Reactivity of Cobalt Acetyl Complexes $(PR_3)(CO)_3CoCOCH_3$ toward Monohydrosilanes

Brian T. Gregg and Alan R. Cutler*

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180

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Monohydrosilanes HSiR$'_3$ (SiR$'_3$ = SiMe$_2$Ph, SiMeEt$_2$, SiEt$_3$, SiPh$_3$) cleave the cobalt acetyl complexes CH$_3$C(O)Co(CO)$_3$(PR$_3$) (PR$_3$ = PPh$_2$Me, PPh$_3$) in C$_6$D$_6$ at room temperature to give the cobalt silyl compounds R$'_3$SiCo(CO)$_3$(PR$_3$) and ethoxysilanes. Neither acetaldehyde nor the α-siloxyethyl complexes CH$_3$CH(OSiR$'_3$)Co(CO)$_3$(PR$_3$) were detected by NMR spectral monitoring, irrespective of whether 1 or 2 equiv of HSiR$'_3$ was used. Six cobalt silyl compounds were isolated in 85–95% yields and were fully characterized, including by ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectroscopy. Further studies involving the reaction between CH$_3$C(O)Co(CO)$_3$(PPh$_2$Me) and HSiMe$_2$Ph afforded the following observations. (1) The presence of CO (1 atm) or free phosphine (1 equiv) inhibits this reaction. (2) Wilkinson's compound, RhCl(PPh$_3$)$_3$, has no effect. (3) Benzaldehyde (1 equiv) inhibits this reaction, whereas acetaldehyde undergoes hydrosilation to give EtOSiMe$_2$Ph. The cobalt acetyl also is an effective acetaldehyde hydrosilation catalyst. (4) The cobalt silyl compound PhMe$_2$SiCo(CO)$_3$(PPh$_2$Me), in contrast, neither undergoes silyl exchange (with HSiEt$_3$) nor catalyzes hydrosilation of acetaldehyde under our standard reaction conditions. These results are compared with those of previous studies involving reactions between CH$_3$C(O)Co(CO)$_3$(PPh$_3$) and HSiEt$_3$ or HSiPh$_3$ in THF at 50 °C/1 atm CO and between the manganese acetyl CH$_3$C(O)Mn(CO)$_5$ and HSiR$'_3$. Mechanistic alternatives are outlined.

Introduction

Treating labile cobalt carbonyl acyl complexes[1] CH$_3$C-(O)Co(CO)$_3$(PPh$_2$Me) (1)[2] or CH$_3$C(O)Co(CO)$_3$(PPh$_3$) (2)[3] with a hydrosilane should release acetaldehyde and form cobalt silyl compounds. This prediction is consistent with the results of hydrogenating 1 and 2 (to release primarily acetaldehyde)[2a,4,5] plus the belief that hydrogenation and hydrosilation of coordinated ligands engender similar mechanisms.[6] Supporting evidence for this prediction comes from a study by Wegman:[4] both Et$_3$SiH and Ph$_3$SiH cleave 2 in THF (at 50 °C and 1 atm of CO) to give a cobalt silyl complex plus acetaldehyde (eq 1).[7] The reaction using Et$_3$SiH (in 10-fold excess) is first-order in 2 and must be studied at 50 °C in order to obtain reasonable rates.
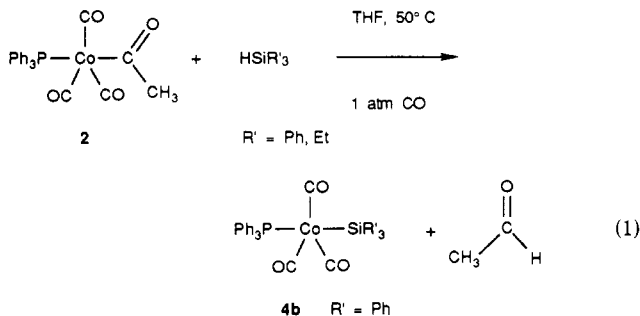
Results of related studies, however, indicate that these hydrosilation reactions are more involved, with at least one competing pathway affording α-siloxyalkyl complexes. Markó and co-workers thus postulated that the α-siloxy-isobutyl compound Me$_2$CHCH(OSiEt$_3$)Co(CO)$_4$ forms as an intermediate during the hydrosilation of the parent acyl complex.[7] The related α-siloxyalkyl compounds RCH-(OSiEt$_3$)Co(CO)$_3$(PPh$_3$) have been advanced by Murai et al.[8,9] as presumed intermediates during Co$_2$(CO)$_8$/PPh$_3$-catalyzed transformation of aldehyde (RCHO), HSiR$'_3$, and CO to the α-siloxyaldehydes RCH(OSiR$'_3$)CHO. A third outcome of these hydrosilation reactions recently was noted by Akita and co-workers for the Et$_3$SiH cleavage of 2 to give CH$_3$CH$_2$OSiEt$_3$.[10a]

The cobalt acyl hydrosilation chemistry could resemble that documented for the isolobal manganese compounds RC(O)Mn(CO)$_5$, a plausible possibility given that both sets of acyl complexes undergo similar reactions.[11] Hydrosilanes selectively transform these manganese acyl complexes (R = CH$_3$, CH$_2$CH$_3$, CH$_2$OMe, Ph, CH$_2$Ph) into a surprising array of hydrosilation products (Figure 1),[12] depending on the choice of reaction conditions.

Distinct features of these manganese acyl hydrosilation reactions are that they (1) occur rapidly and quantitatively

(1) (a) Galamb, V.; Pályi, G. *Coord. Chem. Rev.* **1984**, *59*, 203. (b) Kemmitt, R. D. W.; Russell, D. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 5, Chapter 34.3. (c) Wender, I., Pino, P., Eds. *Organic Synthesis via Metal Carbonyls*; Wiley: New York, 1977; Vol. 2, Chapters 1–3.

(2) (a) Martin, J. T.; Baird, M. C. *Organometallics* **1983**, *2*, 1073. (b) Tso, C. C.; Cutler, A. R. *Organometallics* **1986**, *5*, 1834.

(3) (a) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1962**, *84*, 2499. (b) Roper, M.; Schieren, M.; Heaton, B. T. *J. Organomet. Chem.* **1986**, *299*, 131.

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

(5) (a) Mirbach, M. F. *J. Organomet. Chem.* **1984**, *265*, 205. (b) Ungváry, F.; Markó, L. *Organometallics* **1983**, *2*, 1608. (c) Kovács, I.; Ungváry, F.; Markó, L. *Organometallics* **1986**, *5*, 209. (d) Verslius, L.; Ziegler, T. *Organometallics* **1990**, *9*, 2985 and references therein. (e) Wood, C. D.; Garrou, P. E. *Organometallics* **1984**, *3*, 170.

(6) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
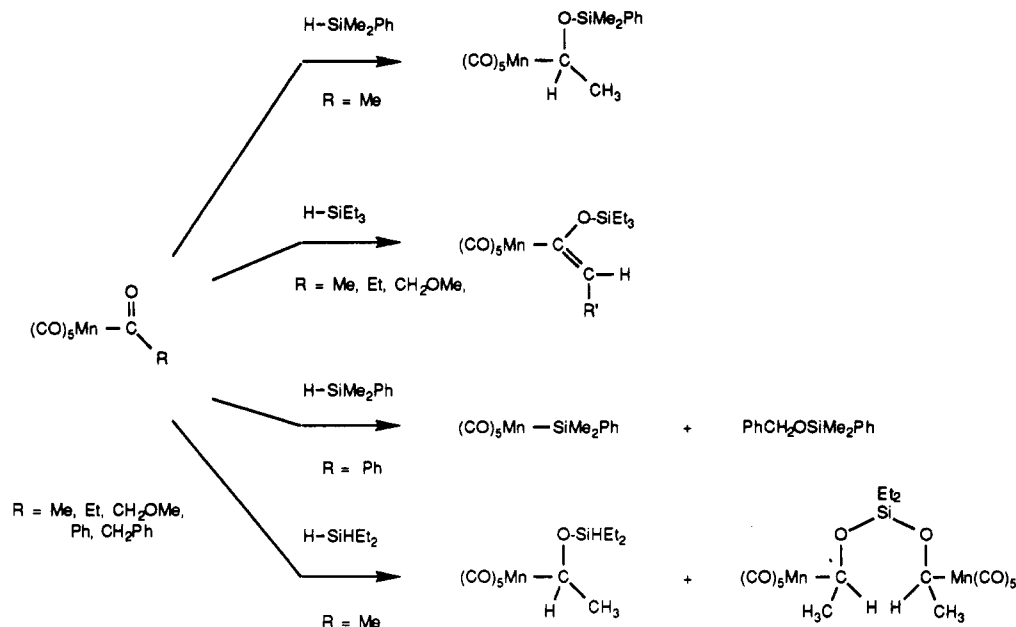
(7) This work has been repeated: Kovács, I.; Sisak, A.; Ungváry, F.; Markó, L. *Organometallics* **1988**, *7*, 1025.

(8) (a) Murai, S.; Toshikazu, K.; Sonoda, N.; Seki, Y.; Kawamoto, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 393. (b) Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837. (c) Murai, S.; Seki, Y. *J. Mol. Catal.* **1987**, *41*, 197.

(9) (a) Typical catalysis conditions: 3 RCHO plus 1 HSiEt$_2$Me in the presence of 50 bar of CO and 0.04 equiv of Co$_2$(CO)$_8$ and PPh$_3$ (1:1) in benzene at 100 °C. The postulated reaction pathway entails first forming Et$_2$MeSiCo(CO)$_3$(PPh$_3$) and then adding it across aldehyde[7,9b] to give RCH(OSiEt$_2$Me)Co(CO)$_3$(PPh$_3$). Subsequent carbonylation and then oxidative addition of hydrosilane presumably releases the observed product. (b) Adding a metal silyl across an aldehyde has been thoroughly documented for Me$_3$SiMn(CO)$_5$: Gladysz, J. A. *Acc. Chem. Res.* **1984**, *17*, 326. Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 147.

(10) (a) Akita, M.; Mitani, O.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 527. (b) Akita, M.; Mitani, O.; Sayama, M.; Moro-oka, Y. *Organometallics* **1991**, *10*, 1394. These publications report Rh(Cl)(PPh$_3$)$_3$-catalyzed hydrosilation of (CO)$_5$MnC(O)R.

(11) (a) Kovács, I.; Hoff, C. D.; Ungváry, F.; Markó, L. *Organometallics* **1985**, *4*, 1347. (b) See ref 1c.

(12) (a) Gregg, B. T.; Hanna, P. K.; Crawford, E. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1991**, *113*, 384. (b) Gregg, B. T.; Cutler, A. R., manuscripts in preparation. (c) Hanna, P. K.; Gregg, B. T.; Tarazano, D. L.; Pinkes, J. R.; Cutler, A. R. *New Science in Transition Metal Catalyzed Reactions*; Advances in Chemistry Series; American Chemical Society: Washington, DC, in press.

Figure 1.

at room temperature using 1–2 equiv of hydrosilane, (2) are inhibited by the presence of CO (1 atm), (3) do not afford free aldehyde, and (4) do not require a catalyst.[10,12] The starting manganese acetyl and benzoyl complexes (R = CH_3, Ph), however, function as excellent hydrosilation catalysts for aldehydes[12a] and other organotransition-metal acyl compounds.[13,14] These results complement those of Wegman,[4] in which $HSiEt_3$ had been reported to cleave the manganese acetyl $CH_3C(O)Mn(CO)_5$ (at 25 °C/1 atm of CO) and eliminate acetaldehyde.

We now document the reactions of monohydrosilanes with the cobalt acetyl complexes $CH_3C(O)Co(CO)_3$-(PPh_2Me) (1), $CH_3C(O)Co(CO)_3(PPh_3)$ (2)[1,2] and CH_3C-$(O)Co(CO)_2(dppe)$ (dppe = $Ph_2PCH_2CH_2PPh_2$)[15] at room temperature in the absence of exogenous CO. Our impetus for the present study was to first find conditions that produce the cobalt α-siloxyalkyl compounds RCH-$(OSiR'_3)Co(CO)_3(PR_3)$ from their acyl precursors and then to link these hydrosilation reactions with a subsequent carbonylation step (thus producing a new acyl complex). These cobalt systems were chosen because of the ease of forming their acyl complexes through carbonylation (typically at 1 atm of CO).[16] Iterating acyl ligand hydrosilation (reduction) and then carbonylation sequences, in principle,[15a] could then generate the homologous siloxymethylene acyl compounds RCH(OSiR'_3)[CH(OSiR'_3)]_nC(O)Co-$(CO)_3(PR_3)$.

Experimental Section

Synthetic manipulations were performed using a combination of standard Schlenk-line (for syringe–septum solution transfer), glovebox, and vacuum-line procedures.[17] 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 cm^{-1}). NMR spectral data were obtained in C_6D_6 and were reported at δ values relative to residual C_6H_6 (^1H, 7.15 ppm), C_6D_6 (^{13}C, 128 ppm), external $SiMe_4$ (^{29}Si, 0 ppm), and external H_3PO_4 (^{31}P, 0 ppm) using Varian Model XL-200 and IBM WP100 spectrometers. $^{29}Si\{^1H\}$ NMR spectra of concentrated C_6D_6 solutions containing $Cr(acac)_3$ (0.5 mol %) were run using single-pulse techniques. These ^{29}Si NMR spectra typically were recorded using inverse gated decoupling for ~500 transients (<1 h) with a pulse angle of 90° and a 1-s delay time. 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. Dichloromethane was distilled under nitrogen from P_2O_5; THF and benzene were distilled from sodium benzophenone ketyl. The cobalt carbonyl dimer $[Co(CO)_3(PPh_2Me)]_2$[2] and $RhCl(PPh_3)_3$[18] were prepared by literature procedures and judged pure by IR and ^1H NMR spectroscopy. The activity of $RhCl(PPh_3)_3$ was checked frequently by carrying out control hydrosilation reactions of $CH_3C(O)Fe(CO)_2Cp$.[14b] The yellow cobalt acetyl complexes $CH_3C(O)Co(CO)_3(PPh_2Me)$ (1),[2] CH_3C-$(O)Co(CO)_2(PPh_3)$ (2),[2a,3] and $CH_3C(O)Co(CO)_2$-$(Ph_2PCH_2CH_2PPh_2)$[15a] were prepared as we previously reported.

NMR spectral data (in C_6D_6) for ethoxysilanes are as follows.[19] $EtOSiMe_2Ph$: ^1H NMR δ 7.57 (m, 2 H, Ph), 7.20 (m, 3 H, Ph), 3.57 (q, J = 7.0 Hz, OCH_2CH$_3$), 1.11 (t, J = 7.0, OCH$_2$CH_3), 0.33 (s, SiCH$_3$); $^{13}C\{^1H\}$ NMR δ 138.7 (ipso Ph), 133.7, 129.6 (Ph), 58.6 (CH_2CH$_3$), 18.7 (CH$_2$CH_3), -1.6 (SiCH$_3$); $^{29}Si\{^1H\}$ NMR δ 6.11. $EtOSiMe_2Et$: ^1H NMR δ 3.52 (q, J = 7.0 Hz, OCH_2CH$_3$), 1.10 (t, J = 7.0, OCH$_2$CH_3), 0.97 (t, J = 8.0, SiCH$_2$CH_3), 0.54 (q, J = 8.0, SiCH_2CH$_3$), 0.07 (s, SiCH$_3$); $^{13}C\{^1H\}$ NMR δ 58.2 (OCH_2CH$_3$), 18.7 (OCH$_2$CH_3), 8.5 (SiCH$_2$CH_3), 6.9 (SiCH_2CH$_3$), -2.5 (SiCH$_3$); $^{29}Si\{^1H\}$ NMR δ 16.44. $EtOSiEt_3$: ^1H NMR δ 3.55 (q, J = 6.9 Hz, OCH_2CH$_3$), 1.11 (t, J = 7.0, OCH$_2$CH_3), 0.96 (m, SiCH$_2$CH_3), 0.56 (m, SiCH_2CH$_3$); $^{13}C\{^1H\}$ NMR δ 58.4 (OCH_2CH$_3$), 18.5 (OCH$_2$CH_3), 6.9 (SiCH$_2$CH_3), 4.9 (SiCH_2CH$_3$); $^{29}Si\{^1H\}$ NMR δ 17.32. $EtOSiPh_3$: ^1H NMR δ 7.61 (m, Ph), 7.20 (m, Ph), 3.78 (q, J = 6.9 Hz, OCH_2CH$_3$), 1.13 (t, J = 6.9, OCH$_2$CH_3); $^{13}C\{^1H\}$ NMR δ 135.2 (ipso Ph), 135.8, 130.1, 128.1 (Ph), 59.8 (CH_2CH$_3$), 18.5 (CH$_2$CH_3); $^{29}Si\{^1H\}$ NMR δ -13.04.

(13) Hanna, P. K.; Gregg, B. T.; Cutler, A. R. *Organometallics* **1991**, *10*, 31.

(14) Other examples of hydrosilation of metal acyl complexes: (a) Reference 10. (b) Crawford, E. J.; Hanna, P. K.; Cutler, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 6891.

(15) (a) Tso, C. C.; Cutler, A. R.; Kullnig, R. K. *J. Am. Chem. Soc.* **1987**, *109*, 5844. (b) Ikariya, T.; Yamamoto, A. *J. Organomet. Chem.* **1976**, *116*, 231.

(16) (a) Heck R. F. *J. Am. Chem. Soc.* **1963**, *85*, 1220. (b) Nagy-magos, Z.; Bor, G.; Markó, L. *J. Organomet. Chem.* **1968**, *14*, 205. (c) Lindner, E.; Neese, P.; Hiller, W.; Fawzi, R. *Organometallics* **1986**, *5*, 2030. (d) Galamb, V.; Pályi, G.; Ungváry, F.; Markó, L.; Boese, R.; Schmid, G. *J. Am. Chem. Soc.* **1986**, *108*, 3344. (e) Galamb, V.; Pályi, G.; Boese, R.; Schmid, G. *Organometallics* **1987**, *6*, 861. (f) Ungváry, F.; Wojcicki, A. *J. Organomet. Chem.* **1990**, *396*, 95.

(17) Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(18) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 67.

(19) (a) Bourhis, R.; Frainnet, E. *J. Organomet. Chem.* **1975**, *86*, 205. (b) Ostdick, T.; McCusker, P. A. *Inorg. Chem.* **1967**, *6*, 98. (c) Rakita, P. E.; Worsham, L. S.; Srebro, J. P. *Org. Magn. Reson.* **1976**, *8*, 310.

NMR Spectral Monitoring of Cobalt Acetyl Reactions with Monohydrosilanes: Reaction between $CH_3C(O)Co(CO)_3[PPh_2(CH_3)]$ (1) and $HSi(CH_3)_2Ph$. A light yellow C_6D_6 solution (400 mg) containing $CH_3C(O)Co(CO)_3[PPh_2(CH_3)]$ (1) (50 mg, 0.13 mmol), $HSi(CH_3)_2Ph$ (35 mg, 0.26 mmol), and ferrocene (4.0 mg, 0.22 mmol) was prepared in a 3-mL vial. This solution then was transferred in the glovebox to a 5-mm NMR tube, which was sealed with a rubber septum. Within 1.5 h, the cobalt acetyl 1 was consumed, as indicated by ^1H NMR spectral monitoring of its acetyl (δ 2.63, d, J = 0.9 Hz) and P-methyl (δ 1.48, d, J = 8.2 Hz) absorptions in the resulting dark yellow-orange solution. Other diagnostic NMR spectral absorptions of 1 that were used in monitoring these reactions include the following: $^{31}P\{^1H\}$, δ 33.41; $^{13}C\{^1H\}$, δ 49.9 (COCH$_3$) and 18.0 (d, J_{PC} = 29 Hz, PCH$_3$).

All ^1H, ^{31}P, and ^{13}C NMR spectral absorptions of this clear solution were accounted for as a 1:1 mixture of $Ph(CH_3)_2SiCo(CO)_3[PPh_2(CH_3)]$ (3a; 95%) and $CH_3CH_2OSi(CH_3)_2Ph$ (93%), with trace amounts of starting $HSi(CH_3)_2Ph$ observed in some experiments. The product yields were arrived at by independent integrations of two absorptions for each product vs the ferrocene internal standard. These analytical results using the integration traces are believed to be accurate within ±5%, on the basis of results of control experiments in which the NMR spectrometer pulse program (pulse angle of 38° and delay time of 6 s) had been optimized for similar mixtures of known concentrations.

Similar reactions, but using half as much $HSi(CH_3)_2Ph$ (17 mg, 0.13 mmol), were performed. The silane was consumed within 1.5 h, as evidenced by elimination of its absorptions at δ 4.39 (quint, J = 3.74 Hz, SiH) and 0.34 (d, J = 3.74, SiCH$_3$). All ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectral absorptions were accounted for as a 1:1:1 mixture of starting $CH_3C(O)Co(CO)_3[PPh_2(CH_3)]$ (1; 47%), $Ph(CH_3)_2SiCo(CO)_3[P(CH_3)Ph_2]$ (3a; 52%), and $CH_3CH_2OSi(CH_3)_2Ph$ (50%). Yields correspond to the starting cobalt acetyl complex 1 according to the stoichiometry noted in Figure 2.

Reaction of $CH_3C(O)Co(CO)_3(PPh_2CH_3)$ (1) and $HSi(CH_3)_2Ph$. A light yellow solution of $CH_3C(O)Co(CO)_3[PPh_2(CH_3)]$ (1; 495 mg, 1.28 mmol) in 1:1 C_6H_6–C_6D_6 (1.2 g) containing 2 mg of $Cr(CH_3COCHCOCH_3)_3$ was treated with 2.2 equiv of $HSi(CH_3)_2Ph$ (384 mg, 2.82 mmol). The solution was transferred to a 10-mm NMR tube, and the reaction was monitored by $^{31}P\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectroscopy. After 5 h, the starting cobalt acetyl 1 and $HSiMe_2Ph$ converted quantitatively to $Ph(CH_3)_2SiCo(CO)_3[PPh_2(CH_3)]$ (3a) and $CH_3CH_2OSi(CH_3)_2Ph$ as judged by ^{31}P and ^{29}Si NMR spectroscopy. The remaining $HSi(CH_3)_2Ph$ (δ -16.83), but not disiloxane $[Ph(CH_3)_2Si]_2O$ (δ -0.84), also was detected by ^{29}Si NMR spectroscopy.

The solvent was evaporated from the clear, dark yellowish orange solution, and the orange-brown gum was triturated with 5 mL of hexane. This afforded a light brown solid that was filtered, washed with hexane (3 × 10 mL) until the filtrates were colorless, and dried under vacuum. The resulting solid (568 mg) was identified as (^1H NMR) spectroscopically pure $Ph(CH_3)_2SiCo(CO)_3[PPh_2(CH_3)]$ (3a; 93% yield).

The cobalt silyl compounds 3b–d and 4a,b were prepared by the same procedure; isolated yields are reported in Table I. Physical properties and combustion microanalytical data are listed in Table III. Satisfactory elemental analyses were not obtained for 4a, although its spectral data (Table II) agree with those of a pure compound of the indicated structure.

Preparation of $Ph(CH_3)_2SiCo(CO)_3[PPh_2(CH_3)]$ (3a). A light green THF solution (50 mL) containing $Co(CO)_3[PPh_2(CH_3)]^-Na^+$ (2.80 mmol) was generated by stirring the reddish brown solution of $\{Co(CO)_3[PPh_2(CH_3)]\}_2$ (1.00 g, 1.46 mmol) over excess 1.5% Na(Hg) for 40 min. This solution was transferred to a 100-mL single-neck round-bottom flask via a stainless steel transfer needle, cooled to -78 °C, and treated dropwise with 1.03 mL (3.10 mmol) of $ClSi(CH_3)_2Ph$. After the brown solution was warmed to room temperature with vigorous stirring (1.5 h), its IR spectrum was consistent with quantitatively generating $Ph(CH_3)_2SiCo(CO)_3[PPh_2(CH_3)]$ (3a): ν(CO) 2022 (w), 1946 (br, vs) cm^{-1}. Solvent was evaporated, and methylene chloride extracts (2 × 20 mL) were filtered through Celite. The combined filtrates were concentrated to 10 mL, layered with hexane (40 mL), and stored at -15 °C for 12 h. This afforded a light brown powder

that was filtered, washed with hexane, and dried under vacuum, giving 1.198 g (86%) of analytically pure 3a (Table III).

The silyl complex $Et(CH_3)_2SiCo(CO)_3(PPh_2Me)$ (3b) was similarly prepared from the reaction between $Co(CO)_3(PPh_2Me)^-Na^+$ and $EtMe_2SiCl$. Hexane extracts of the reaction mixture were cooled to -78 °C (precipitating small amounts of $[Co(CO)_3-(PPh_2Me)]_2$ as a brown powder), filtered, and then evaporated to give spectroscopically pure 3b as a brown solid (yield 81%).

Preparation of $Ph(CH_3)_2SiCo(CO)_3[PPh_2(CH_3)]$ (3a) from $Co_2(CO)_8$. A dark red-brown solution of $Co_2(CO)_8$ (2.00 g, 5.85 mmol) in benzene (60 mL) was treated with 2.3 equiv of $HSiMe_2Ph$ (1.80 g, 13.21 mmol). Immediate gas evolution (presumably H$_2$) ensued, and after 1 h the solution turned light yellow-brown. Its IR spectrum was consistent with quantitatively generating $PhMe_2SiCo(CO)_4$ (ν(CO) 2090 (s), 2027 (s), 1995 (vs, br) cm^{-1}). The phosphine PPh_2Me (2.42 mL, 12.9 mmol) the was added by syringe to the reaction mixture, which then slowly evolved gas (presumably CO). After 3 h, <30% conversion to $PhMe_2SiCo-(CO)_3(PPh_2Me)$ (3a; ν(CO) 1948 cm^{-1}) was detected, and heating at 56 °C for 20 h was required to quantitatively consume $PhMe_2SiCo(CO)_4$. The resulting light yellow-orange solution was evaporated, and methylene chloride extracts (20 mL) of the residue were filtered through Celite, which was washed with additional methylene chloride (15 mL). A layer of hexane (250 mL) was settled carefully over the combined methylene chloride extracts (40 mL), before this mixture was set aside at -20 °C for 12 h. Dark red crystals of analytically pure 3a (2.69 g, 48% yield) were collected, washed with hexane, and vacuum-dried.

Results and Discussion

Reactions between Cobalt Acetyl Complexes $CH_3C(O)Co(CO)_3(PR_3)$ and Monohydrosilanes. Treating the cobalt acetyl complexes $CH_3C(O)Co(CO)_3-(PPh_2Me)$ (1) and $CH_3C(O)CoC(O)_3(PPh_3)$ (2) with the monohydrosilanes noted in Figure 2 cleanly affords the cobalt silyl complexes 3a–d and 4a,b plus the requisite ethoxysilanes. Operationally, these reactions involved mixing 1 or 2 (on a reaction scale of either 50 or 200–500 mg) in C_6D_6 with 1–3 equiv of monohydrosilane at room temperature. Results for a selection of these reactions appear in Table I; products were identified by ^1H, ^{13}C, ^{31}P, and ^{29}Si NMR spectroscopy and were quantified by ^1H NMR spectroscopy using an internal standard. All cobalt silyl complexes were isolated in 85–95% yield (using ≥2 equiv of $HSiR_3$ in the larger scale reactions) and were fully characterized (vide infra). The ethoxysilanes, all known compounds,[19] were not isolated, but their ^1H and ^{13}C NMR spectral data closely match those reported in the literature, obtained from commercially available samples (EtOSiMe$_2$Ph and EtOSiPh$_3$), and independently observed during our studies on manganese acetyl catalyzed hydrosilation of aldehydes.[12,13]

We never detected the presence of acetaldehyde during NMR spectral monitoring of these reactions. Limiting the amount of hydrosilane to 1 equiv (Figure 2) consumes 50% of the starting cobalt acetyl 1 or 2 and releases a 1:1 mixture of the cobalt silyl complex 3 or 4 and ethoxysilane. These mixtures were quantified by ^1H NMR spectroscopy, as illustrated in Figure 3 for the reaction between 1.4 equiv of $HSiMe_2Ph$ and 1 (cf. entry 3 in Table I). (Our choice of 1 and $HSiMe_2Ph$ conveniently provided distinctive ^1H NMR spectral tags for the cobalt (P-methyl) and silicon centers.) The lower ^1H NMR spectral scan in Figure 3, recorded after 2 h, shows that the starting hydrosilane has been quantitatively replaced by 3a plus $CH_3CH_2OSiMe_2Ph$ (1:1), thus leaving the requisite amount of unreacted acetyl complex 1. This absence of competing side reactions prevails for the reactions between 1 and all four monohydrosilanes, as well as between 2 and $HSiMe_2Ph$ or $HSiEt_3$. We used four hydrosilanes in this study because the parallel reactions involving $CH_3C(O)Mn(CO)_5$ and

Figure 2.

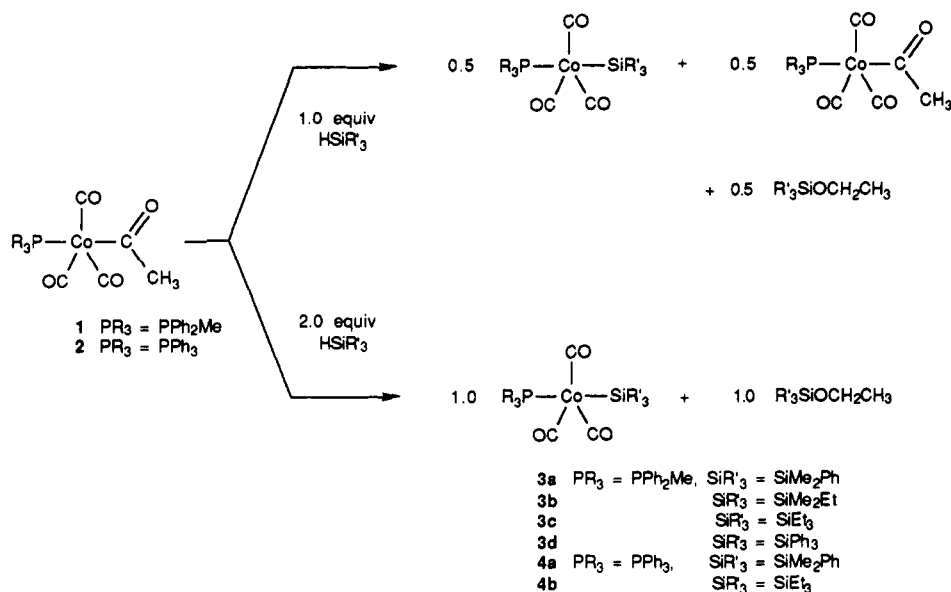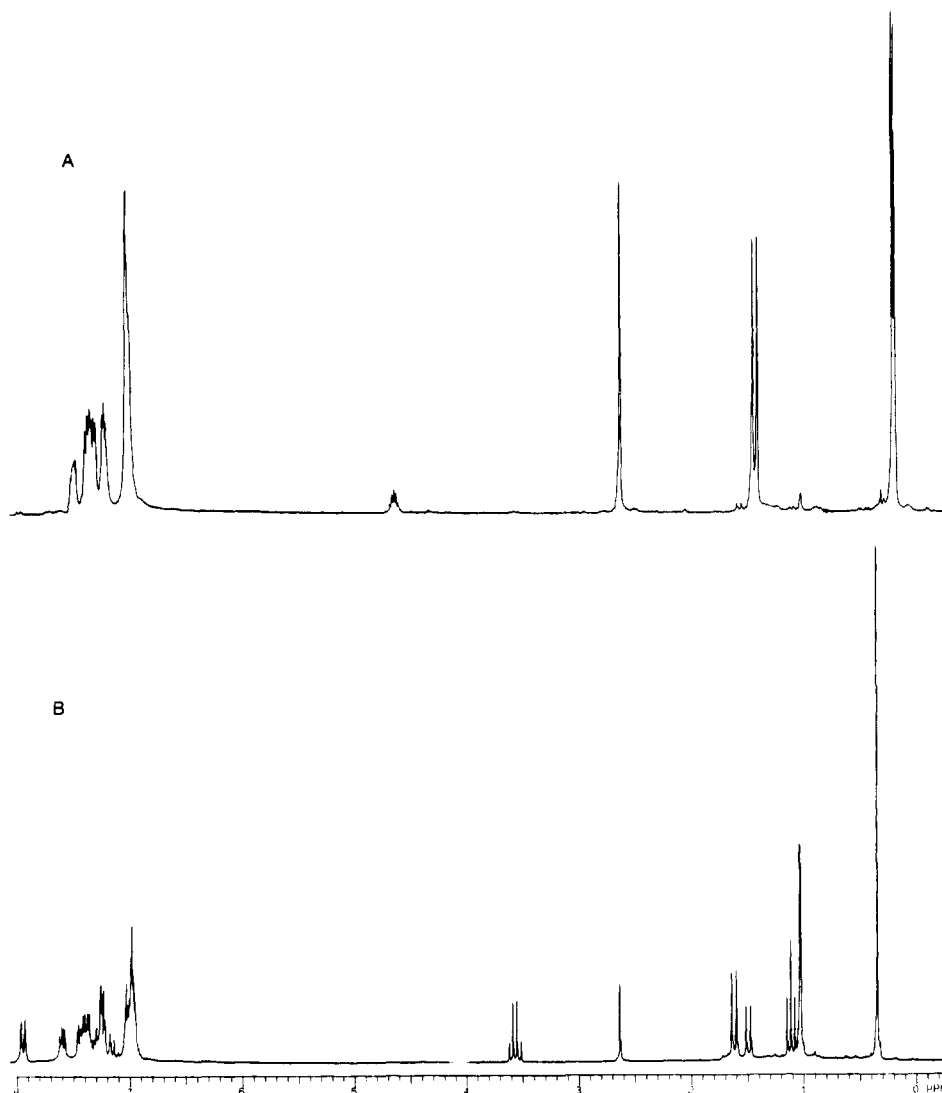**Figure 3.** ^{1}H NMR spectra for reaction of CH$_3$C(O)Co(CO)$_3$(PPh$_2$Me) (1; 200 mg, 0.52 mmol) and HSiMe$_2$Ph (97 mg, 0.71 mmol) in 400 mg of C$_6$D$_6$: (A) t = 0; (B) t = 2 h.

HSiR$'_3$ had proved to be critically dependent on the mo-nohydrosilane (Figure 1).[12]

In contrast to the previously reported hydrosilation chemistry for the manganese acetyl compounds,[12] reactions between monohydrosilanes and the cobalt acetyl complexes **1** and **2** do not afford α-siloxyethyl products CH$_3$CH-(OSiR$'_3$)Co(CO)$_3$(PR$_3$). Such products should have diag-nostic ^{1}H and ^{13}C NMR spectra that resemble those of our

<div style="text-align:center">Table I. Reactions between Cobalt Acetyl Complexes and Monohydrosilanes</div>

entry no.	Co acetyl (amt, mmol)	hydrosilane (amt, equiv)	amt of C_6D_6, g	reacn time, h	% Co acetyl consumed[a]	Co silyl (% yield)
1	$CH_3C(O)Co(CO)_3(PPh_2Me)$ (1) (0.13)	$HSiMe_2Ph$ (1.0)	0.4	1.5	47–50[b]	$PhMe_2SiCo(CO)_3(PPh_2Me)$ (3a) (52)[a]
2	1 (0.13)	$HSiMe_2Ph$ (2.0)	0.4	1.5	98	3a (97)[a]
3	1 (0.52)	$HSiMe_2Ph$ (1.4)[c,d]	0.4	2.0	63	3a (68)[a]
4	1 (1.28)	$HSiMe_2Ph$ (2.2)	1.2	5	100	3a (93)[e]
5	1 (0.13)	$HSiMe_2Et$ (2.0)	0.4	2.5	100	$EtMe_2SiCo(CO)_3(PPh_2Me)$ (3b) (100)[a]
6	1 (1.29)	$HSiMe_2Et$ (2.2)	1.2	6	100	3b (85)[e]
7	1 (0.13)	$HSiEt_3$ (2.0)	0.4	2.5	100	$Et_3SiCo(CO)_3(PPh_2Me)$ (3c) (100)[a]
8	1 (1.29)	$HSiEt_3$ (2.3)	1.2	8	100	3c (91)[e]
9	1 (0.13)	$HSiPh_3$ (1.0)	0.4	4	49[b]	$Ph_3SiCo(CO)_3(PPh_2Me)$ (3d) (50)[a]
10	1 (0.13)	$HSiPh_3$ (2.7)	0.4	14	100	3d (100)[a]
11	1 (1.29)	$HSiPh_3$ (2.3)	1.2	10	100	3d (86)[e]
12	1 (0.05)	$HSiMe_2Ph$ (2.1)	0.6	5	76	3a (63)[a,g]
13	$CH_3C(O)Co(CO)_3(PPh_3)$ (2) (0.22)	$HSiMe_2Ph$ (1.2)	0.4	8	60	$PhMe_2SiCo(CO)_3(PPh_3)$ (4a) (60)[a]
14	2 (0.22)	$HSiMe_2Ph$ (2.0)	0.4	8	100	4a (100)[a]
15	2 (1.12)	$HSiMe_2Ph$ (2.2)	1.2	10	100	4a (90)[e]
16	2 (1.12)	$HSiEt_3$ (2.2)	1.2	10	100	$Et_3SiCo(CO)_3(PPh_3)$ (4b) (94)[e]
17	$CH_3C(O)Co(CO)_2(dppe)$[f] (0.19)	$HSiMe_2Ph$ (1.2)	0.4	3	no reacn	

[a] ^{1}H NMR spectral monitoring using a ferrocene internal standard; yields based on starting cobalt acetyl. ^{31}P and ^{13}C NMR spectral data qualitatively used for materials balance. [b] Hydrosilane was consumed. [c] Identical results when reaction was repeated with $RhCl(PPh_3)_3$ (2%) present. [d] Presence of either CO (1 atm) or of $PPh_2(p$-tolyl) (1.2 equiv) quantitatively blocks this reaction. [f] Dppe is $Ph_2PCH_2CH_2PPh_2$; no reaction after 18 h in the presence of $RhCl(PPh_3)_3$ (2%). [g] Also, 12% of $[Co(CO)_3PPh_2Me]_2$ and 59% of $CH_3CH_2OSiMe_2Ph$ were detected. Reaction was complete within 15 h, 45% of $[Co(CO)_3PPh_2Me]_2$ and 55% of 3a were detected.

recently characterized (α-ethoxyethyl)cobalt complex $CH_3CH(OEt)Co(CO)_3(PPh_3)^{20}$ and, of course, several examples of the manganese and iron α-siloxyethyl complexes $CH_3CH(OSiR'_3)ML_x$ ($ML_x = Mn(CO)_5$, $Fe(CO)_2Cp$).[10,12–14] The parent siloxymethyl compound $Me_3SiOCH_2Co(CO)_4$ has been reported as the product from the photolysis of $Me_3SiCo(CO)_4$ in the presence of formaldehyde and CO.[21]

We further looked for potential catalysis or inhibition of the reaction between $CH_3C(O)Co(CO)_3(PPh_2Me)$ (1) and $HSiMe_2Ph$ by NMR spectral monitoring of experiments that included carbon monoxide, a phosphine, an aldehyde, or Wilkinson's compound, $RhCl(PPh_3)_3$. The presence of 2–5% of Wilkinson's compound, a potential acyl ligand hydrosilation catalyst,[10,12,13] affords the same reaction time and product distribution under our standard conditions. Complying with these standard conditions, especially the concentration of 1, proved to be critical, however. When these reactions were run more dilute in 1 (with or without $RhCl(PPh_3)_3$ present), they proceeded slowly and generated substantial amounts of $[Co(CO)_3$-$(PPh_2Me)]_2$ (e.g., entry 12, Table I).

The presence of excess carbon monoxide or phosphine dramatically inhibits the hydrosilation of 1. No reaction occurs between 1 and $HSiMe_2Ph$ (1.0–1.4 equiv) for at least 2 h in the presence of CO (1 atm) or 1.0 equiv of PPh_2-(p-tolyl). In the absence of these added ligands, the cobalt acetyl 1 consumes all of the $HSiMe_2Ph$ within 2 h under otherwise identical reaction conditions. Although only these starting materials are detected during the carbon monoxide runs, reactions containing $PPh_2(p$-tolyl) produced up to 20% free PPh_2Me and incorporated $PPh_2(p$-tolyl) into 1 to give the new acetyl complex $CH_3C(O)Co$-$(CO)_3[PPh_2(p$-tolyl)]$. This apparent phosphine exchange occurs independently of the hydrosilane, since a control reaction between 1 and $PPh_2(p$-tolyl) in the absence of added $HSiR_3$ affords the same 20% phosphine exchange in 2 h.

Acetaldehyde and benzaldehyde interrupt the reaction of 1 with $HSiMe_2Ph$, albeit by very different pathways (Figure 4). Acetaldehyde selectively undergoes hydro-
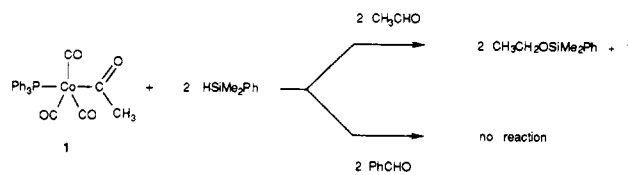
Figure 4.

silation: a mixture of 1 (0.26 mmol), $HSiMe_2Ph$ (0.57 mmol), and acetaldehyde (0.57 mmol) in 600 mg of C_6D_6 quantitatively transformed the aldehyde to $CH_3CH_3OSiMe_2Ph$, while leaving the cobalt acetyl 1 intact. The same results prevailed irrespective of whether 1 and $HSiMe_2Ph$ were premixed before added CH_3CHO or if separate C_6D_6 solutions of 1 and $HSiMe_2Ph$ plus CH_3CHO were combined. During these acetaldehyde hydrosilation reactions, 1 remained as the only cobalt species detected by ^{1}H NMR spectroscopy (monitoring the P-methyl doublet region) until the aldehyde disappeared; then 1 converted to 3a.

Acetaldehyde hydrosilation also can be carried out catalytically in 1 (10%), but under otherwise identical conditions, to quantitatively transform acetaldehyde to $CH_3CH_3OSiMe_2Ph$ in under 2 h.[22] Workup under these reactions was not attempted, but no other organic products were detected by ^{1}H and ^{13}C NMR spectroscopy.

Benzaldehyde under similar conditions (0.13 mmol of 1, 0.26 mmol of $HSiMe_2Ph$, and 0.26 mmol of PhCHO in 300 mg of C_6D_6) effectively sequesters 1 and blocks all hydrosilation activity. No discernible reaction occurred, including aldehyde hydrosilation, for over 2 h. (In contrast, hydrosilation of PhCHO with $HSiMe_2Ph$ and catalytic $CH_3C(O)Mn(CO)_5$ is quite facile under these conditions.[12]) Even including an equivalent amount of acetaldehyde (0.27 mmol) failed to induce any hydrosilation reaction; the

(20) Tso, C. C.; Cutler, A. R. Electrophilic Activation, Reduction, and Carbonylation of the Acetyl Ligand on $CH_3C(O)Co(CO)_3PPh_3$. Manuscript submitted for publication.

(21) Sisak, A.; Sámpár-Szerencsés, E.; Galamb, V.; Németh, L.; Ungváry, F.; Pályi, G. *Organometallics* 1989, 8, 1096 and references cited therein.

(22) (a) $Co_2(CO)_8$ has been reported to catalyze the hydrosilation of ketones: Sakurai, H.; Miyoshi, K.; Nakodaira, Y. *Tetrahedron Lett.* 1977, 2671. (b) Reviews on catalytic aldehyde/ketone hydrosilation: Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *Top. Stereochem.* 1984, 15, 45. Ojima, I.; Hirai, K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York. 1985; Vol. 5, p 103. Chaloner, P. A. *Handbook of Coordination Catalysis in Organic Chemistry*; Butterworths: Boston, 1986; Chapter 7.2. Brunner, H. *Top. Stereochem.* 1988, 18, 129; *Synthesis* 1988, 645. Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1989; Part 2p, Chapter 25.

Table II. Spectroscopic Characterization of Cobalt Silyl Complexes

complex [IR (C_6D_6), cm^{-1}]	^{1}H NMR (C_6D_6), ppm (J, Hz)	$^{13}C\{^1H\}$ NMR (C_6D_6), ppm (J, Hz)	$^{29}Si\{^1H\}$ NMR (C_6D_6), ppm (J, Hz)	$^{31}P\{^1H\}$ NMR (C_6D_6), ppm
PhMe$_2$SiCo(CO)$_3$(PPh$_2$Me) (3a) [ν(CO) 2021 (w), 1944 (s)]	7.98 (m, 2 H, o SiPh) 7.40 (m, 4 H, o PPh) 7.34 (m, 3 H, m,p SiPh) 7.12 6.95 (m, 6 H, m,p PPh$_3$) 1.54 (d, J_{PH} = 8.3, PCH_3) 1.04 (d, J_{PH} = 1.7, SiCH_3)	201.4 (br d, J_{PC} = 13.6, CO) 136.9 (d, J_{PC} = 43.4, ipso PPh) 133.4 (SiPh) 131.6 (d, J_{PC} = 11.2, o PPh) 130.3 (d, J_{PC} = 1.3, m PPh) 128.9 (SiPh) 128.7 (SiPh) 19.1 (d, J_{PC} = 30.0, PCH$_3$) 6.6 (d, J_{PC} = 2.7, SiCH$_3$)	32.29 (d, J_{PSi} = 28.9)	39.87
EtMe$_2$SiCo(CO)$_3$(PPh$_2$Me) (3b) [ν(CO) 2023 (w), 1948 (s)]	7.43 (m, 4 H, Ph) 6.96 (m, 6 H, Ph) 1.66 (d, J_{PH} = 8.2, PCH_3) 1.18 (m, 5 H, SiEt) 0.70 (s, SiCH_3)	202.8 (br d, J_{PC} = 14.2, CO) 137.1 (d, J_{PC} = 42.7, ipso Ph) 131.6 (d, J_{PC} = 11.3, o Ph) 130.3 (d, J_{PC} = 2.2, m Ph) 128.8 (s, p Ph) 19.3 (d, J_{PC} = 29.6, PCH$_3$) 16.7 (d, J_{PC} = 2.1, SiCH$_2$CH$_3$) 9.1 (s, SiCH$_2$CH$_3$) 5.5 (d, J_{PC} = 2.1, SiCH$_3$)	42.22 (d, J_{PSi} = 26.0)	40.07
Et$_3$SiCo(CO)$_3$(PPh$_2$Me) (3c) [ν(CO) 2022 (w), 1947 (s)]	7.45 (m, 4 H, o Ph) 6.99 (m, 6 H, m,p Ph) 1.66 (d, J_{PH} = 8.3, PCH_3) 1.23 (br s, 15 H, SiEt)	201.7 (br d, J_{PC} = 13.6, CO) 137.1 (d, J_{PC} = 42.9, ipso Ph) 131.6 (d, J_{PC} = 11.1, o Ph) 130.4 (d, J_{PC} = 2.0, m Ph) 128.6 (s, p Ph) 19.1 (d, J_{PC} = 29.7, PCH$_3$) 12.8 (d, J_{PC} = 2.7, SiCH$_2$CH$_3$) 9.3 (SiCH$_2$CH$_3$)	51.86 (d, J_{PSi} = 25.0)	40.03
Ph$_3$SiCo(CO)$_3$(PPh$_2$Me) (3d) [ν(CO) 2027 (w), 1951 (s)]	8.02 (m, 6 H, o SiPh) 7.40 (m, 4 H, o PPh) 7.16 (m, 9 H, m,p SiPh) 6.92 (m, 6 H, m,p PPh) 1.63 (d, J_{PH} = 8.4, PCH_3)	201.3 (br s, CO) 136.1 (Ph) 131.5 (d, J_{PC} = 10.9, o PPh) 130.4 (d, J_{PC} = 2.2, m PPh) 129.1 (Ph: overlap C$_6$D$_6$) 128.7 (Ph: overlap C$_6$D$_6$) 128.0 (Ph: overlap C$_6$D$_6$) 18.9 (d, J_{PC} = 30.9, PCH$_3$)	29.81 (d, J_{PSi} = 33.0)	40.49
PhMe$_2$SiCo(CO)$_3$(PPh$_3$) (4a) [ν(CO) 2023 (w), 1947 (s)]	8.00 (m, 2 H, o SiPh) 7.55 (m, 6 H, o Ph) 7.25 (m, 3 H, m,p SiPh) 6.96 (m, 9 H, m,p PPh) 1.09 (d, J_{PH} = 1.7, SiCH_3)	202.0 (br d, CO) 143.6 (ipso SiPh) 135.1 (d, J_{PC} = 44.1, ipso PPh) 133.3 (d, J_{PC} = 11.1, o PPh) 130.5 (Ph) 129.0 (Ph: overlap C$_6$D$_6$) 128.7 (Ph: overlap C$_6$D$_6$) 6.7 (d, J_{PC} = 1.8, SiCH$_3$)	33.09 (d, J_{PSi} = 29.4)	57.54
Et$_3$SiCo(CO)$_3$(PPh$_3$) (4b) [ν(CO) 2020 (w), 1943 (s)]	7.62 (br m, 6 H, o Ph) 6.96 (m, 9 H, m,p Ph) 1.29 (br s, 15 H, SiEt)	201.3 (br s, CO) 133.3 (d, J_{PC} = 11.4, o Ph) 130.4 (Ph) 128.9 (Ph: overlap C$_6$D$_6$) 12.8 (SiCH$_2$CH$_3$) 9.3 (SiCH$_2$CH$_3$)	52.94 (d, J_{PSi} = 25.4)	58.02

Table III. Analytical Data for Cobalt Silyl Complexes

complex	color	mp behavior,^{a} °C	microanal. data, %	
			C obsd (calcd)	H obsd (calcd)
PhMe$_2$SiCo(CO)$_3$(PPh$_2$Me) (3a)	dark red cryst	134–135	59.96 (60.25)	4.97 (5.06)
EtMe$_2$SiCo(CO)$_3$(PPh$_2$Me) (3b)	brown oil		55.59 (55.81)	5.43 (5.62)
Et$_3$SiCo(CO)$_3$(PPh$_2$Me) (3c)	brown oil			
Ph$_3$SiCo(CO)$_3$(PPh$_2$Me) (3d)	light yellow powder	210–212	67.29 (68.00)	4.53 (4.36)
PhMe$_2$SiCo(CO)$_3$(PPh$_3$) (4a)	light brown powder	201–204	63.83 (64.44)	4.94 (4.85)
Et$_3$SiCo(CO)$_3$(PPh$_3$) (4b)	brown powder		62.44 (62.30)	5.67 (5.81)

^{a} In vacuo; decomposition points for **3b–d** and **4a,b**.

benzaldehyde now blocked hydrosilation of the acetaldehyde.

The high reactivity of the cobalt acetyl complexes 1 and 2 toward monohydrosilanes does not carry over to the diphosphine-substituted cobalt acetyl CH$_3$C(O)Co(CO)$_2$-(dppe). It is unreactive to HSiMe$_2$Ph (1.4 equiv) under otherwise comparable reaction conditions (Table I, entry 18).

Synthesis and Characterization of Cobalt Silyl Complexes. The six cobalt silyl complexes **3a–d** and **4a,b** were isolated conveniently from the reactions of 2.2 equiv of HSiR'$_3$ with the cobalt acetyl compounds 1 and 2 (Figure

1 and Table I). These robust silyl complexes, which are only moderately air sensitive and hygroscopic, vary in appearance from brown oils (**3b,c**) to yellow or brown powders (**3d, 4a,b**) to a red crystalline solid (**3a**). Tables II and III collect their spectroscopic and analytical data, respectively. We did not get an acceptable elemental analysis for Et$_3$SiCo(CO)$_3$(PPh$_2$Me) (**3c**), although it was obtained spectroscopically pure. Its spectral data closely resembles those obtained for the other cobalt silyl complexes reported in this study.

Spectral data for the cobalt silyl complexes **3a–d** and **4a,b** are consistent with the expected trigonal-bipyramidal
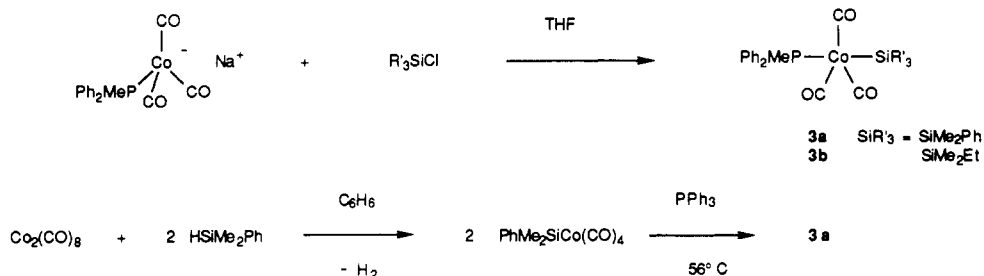
Figure 5.

structures that retain a trans-axial array of silyl and phosphine ligands.[23] This localized C_{3v} symmetry agrees with the diagnostic pattern of terminal carbonyl $\nu(CO)$ bands in the IR spectra,[1,16] a weak absorption near 2023 cm^{-1}, and a broad, intense band centered at 1947 cm^{-1} (for the almost degenerate E-mode vibrations). The appearance of these $\nu(CO)$ bands also closely resembles those of related alkyl cobalt complexes $RCo(CO)_3(PR_3)$,[1,2,20] which are known to retain diaxial-substituted trigonal-bipyramidal structures with pseudo-C_{3v} symmetry.[16d,e,24]

^{1}H, ^{13}C, and ^{29}Si NMR spectra of these cobalt silyl complexes feature distinctive phosphorus spin–spin splittings of the silyl ligand absorptions. The ^{29}Si absorptions thus appear as doublets ($^2J_{PSi}$ = 25–33 Hz) with chemical shifts that vary from 29.8 ppm (Ph$_3$SiCo(CO)$_3$-(PPh$_2$Me)) (**3d**) to 52.9 ppm (Et$_3$SiCo(CO)$_3$(PPh$_3$) (**4b**)). This chemical shift range[25] parallels a similar spread of ^{29}Si chemical shifts that we tabulate for the ethoxysilanes (Experimental Section: δ −13.04 (Ph$_3$SiOEt) to 17.32 (Et$_3$SiOEt)). The starting hydrosilanes likewise vary in ^{29}Si chemical shift from δ −17.55 (HSiPh$_3$) to 0.42 (HSiEt$_3$).

A ^{29}Si chemical shift of δ 42.22 for EtMe$_2$SiCo(CO)$_3$-(PPh$_2$Me) (**3b**) should be compared with that reported by Gladysz and co-workers[26] for Me$_3$SiCo(CO)$_4$ (37.45 ppm, also in C$_6$D$_6$). This 4.8 ppm increase in ^{29}Si shifts when ligated CO is replaced by phosphine is surprising, since a 6–8 ppm *decrease* might be expected. Pannell[27] established just such a trend with the iron silyl complexes R$_3$SiFe(CO)LCp.

^{31}P NMR chemical shifts for the cobalt silyl complexes **3a–d** (ca. δ 40) and for **4a,b** (ca. δ 58) depend on the ligated phosphine and remain independent of the silyl group. Not surprisingly, these ^{31}P NMR chemical shifts are very close to those that we reported for the corresponding alkyl compounds $RCo(CO)_3(PR_3)$ (PR$_3$ = PPh$_2$Me,[2b] PPh$_3$).[20]

A number of cobalt silyl complexes[28] of the general type R$'_3$SiCo(CO)$_3$(PR$_3$) previously had been at least partially

characterized. Of the silyl complexes that are reported in this study, Ph$_3$SiCo(CO)$_3$(PPh$_2$Me) (**3d**) is known,[23b] and Et$_3$SiCo(CO)$_3$(PPh$_3$) (**4a**) is Wegman's assumed product from the HSiEt$_3$ cleavage of **2**.[4] General procedures for preparing analogous cobalt silyl complexes include (1) metalating a silyl chloride with Co(CO)$_3$(PR$_3$)$^-$ (e.g., Ph$_3$SiCo(CO)$_3$(PPh$_3$)[29a]),[29] (2) substituting PR$_3$ for CO on R$'_3$SiCo(CO)$_4$ (e.g., Me$_3$SiCo(CO)$_3$(PPh$_3$)[23,29a,30a] and Ph$_3$SiCo(CO)$_3$(PPh$_2$Me) (**3d**)[23b]), and (3) cleaving dimeric [Co(CO)$_3$(PR$_3$)]$_2$ with HSiR$'_3$ (e.g., MePh(1-C$_{10}$H$_7$)SiCo-(CO)$_3$(PPh$_3$)).[31a] A nongeneral procedure of adding a hydrosilane to (η^3-allyl)Co(CO)$_2$(PPh$_3$) has been used to generate Ph$_2$MeSiCo(CO)$_3$(PPh$_3$).[31b]

We independently synthesized both PhMe$_2$SiCo(CO)$_3$-(PPh$_2$Me) (**3a**) and EtMe$_2$SiCo(CO)$_3$(PPh$_2$Me) (**3b**) by using two of the established procedures (Figure 5). Reacting Co(CO)$_3$(PPh$_2$Me)$^-$Na$^+$ in THF with silyl chlorides affords **3a,b** in 80% yields after a standard workup procedure. Interestingly, these cobalt silyl complexes do not cleave THF[29a,32] at room temperature. The other procedure entails first cleaving Co$_2$(CO)$_8$ with excess HSiMe$_2$Ph in benzene, an established reaction,[33] and then treating the resulting PhMe$_2$SiCo(CO)$_4$ at 56 °C with PPh$_2$Me. This convenient method provides **3a** in ca. 50% yield. In the present study, **3a** serves as the prototypical cobalt silyl complex R$'_3$SiCo(CO)$_3$(PR$_3$) in studies probing the reactivity of the Co–Si bond.

The cobalt silyl complexes R$'_3$SiCo(CO)$_3$(PR$_3$) (**3, 4**) certainly are byproducts of treating the cobalt acetyl compounds **1** and **2** with hydrosilanes, but are they mechanistically involved in transforming the acetyl ligand to an ethoxysilane? Such reactivity presumably would require **3** or **4** to bind and then catalytically hydrosilate acetaldehyde (vide infra). This possibility was addressed by running several control experiments using Me$_2$PhSiCo(CO)$_3$(PPh$_2$Me) (**3a**). The objectives were to detect (1) **3a** functioning as an acetaldehyde hydrosilation catalyst[22] and (2) CO or phosphine ligand lability on **3a**. The probe for thermal lability of **3a** (at room temperature) involved looking for silane exchange (eq 2) analogous to

(23) (a) Kahn, O.; Bigorgne, M. *J. Organomet. Chem.* **1967**, *10*, 137. (b) Haszeldine, R. N.; Mather, A. P.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1980**, 923.

(24) (a) Heiber, W.; Lindner, E. *Chem. Ber.* **1962**, *95*, 273. (b) Lindner, E.; Stich, H.; Geibel, K.; Kranz, H. *Chem. Ber.* **1971**, *104*, 1524. (c) Galamb, V.; Pályi, G.; Cser, F.; Furmanova, M. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1981**, *209*, 183. (d) España, N.; Gomez, P.; Royo, P.; Vazquez De Miguel, A. *J. Organomet. Chem.* **1983**, *256*, 141. (e) Tasi, M.; Palyi, G. *Organometallics* **1985**, *4*, 1523.

(25) (a) Williams, E. A. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 235. (b) Coleman, B. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983.

(26) Li, S.; Johnson, D. L.; Gladysz, J. A.; Servis, K. L. *J. Organomet. Chem.* **1979**, *166*, 317.

(27) (a) Pannell, K. H.; Bassindale, A. R. *J. Organomet. Chem.* **1982**, *229*, 1. (b) Pannell, K. H.; Lin, S.-H.; Kapoor, R. N.; Cervantes-Lee, F.; Pinon, M.; Parkanyi, L. *Organometallics* **1990**, *9*, 2454.

(28) (a) Mackay, K. M.; Nicholson, B. K. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 6, Chapter 43. (b) Aylett, B. J. *Adv. Inorg. Chem. Radiochem.* **1982**, *25*, 1. (c) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley-Interscience: New York, 1989; Part 2, Chapter 24.

(29) (a) Curtis, M. D. *Inorg. Chem.* **1972**, *11*, 802. (b) Hengee, E.; Eibl, M. *Organometallics* **1991**, *10*, 3185.

(30) (a) Bald, J. F., Jr.; MacDiarmid, A. G. *J. Organomet. Chem.* **1970**, *22*, C22. (b) Aylett, B. J.; Campbell, J. M. *J. Chem. Soc. A* **1969**, 1910. (c) Ogino, K.; Brown, T. L. *Inorg. Chem.* **1971**, *10*, 517. (d) Reichel, C. L.; Wrighton, M. S. *Inorg. Chem.* **1980**, *19*, 3858.

(31) (a) Cerveau, G.; Colomer, E.; Corriu, R. J. P. *J. Organomet. Chem.* **1982**, *236*, 33. (b) Schubert, U.; Mueller, J. *J. Organomet. Chem.* **1988**, *340*, 101.

(32) (a) Ingle, W. M.; Preti, G.; MacDiarmid, A. G. *J. Chem. Soc., Chem. Commun.* **1973**, 497. (b) Nicholson, B. K.; Simpson, J. *J. Organomet. Chem.* **1978**, *155*, 237.

(33) (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 1133. (b) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1967**, *89*, 1640. (c) Baay, Y. L.; MacDiramid, A. G. *Inorg. Chem.* **1969**, *8*, 986. (d) Sommer, L. H.; Lyons, J. E.; Fujimoto, H. *J. Am. Chem. Soc.* **1969**, *91*, 7051. (e) Bradley, G. F.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.* **1974**, 264. (f) Harrod, J. F.; Chalk, A. J.; In *Organic Syntheses via Metal Carbonyls*; Wiley: New York, 1977; Vol. 2, pp 687–690 and references therein. (g) Sisak, A.; Ungváry, F.; Markó, L. *Organometallics* **1986**, *5*, 1019.
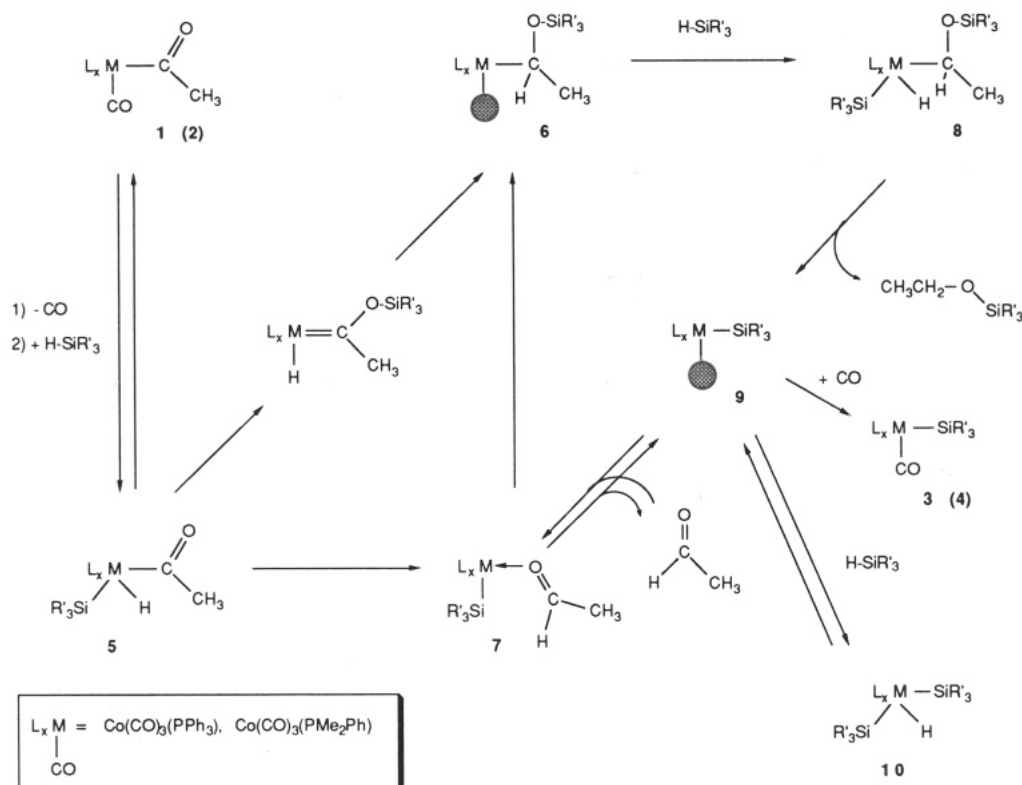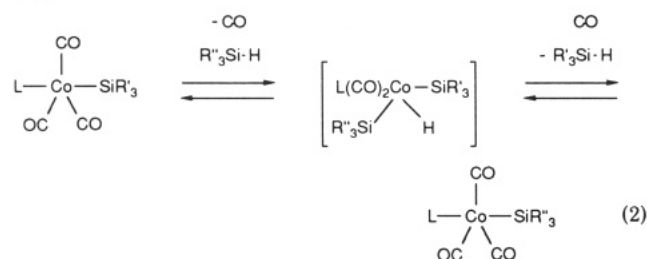
Figure 6.

that observed for the cobalt tetracarbonyl analogs (L = CO).[34]

Silane exchange does not occur in C_6D_6 solutions (600 mg) containing **3a** (50 mg) and 1 equiv of $HSiEt_3$. ^{1}H NMR detectable quantities of the plausible silane exchange products $Et_3SiCo(CO)_3(PPh_2Me)$ (**3c**) and free $HSiMe_2Ph$ were not evident at room temperature (20 h) or even upon warming at 56 °C (8 h). Under these more extreme conditions, **3a** degraded approximately 15% to an unidentified cobalt complex, having its *P*-methyl doublet absorption shifted to δ 1.55 (d, $J = 8.4$ Hz), and the disiloxane $(PhMe_2Si)_2O$ (δ 0.34). Dimeric $[Co(CO)_3(PMe_2Ph)]_2$ (δ 1.67, m, PMe) was not detected.

Acetaldehyde likewise undergoes no reaction with $Me_2PhSiCo(CO)_3(PPh_2Me)$ (**3a**) at room temperature. Thus, **3a** does not interact with excess CH_3CHO in C_6D_6 (5 h), nor does **3a** (5%) catalytically add $HSiMe_2Ph$ (0.25 mmol/600 mg C_6D_6 to CH_3CHO (0.5 mmol) over 5 h. Under these conditions, $CH_3C(O)Co(CO)_3(PPh_2Me)$ (**1**) efficiently catalyzes the hydrosilation of acetaldehyde. In contrast to the inertness of the cobalt silyl **3a** toward acetaldehyde, the more reactive cobalt tetracarbonyl silyl complexes $R''_3SiCo(CO)_4$ ($R'' = Me, Et$) easily add isobutyraldehyde[7] and apparently provide the (undetected)

α-siloxyalkyl intermediates $Me_2CHCH(OSiR''_3)Co(CO)_4$.[7-9] These intermediates ultimately degrade to several organic products, including the silyl ethers $Me_2CHCH_2OSiR''_3$.

Plausible Cobalt Acetyl Hydrosilation Pathways. The inertness of $PhMe_2SiCo(CO)_3(PPh_2Me)$ (**3a**) toward acetaldehyde, even in the presence of excess $HSiMe_2Ph$, clearly limits the mechanistic options that are available for transforming cobalt acetyl compounds **1** and **2** into their silyl derivatives **3** and **4**, respectively, plus ethoxysilane. Figure 6 outlines two plausible options, one intramolecular and one intermolecular, for the hydrosilation of **1** and **2**.

According to the intramolecular pathway, the starting acetyl complex **1** or **2** reversibly dissociates CO (or phosphine)[35] and oxidatively adds hydrosilane[36] to give the hydridoacetyl(silyl)cobalt(III) species **5**. This cobalt(III) transient **5** then transforms to the coordinatively unsaturated α-siloxyethyl intermediate **6** by two likely pathways: either **5** reductively eliminates ligated acetaldehyde as **7**, which rearranges to **6**, or **5** undergoes a 1,3-silatropic shift[37] followed by hydride migration to also generate **6**. Either way, **6** then added $HSiR'_3$, giving another Co(III) species (**8**), and reductively eliminates the observed ethoxysilane.

This overall pathway resembles those advanced by Murai et al. for $Co_2(CO)_8$-catalyzed siloxymethylation of aldehydes (with $HSiR_3$ and CO) to higher α-siloxy aldeh-

(34) (a) This silyl group exchange has been studied under thermal[33d,f] and photochemical[34b] conditions. (b) Reichel, C. L.; Wrighton, M. S. *Inorg. Chem.* **1980**, *19*, 3858. Anderson, F. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 995.

(35) The extent to which this phosphine lability, as opposed to the established carbonyl lability,[1] contributes to the hydrosilation pathway of **1** is unclear and will have to be examined by a future kinetic study. This discussion emphasizes the role of carbonyl lability.

(36) Alternatively, reactions involving hydrosilane ligand (η^2-H–Si) on intermediates analogous to **5** and **8** could supplant the oxidative-addition–reductive-elimination steps: Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527. Transience of these intermediates should be preferred to a σ-bond metathesis-type mechanism in which noncoordinated hydrosilane directly reacts with a (typically) early-transition-metal–carbon bond: Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043.

(37) Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *3*, 1325.

ydes[7,8b,c,9b,38] and by Akita, Moro-oka, et al. for their reduction of the acyl ligand on $Cp(L)(CO)FeC(O)CH_2CH_2Ph$ complexes via catalytic hydrosilation.[39] Indirect evidence supporting the transience of the Co(III) species 5 and 8 during oxidative-addition–reductive-elimination sequences at cobalt follows from characterization of several examples of (hydrido)(silyl)(alkyl)Co[III],[40] (hydrido)(silyl)$_2$Co[III],[34] and (hydrido)(silyl)$_2$Fe(CO)Cp[41] species.

The intermolecular pathway differs in that the putative (silyl)(acetaldehyde)cobalt complex 7 would dissociate its acetaldehyde and (after associating CO) afford the inert silyl complex 3 or 4. Steady-state concentrations of acetaldehyde then would undergo catalytic hydrosilation and convert to the observed ethoxysilane. Plausible catalysts that would derive from the acetyl compounds 1 or 2 include the hydridosilyl(acetyl)cobalt(III) species 5 and the coordinatively unsaturated silyl intermediate 9. The former might engage in a free-radical mechanism involving 17-/19-electron intermediates analogous to that postulated for $(CO)_5MnCOR$-catalyzed hydrosilation of $FpC(O)CH_3$ or aldehydes,[12] and the latter could associate CH_3CHO and enter the catalytic sequence 9–7–6–8–9 plus $CH_3CH_2OSiR'_3$. This latter pathway mimics those suggested by Akita, Moro-oka, et al.[39] and by Brunner et al.[41a] for $Cp(LK)FeSiR'_3$ (cf. 9) as an aldehyde hydrosilation catalyst.

Conclusions

Although monohydrosilanes $HSiR'_3$ readily react with the cobalt acetyl compounds $CH_3C(O)Co(CO)_3(PR_3)$ (1,

$PR_3 = PPh_2Me$; 2, $PR_3 = PPh_3$) at room temperature (Figure 2), they do not release detectable quantities of acetaldehyde. Instead, these acetyl compounds cleanly transform into cobalt silyl complexes 3 or 4 and ethoxysilanes $EtOSiR'_3$, irrespective of whether 1 or 2 equiv of hydrosilane is used. The presence of either CO (1 atm) or 1 equiv of free phosphine inhibits these reactions, and adding catalytic quantities of Wilkinson's compound, $RhCl(PPh_3)_3$, affects neither the rate nor the outcome of the reaction.

Our results differ from those reported by Wegman[4] for the reactions of $HSiEt_3$ and $HSiPh_3$ with 2 in THF at 50 °C. The critical difference is that Wegman's studies were done under a CO atmosphere, which apparently alters the reactions to favor acetaldehyde as the sole organic product. The presence of CO would account for the more forcing reaction conditions, if not actually initiating an alternative pathway, that apply to Wegman's studies. By efficiently shunting the coordinatively unsaturated intermediates such as 9 (Figure 6) to the nonlabile cobalt silyl byproducts 3 and 4, the presence of CO could thus ensure that the acetaldehyde primary product does not further hydrosilate. Indeed, the present study establishes that the coordinatively saturated silyl complex 3a does not catalyze the hydrosilation of acetaldehyde.

The cobalt acetyl compounds 1 and 2 also differ from the manganese acetyl $CH_3C(O)Mn(CO)_5$ in their reactivity toward monohydrosilanes. We find no evidence for forming (α-siloxyethyl)cobalt complexes $CH_3CH(OSiR'_3)Co(CO)_3(PR_3)$ of the type that readily derive from $CH_3C(O)Mn(CO)_5$ under comparable conditions. A possibly related observation is that 1 is not nearly as effective an aldehyde hydrosilation catalyst as is the manganese acetyl. For example, $CH_3C(O)Mn(CO)_5$ catalytically adds $HSiMe_2Ph$ to acetaldehyde and benzaldehyde, whereas 1 is catalytically inactive toward the latter. Studies in progress are addressing mechanistic details of cobalt and manganese acyl complexes as hydrosilation catalysts.

(38) (a) Chatani, N.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 1370. (b) Chatani, N.; Fugii, S.; Yamasaki, Y.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1986**, *108*, 7361. (c) Murai, T.; Yasui, E.; Kato, S.; Hatayama, Y.; Suzuki, S.; Yamasaki, Y.; Sonoda, N.; Kurosawa, H.; Kawasaki, Y.; Murai, S. *J. Am. Chem. Soc.* **1989**, *111*, 7938.

(39) (a) Akita, M.; Oku, T.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1790. (b) Akita, M.; Oku, T.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1991**, *10*, 3080.

(40) Wrighton, M. S.; Seitz, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289. (b) Hardin, S.; Turney, T. W. *J. Mol. Catal.* **1987**, *39*, 237. (c) Archer, N. J.; Haszeldine, R. N.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1979**, 695.

(41) (a) Brunner, H.; Fisch, K. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1131; *J. Organomet. Chem.* **1991**, *412*, C11. (b) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366. (c) For Cp*Ru congeners, see: Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673.