}C NMR, and IR spectroscopy and by microanalysis. In particular, the ^{13}C NMR spectrum of (*Z*)-$(CO)_5MnC(OSiEt_3){=}CHCH_3$ (**3b**) has C_α and C_β resonances (δ 163.4 and 116.4) that are similar to values reported for (*Z*)-$Cp(PPh_3)(NO)ReC(OCH_3){=}CHCH_3$ (δ 162.6 and 102.9).[12] The *Z*-configurations for **3b** and **3c** were assigned from the results of difference NOE ^1H NMR experiments.[13] Irradiation of the triethysilyl methylene groups for **3b** and **3c** thus gave positive enhancements for the vinyl hydrogen absorptions and less intense negative enhancements (indirect NOE) for geminal vinyl methyl and methoxy resonances.

A number of similar mono- and bimetallic 1-oxyvinyl complexes had been characterized. Interest in these 1-oxyvinyl systems centers on (1) using nucleophilic α-metaloxyvinyl or α-alkoxyvinyl compounds $L_xMC(OR){=}CHR$ to form carbon–carbon bonds[14] and (2) transforming acyl ligands to bimetallic $\mu(\eta^1\text{-C}:\eta^1\text{-O})$ ketene (or enolate) complexes.[15] α-Alkoxyvinyl compounds, for example, typically result from deprotonating alkoxycarbene compounds,[16] as exemplified by syntheses of the (*Z*)-rhenium and iron alkoxy-1-propenyl compounds (eq 2) by the Gladysz[12] and Davies[17] groups, respectively.



L_xM = Re(NO)(PPh3)Cp, Fe(CO)(PPh3)Cp

(**2**)

Organometallic 1-oxyvinyl enolates[18,19] $L_xMC(O^-){=}CHR$ are precursors to other 1-oxyvinyl compounds. Floriani accordingly trapped $Cp(PPh_3)(CO)FeC(O){=}CH_2^-$ as its titanoxy and zirconoxy derivatives $Cp(PPh_3)(CO)FeC(OMClCp_2){=}CH_2$.[20] Attempts to generate the corresponding α-siloxyvinyl complex $Cp(PPh_3)(CO)FeC(OSiMe_3){=}CH_2$ by silylating the same enolate instead gave $Cp(PPh_3)(CO)FeC(O)CH_2SiMe_3$.[18b,c] Gladysz converted the analogous rhenium α-silylacetyl to its α-siloxyvinyl tautomer $Cp(PPh_3)(NO)ReC(OSiMe_3){=}CH_2$.[18g]

The extensive literature of $Mn(CO)_5$ chemistry[21] also includes several examples of 1-oxyvinyl complexes. Thus 5-$(CO)_5$Mn-2(3*H*)-furanone and 6-$(CO)_5$Mn(−3,4-dihydro-2*H*)-pyran-2-one complexes **7**[22] and the recently reported $Mn_2(CO)_9\{\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$ (**8**)[23] con-

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[11] These fundamental carbonyl $\nu(CO)$ stretching frequencies are assigned (in decreasing frequency) as having A_1, B_1, and ($E + A_1$) symmetry. Some $Mn(CO)_5R$ complexes reported herein have four terminal carbonyl $\nu(CO)$ bands due to the appearance of separate E (very intense, broad) and A_1 (medium-intensity, 20–40 cm^{-1} lower in energy) fundamentals. This band splitting is associated with the presence of "less symmetrical" alkyl or acyl ligands R on $(CO)_5MnR$. (a) Cotton, F. A.; Musco, A.; Yagupsky, G. *Inorg. Chem.* **1967**, *6*, 1357. (b) Kaesz, H. D.; Bau, R.; Hendrickson, D.; Smith, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2844. (c) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, 1975; pp 72, 223.

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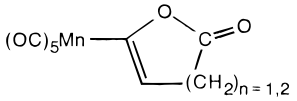
tain 1-oxyvinyl functionalities. A particularly intriguing example is the trimethylsilyl enol ether derivative **9** of the bimetallic μ-malonyl compound Cp*(NO)(PPh$_3$)Re[μ-(COCH$_2$CO)-C^1,O^3:C^3]Mn(CO)$_4$, which O'Connor used in establishing keto–enol tautomerization of metal acyl systems.[24]



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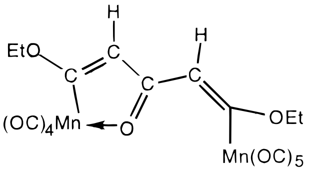

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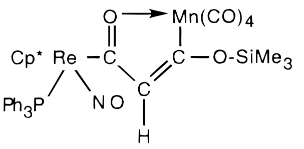
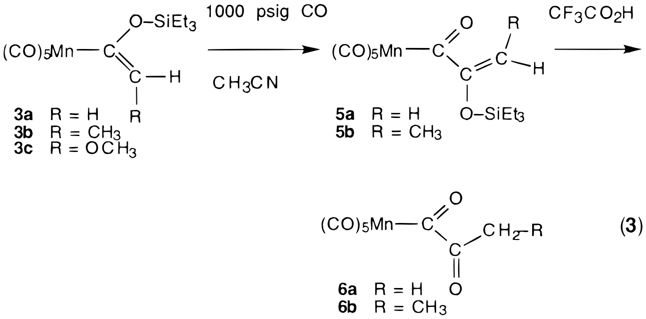


9

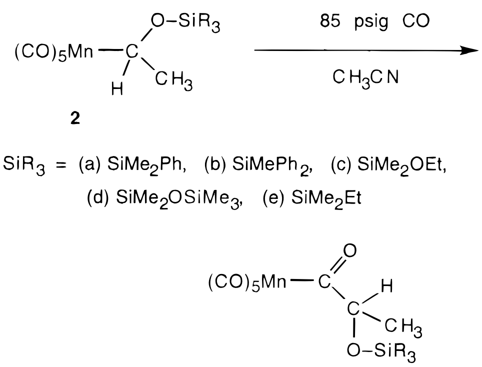
Carbonylation of the α-(Triethylsiloxy)vinyl Complexes (CO)$_5$MnC(OSiEt$_3$)=CH$_2$ (3a) and (*Z*)-(CO)$_5$MnC(OSiEt$_3$)=CHCH$_3$ (3b): Synthesis of Their α-Ketoacyl Derivatives (CO)$_5$MnC(O)C(O)R, R = Me, Et. Carbonylation of (CO)$_5$MnC(OSiEt$_3$)=CH$_2$ (**3a**) and (*Z*)–(CO)$_5$MnC(OSiEt$_3$)=CHCH$_3$ (**3b**) afforded (pentacarbonyl)manganese (α-triethylsiloxy)acryloyl **5a** and (*E*)-(α–triethylsiloxy)crotonyl **5b** complexes (eq 3) in over 80% isolated yields. These reactions required 1000 psig CO for 3 days in acetonitrile; attempted carbonylation of **3a** at 80 psig CO in benzene, THF, or acetonitrile returned starting material. Even in acetonitrile at 1000 psig CO, (*Z*)-(CO)$_5$MnC(OSiEt$_3$)=CH(OCH$_3$) (**3b**) proved inert.



(3)

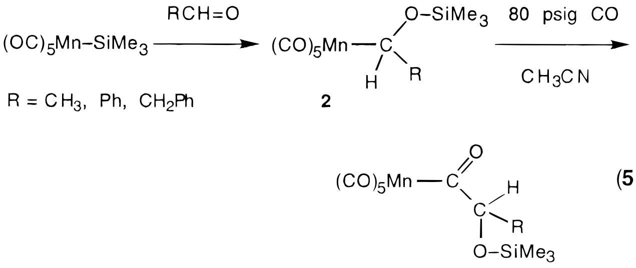
Both **5a** and **5b** are stable, yellow oils that have distinctive ^{1}H and ^{13}C NMR and IR spectra. Medium-intensity IR ν(C=O) bands at 1634 and 1630 cm^{-1}, respectively, and ^{13}C NMR absorptions at δ 251 are consistent with the presence of an acyl ligand. Similar acyl absorptions (1653 cm^{-1}, δ 251) occur for (CO)$_5$MnC(O)CH$_3$ (**1a**). Remaining IR ν(CO) bands for the terminal carbonyls on **5a** and **5b** closely resemble those of their (α-triethylsiloxy)vinyl precursors **3a** and **3b**. ^{1}H and ^{13}C NMR spectral absorptions for the vinyl positions on **5a** and **5b** show distinct upfield shifts, 0.8–1.3 ppm (^{1}H NMR) and 6–18 ppm (^{13}C NMR), with respect to **3a** and **3b**.

The rather demanding carbonylation conditions for generating **3a** and **3b** contrast the 85 psig CO that we used in carbonylating (α-trialkylsiloxy)ethyl complexes **2**.[2a] For these reactions, 1 h of carbonylation in CH$_3$CN produced (CO)$_5$MnC(O)CH(OSiR$_3$)CH$_3$ in high yields (eq 4). Gladysz and co-workers[25] previously used up to 200 psig CO to intercept and derivatize their unstable (α-trimethylsiloxy)alkyl complexes **2** (eq 5).



SiR$_3$ = (a) SiMe$_2$Ph, (b) SiMePh$_2$, (c) SiMe$_2$OEt, (d) SiMe$_2$OSiMe$_3$, (e) SiMe$_2$Et

(**4**)



(**5**)

The difficulty experienced in carbonylating **3a** and **3b** presumably corresponds to the sluggish alkyl–CO migratory insertion step,[26,27] since **5a** only slowly decarbonylated to **3a** in the absence of a CO atmosphere (30% deinsertion over 3 h). The same electronic effects[27] that inhibit carbonylation of (CO)$_5$MnCH$_2$OR (R = CH$_3$, SiMe$_3$)[8,28] and (CO)$_5$MnPh vs (CO)$_5$MnCH$_3$[27b] evidently apply to carbonylating **3a** and **3b**. The vinyl and α-siloxy functionalities on **3a** and **3b** thus retard their carbonylation, and the presence of an additional electronegative methoxy group on (*Z*)-(CO)$_5$MnC(OSiEt$_3$)=CH(OCH$_3$) (**3c**) ultimately prevented CO incorporation.

Protonolysis of (α-triethylsiloxy)vinyl compounds **5a** and **5b** with excess trifluoroacetic acid in benzene provided the α-ketoacyl complexes (CO)$_5$MnC(O)C(O)R

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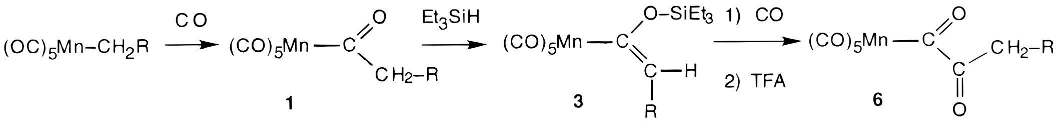
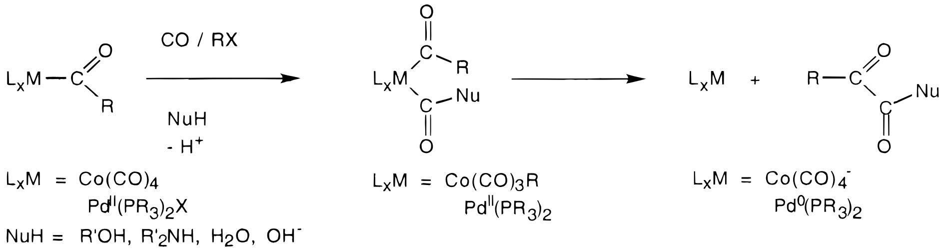
Scheme 4



Scheme 5



[R = CH_3 (**6a**), CH_3CH_2 (**6b**)] (eq 3). These α-ketoacyl complexes were isolated in 86–89% yields as stable pink solids after column chromatography of the reaction mixtures. The pyruvoyl **6a** previously had been synthesized by Casey[10] as the metathesis product of $(CO)_5Mn^-Na^+$ and pyruvoyl chloride; its X-ray crystallographic structure determination established an s-trans conformation for the acyl carbonyls. The appearance of several IR ν(CO) bands for **6a** in the 1720–1600 cm^{-1} region (three to five, depending on the solvent) suggests that syn and anti conformers equilbrate in solution. IR and ^{13}C NMR spectral data for the fully characterized manganese-2-ketobutyryl **6b** closely correspond to those of **6a**; for example, ^{13}C NMR absorptions for the manganese acyl and keto carbons occur at δ 261, 197 (**6b**) and δ 262, 194 (**6a**).

Double Carbonylation. The set of ligand reactions involved in transforming manganese methyl and ethyl complexes $(CO)_5MnCH_2R$ into their α-ketoacyl derivatives $(CO)_5MnC(O)C(O)CH_2R$ (**6a**, R = H; **6b**, R = CH_3) (Scheme 4) represents a novel form of double carbonylation. Hydrosilation of the acetyl **1a** and propionyl **1b** intermediates—the single carbonylation products[26]—yields their (α-triethylsiloxy)vinyl derivatives $(CO)_5MnC(OSiEt_3){=}CHR$ (**3a** and **3b**). These siloxyvinyl derivatives, after carbonylation and protonolysis, then afford the double-carbonylation products **6a** and **6b** (Scheme 4).

These α-ketoacyl derivatives **6a** and **6b** are not accessible by direct carbonylation of **1a**[10] and **1b**. Indeed, few examples of acyl-to-CO migratory insertion are known,[29] since equilibria involving acyl to α-ketoacyl complexes generally are disfavored.[8,10,30] Masking **1a** and **1b** as their siloxyvinyl derivatives **3a** and **3b**, however, facilitates the second carbonylation. The double-carbonylation sequence presented in Scheme 4 thus is unusual in that α-ketoacyl products originate through carbonylation of the initial acyl complex only after it is converted to a more labile siloxyvinyl derivative. Subsequent hydrolysis reinstates the original acyl group that is now part of the new ketoacyl ligand.

Double carbonylation usually refers to metal-catalyzed transformation of an aryl or benzyl halide, base, and two CO molecules into organic α-ketoacid derivatives.[4,31] Typical double-carbonylation catalytic systems incorporate bis-phosphine palladium complexes or $Co_2(CO)_8$ under basic (phase-transfer catalytic) conditions. Scheme 5 outlines the accepted mechanism by which both catalytic systems promote double carbonylation of aryl halides to give either α-ketoamides[32] and α-ketoesters[33] (with Pd) or α-ketoacids[9c,34a] (with Co). Both catalytic systems have in common generating $(PR_3)_2Pd$(acyl)(carbamoyl) and $(PR_3)_2Pd$(acyl)(alkoxycarbonyl) or $(CO)_3(CH_3)Co$(aroyl)(hydroxycarbonyl) intermediates that reductively eliminate their organic dione products.

Organometallic α-ketoacyl complexes evidently are not involved in these double-carbonylation catalytic cycles. Although a number of α-ketoacyl complexes have been characterized,[29,30,35] including $(CO)_5MnC(O)C(O)R$, R = CH_3, CH_2Ph, OEt, and Ph,[8,9,10,36] mecha-

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[31] Other versions of double carbonylation include oxidation of nucleophilic metal acyl complexes,[31a] carbonylation of η^1-allenyl compounds,[31b] and carbonylation of group 4 transition metal, lanthanide, and actinide alkyl complexes.[31c] (a) Periasamy, M.; Devasagayaraj, A.; Radhakrishnan, U. *Organometallics* **1993**, *12*, 1424. (b) Wouters J. M. A.; Avis, M. W.; Elsevier: C. J.; Kyriakidis, C. E.; Stam, C. H. *Organometallics* **1990**, *9*, 2203. (c) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. Petersen, J. L.; Egan, J. W. *Organometallics* **1987**, *6*, 2007, and references therein.

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nistic studies involving independently prepared $(PR_3)_2$-(X)PdC(O)C(O)R have proved to be the most informative.[30c,35] These fully characterized palladium α-ketoacyl complexes neither transform into organic α-ketoacid derivatives nor enter into the double-carbonylation catalytic cycle. In contrast, several acyl–carbamoyl and acyl–alkoxycarbonyl palladium compounds $(PR_3)_2Pd[C(O)R][C(O)Nu]$ (Nu = NR_2, OR) have been established as intermediates for these double-carbonylation systems.[37] Analogous but more stable platinum bis-acyl complexes are proving to be useful for elucidating finer points of this bis-acyl double-carbonylation mechanism, such as cis–trans isomerization of the bis-acyl intermediates.[38]

Tetracarbonylcobalt α-ketoester complexes also are known,[30e,f] but they are not likely intermediates in $Co_2(CO)_8$-catalyzed double carbonylation.[4] Double carbonylation of aryl halides under these conditions involves transient anionic aroyl–hydroxycarbonyl cobalt compounds $(CO)_3Co[C(O)Ar][C(O)OH]^-$ and $(CO)_3Co$-$[C(O)Ar][C(O)OH](CH_3)$.[34,39] Recently, Yamamoto and co-workers reported similar benzoyl–carbamoyl complexes $(PR_3)(CO)_2Co[C(O)Ph][C(O)NR_2]^-$, which underwent oxidatively induced reductive elimination of PhC-(O)C(O)NR_2.[40]

An alternative to the bis-acyl mechanism (Scheme 5) has been advanced for $Co_2(CO)_8$-catalyzed double carbonylation of benzylic halides.[4,41] Foá and co-workers proposed that the second carbonylation intercepts a cobalt acyl enol $(CO)_4CoC(OH)=CHPh$ to give $(CO)_4CoC$-(O)C(OH)=CHPh, which tautomerizes to $(CO)_4CoC$-(O)C(O)CH_2Ph. Basic hydrolysis then releases arylglyoxylic acids and regenerates $Co(CO)_4^-$. Unfortunately, only indirect evidence exists for the hypothesized equilibration of cobalt carbonyl acyl complexes with their enol tautomers.[41e,42]

Conclusions

Treatment of the manganese acyl complexes $(CO)_5$-$MnC(O)CH_2R$ [R = H (**1a**), CH_3 (**1b**), OCH_3 (**1c**)] with triethylsilane in benzene afforded stable α-triethylsiloxyvinyl compounds (*Z*)-$(CO)_5MnC(OSiEt_3)=CHR$ (**3a**–**c**) (eq 1), which were isolated in moderate yields (56–76%). Carbonylation of the α-triethylsiloxyvinyl complexes **3a** and **3b** at 1000 psig CO (in acetonitrile), followed by protonolysis of the resulting acyl compounds $(CO)_5MnC(O)C(OSiEt_3)=CHR$ [R = H (**5a**), CH_3 (**5b**)], provided their α-ketoacyl derivatives $(CO)_5MnC(O)C$-(O)CH_2R **6a** and **6b** (eq 3). Since the starting acyl complexes **1** are available through carbonylation of their aklyl precursors $(CO)_5MnCH_2R$, the subsequent transformation of **1** to their α-ketoacyl derivatives **6** amounts to a novel double-carbonylation procedure (Scheme 4). The novelty of this procedure lies in the formation of the α-ketoacyl compounds **6** as the final products, which are not the anticipated products for other examples of double-carbonylation procedures.

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