Alkyl–CO Insertion Reactions of $(PMePh_2)(CO)_3Co$ η^1-Methyl, Methoxymethyl, and Carbomethoxymethyl Complexes

Chung C. Tso and Alan R. Cutler*

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180–3590

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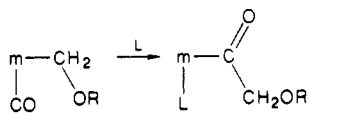
The reactions of CO (1 atm) or excess $PMePh_2$ with $(PMePh_2)(CO)_3Co$–R [R = CH_3 (**5**), CH_2OCH_3 (**8**), $CH_2CO_2CH_2CH_3$ (**12**)] and with $(PMePh_2)_2(CO)_2Co$–CH_2OCH_3 (**10**) are reported. The mono(phosphine) cobalt methyl (**5**) and methoxymethyl (**8**) compounds quickly add CO and give their stable acyl complexes $(PMePh_2)(CO)_3Co$–COR [R = CH_3 (**6**), CH_2OCH_3 (**9**)]. Neither acyl dissociates CO or phosphine in solution. Reactions of **5** and **8** with $PMePh_2$ afford the unstable bis(phosphine) acyl complexes $(PMePh_2)_2(CO)_2Co$–COR [R = CH_3 (**7**), CH_2OCH_3 (**11**)]. These acyl complexes readily dissociate $PMePh_2$ in solution and regenerate **5** and **8**, respectively; upon treating with CO, **11** accordingly generates **9**. Thus, carbonylating **10** affords first **11** and then **9**. Carbethoxymethyl compound **12** is inert to CO under these conditions. The desired carbethoxyacetyl complex $(PMePh_2)(CO)_3CoCOCH_2CO_2CH_2CH_3$ (**13**) interestingly is independently available by either metalating ethyl malonyl chloride or by treating $(CO)_4CoCH_2CO_2CH_2CH_3$ with $PMePh_2$. Once prepared, **13** deinserts CO and generates **12** (half-life in CH_2Cl_2 solution, 9 h). Therefore, if **13** did form in appreciable concentration from carbonylation attempts on **12** (typically 1–2-h duration), then it would have been detected. All organocobalt complexes were purified by column chromatography and were characterized by IR and ^1H, ^{13}C, and ^{31}P NMR spectral procedures and in some cases by elemental analysis.

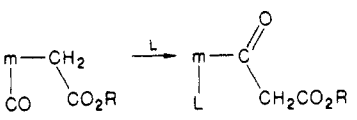
Introduction

Carbonylation reactions that convert a transition organometallic alkoxymethyl complex (**1**) to its alkoxyacetyl derivative **2**, and carbalkoxymethyl **3** to its carbalkoxyacetyl derivative **4**, could model pivotal steps in synthesizing C_2 and C_3 organic products, respectively, from synthesis gas (CO–H_2 mixtures) and homogeneous metal catalysts.[1] Several examples of the former reaction (eq



(1)

1 2



(2)

3 4

1, L = CO) have been recorded,[2] although most alkoxyacetyl compounds have been prepared by using phosphine- or phosphite-promoted alkyl–CO migratory insertion (eq 1, L = PR_3).[3,4] Very little is known concerning carbalkoxyacetyl compounds **4**: two examples were prepared by reacting triphenylphosphine with the requisite **3** (eq 2, L = PPh_3).[3a,5a] Carbonylating **3**, in contrast, requires an oxidizing agent and an alcoholic solvent, which then gives a malonic ester[6] via a net carbalkoxylation reaction.[7]

In previous studies we used organoiron $Cp(CO)(L)Fe$ complexes [L = CO, PPh_3, $P(OMe)_3$] in synthesizing C_2 alkoxyacetyl and carbalkoxyacetyl ligands from carbon monoxide. Thus $Cp(CO)_2Fe$ alkoxymethyl ($FpCH_2OR$), its CH_2OR group originating in the reduction of coordinated CO on $FpCO^+$ in ROH,[8a] readily affords alkoxyacetyl complexes via PPh_3- and $P(OMe)_3$-induced CO insertion (eq 1, MCO = Fp).[4] Carbalkoxymethyl complexes $Cp(CO)(L)FeCH_2CO_2R$ (**3**) then derive either from (1) isomerizing (with a trace of acid) the requisite alkoxyacetyl compound **2**,[4] or (2) carbonylating and then solvolyzing $FpCH_2^+$, which results from protonating $FpCH_2OR$.[8b] Both procedures have in common transcience of an η^2-C,C-ketene complex $Cp(CO)(L)Fe(CH_2{=}C{=}O)^+$ that adds ROH and gives the observed **3**. We were unsuccessful, however, in carbonylating these iron alkoxymethyl and carbalkoxymethyl complexes (eq 1 and 2, L = CO) under conditions where the analogous methyl compounds readily added CO.[8c,d]

Our present approach is to use more labile Co(I) carbonyl complexes in attempting to carbonylate alkoxymethyl and carbalkoxymethyl ligands. The question that we address is the following: If these examples of 1 accordingly give **2** and in sequence **3**, will **3** subsequently add

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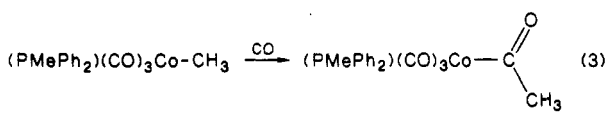
CO under comparable conditions and generate the C_3 carbalkoxyacetyl 4? The cobalt system chosen corresponds to $(MePPh_2)(CO)_3Co$ alkyl and acyl complexes that retain the high Co–CO reactivity but engender increased thermodynamic stability with respect to the parent $(CO)_4Co$ compound.[9] Martin and Baird[10] recently reported, for example, that the methyl complex **5** readily adds CO (1 atm in THF) and affords its fully characterized acetyl derivative **6** (eq 3). We now report results of independ-



(3)

5 **6**

ently reacting CO or excess $PMePh_2$ with **5**, $(PMePh_2)(CO)_3CoCH_2OMe$ (**8**), $(PMePh_2)_2(CO)_2CoCH_2OMe$ (**10**), and $(PMePh_2)(CO)_3CoCH_2CO_2Et$ (**12**).

Experimental Section

All synthetic manipulations were performed under a nitrogen atmosphere by using standard syringe/septum and Schlenk-type bench-top techniques for handling moderately air-sensitive organometallics.[11] Solvents for synthetic work and for recording spectral data were deoxygenated by purging with nitrogen for ca. 20 min. Otherwise, yellow solutions containing alkyl complexes of $(MePh_2P)(CO)_3Co$ and especially of $(MePh_2P)_2(CO)_2Co$ rapidly afford dark green residues. Camag alumina (neutral, activity 3) was used in column chromatography.

Infrared spectra were taken of CH_2Cl_2 solutions (0.10 mmol/2.5 mL) in a NaCl amalgam-spaced (0.10-mm) solution cell and were recorded on a Perkin-Elmer Model No. 297 spectrophotometer. The ν(CO) frequencies (2100–1600 cm^{-1}) were calibrated against the polystyrene 1601 cm^{-1} absorption; they are accurate to ±2 cm^{-1} below and ±5 cm^{-1} above 2000 cm^{-1}. NMR spectral data were recorded in concentrated $CDCl_3$ solutions, after trace amounts of insoluble residues were centrifuged. Varian Model XL-200 and IBM-WP100 instruments supplied the NMR spectra, which are reported as δ values downfield from internal $(CH_3)_4Si$ (^1H and ^{13}C NMR spectra) and in parts per million relative to external H_3PO_4 ($^{31}P\{^1H\}$ NMR spectra). (The PF_6^- absorption in its ^{31}P NMR spectrum is centered at δ −143.2 (J_{PF} = 710 Hz).) Combustion microanalyses were performed by Mic Anal, Tucson, AZ, although acceptable elemental analyses could not be obtained (despite numerous attempts) for most of these unstable cobalt alkyl compounds.

Organic reagents were procured commercially and used as received. Tetrahydrofuran (THF) was additionally distilled under nitrogen from sodium benzophenone ketyl; methylene chloride was likewise obtained as needed from P_2O_5. The anhydrous ether used either was taken from a freshly opened can, or it was distilled from sodium benzophenone ketyl. Metal carbonyl complexes $[(PMePh_2)(CO)_3Co]_2$,[10] $[(PMePh_2)_2(CO)_2Co]_2Hg$,[12] $(CO)_4CoCH_2CO_2CH_2CH_3$ (**14**),[3,13] and $(PMePh_2)(CO)_3CoCH_3$[10] were prepared by literature procedures and judged pure by IR and NMR spectroscopy. $(PMePh_2)(CO)_3CoCOCH_3$ (**6**) was prepared according to the procedure of Martin and Baird:[10] carbonylation of $(PMePh_2)(CO)_3CoCH_3$ (**5**) in THF solution (2 h, 1 atm of CO) and column chromatography afforded spectroscopically pure **6** (91% yield) as a yellow solid.

Preparation of $(PMePh_2)(CO)_3CoCH_2OCH_3$ (8). A light green THF solution (40 mL) containing $(PMePh_2)(CO)_3Co^-Na^+$ (2.92 mmol) [IR 1936 (sh), 1928 (m), 1850 (vs), 1807 (m) cm^{-1}] was generated by stirring a reddish brown solution of $[(PMePh_2)(CO)_3Co]_2$ (1.00 g, 1.46 mmol) over excess Na(Hg) for 0.5 h.[14] This solution was transferred via a stainless-steel needle, cooled to −80 °C, and treated with 0.23 mL (2.92 mmol) of $ClCH_2OCH_3$. After being warmed to and stirred at room temperature (1.5 h), the pale green suspension was filtered through Celite, and the filtrate was evaporated. The light yellow-green oil remaining was chromatographed (20 g of alumina) by using CH_2Cl_2; a yellow band was eluted cleanly that afforded a light yellow-green syrup (1.06 g). This represented a 94% yield of spectroscopically pure $(PMePh_2)(CO)_3CoCH_2OMe$ (**8**).

Preparation of $(PMePh_2)(CO)_3CoCOCH_2OCH_3$ (9). A THF solution (40 mL) containing 4.38 mmol of $(PMePh_2)(CO)_3CoCH_2OCH_3$ (**8**), generated from 1.50 g (2.19 mmol) of $[(PMePh_2)(CO)_3Co]_2$, was filtered. An IR spectrum indicated quantitative alkylation to give **8**, ν(CO) 1956 (br) cm^{-1}. Into this solution was bubbled carbon monoxide (1 atm) for 2 h, and although the pale green solution was unchanged in physical appearance, its IR spectrum was consistent with quantitative conversion of **8** to $(PMePh_2)(CO)_3CoCOCH_2OCH_3$ (**9**): ν(CO) (THF) 1976, 1955 cm^{-1} (C≡O), 1678 cm^{-1} (C=O). The product was filtered through Celite and evaporated, redissolved in 15 mL of CH_2Cl_2, and chromatographed on 20 g of alumina. A light yellow band that cleanly eluted with CH_2Cl_2 afforded spectroscopically pure **9** as a yellow syrup, 1.67 g (92% yield). The product formed bright yellow crystals at −78 °C (from CH_2Cl_2–hexane), but these melted to give a gum upon removing supernatant and warming to room temperature. A similar gum formed when these crystals were warmed to room temperature under vacuum (1 h); **9** did not decarbonylate to **8** under these conditions, as demonstrated by NMR spectral examination.

Preparation of $(PMePh_2)(CO)_3CoCH_2CO_2CH_2CH_3$ (12). To a light green THF solution (40 mL) containing 2.92 mmol of $(PMePh_2)(CO)_3Co^-Na^+$, precooled to −78 °C, was added $BrCH_2CO_2CH_2CH_3$ (0.33 mL, 2.92 mmol). As the mixture was warmed to room temperature (0.75 h), the light yellow-green suspension gradually turned yellow-brown. The reaction was judged complete within 3 h by IR spectral monitoring [ν(CO) 1975, 1966 cm^{-1} (C≡O), 1701 cm^{-1} (C=O)], and the brown suspension was filtered through Celite and evaporated. Column chromatography and vacuum drying of the yellow CH_2Cl_2 eluate afforded a yellow-brown gum (1.09 g), which was $(PMePh_2)(CO)_3CoCH_2CO_2CH_2CH_3$ (**12**) (87% yield).

Anal. Calcd for $C_{20}H_{20}O_5PCo$: C, 55.78; H, 4.65. Found: C, 56.08; H, 4.73.

A Fisher-Porter tube containing a CH_2Cl_2 solution (10 mL) of **12** (0.11 g, 0.23 mmol) was pressurized (70 psig) under carbon monoxide, as the yellow solution was stirred vigorously. After 8 h, an IR spectrum of the unchanged solution indicated only unreacted starting **12**.

Preparation and Carbonylation of $(PMePh_2)_2(CO)_2CoCOCH_3$ (7). Dimeric $[(PMePh_2)(CO)_3Co]_2$ (1.00 g, 1.46 mmol), upon reducing with Na(Hg) to $(PMePh_2)(CO)_3Co^-Na^+$ in THF solution (50 mL) and alkylating with CH_3I (0.19 mL, 2.92 mmol) at −78 °C, afforded $(PMePh_2)(CO)_3CoCH_3$ (**5**). IR spectral monitoring established that **5** [ν(CO) 1956 (br) cm^{-1}] was formed quantitatively after the pale green reaction mixture was stirred for 1 h at room temperature. To the filtered solution was added 0.54 mL of $PMePh_2$ (2.92 mmol), and IR spectral monitoring was consistent with **5** being consumed within 0.5 h: ν(CO) 1964 (m), 1907 (vs) cm^{-1} (C≡O), 1655 (m) cm^{-1} (C=O). The pale yellow-green solution then was evaporated on a rotary evaporator, redissolved in CH_2Cl_2 (10 mL), and chromatographed on 20 g of alumina. The resulting dark yellow eluate (with CH_2Cl_2) afforded a golden yellow syrup (1.53 g after vacuum drying). ^1H NMR data

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Table I

reactn time, h	% 10	% 11	% 9
1	70	25	5
2	33	33	33
3	10	32	58

was consistent with it containing 85% $(PMePh_2)_2(CO)_2CoCOCH_3$ (7) (overall yield 79%), while the ^{31}P NMR spectrum exhibited the assigned absorption, δ 26.5, plus four others at δ 45.0 (33%), 39.9 (23%), 15.4 (22%), and 8.7 (12% relative intensity).

Into a CH_2Cl_2 solution (3.0 mL) containing 59 mg (0.11 mmol) of the above syrup was bubbled CO for 0.5 h. The initially yellow solution had turned yellow-green, and IR spectral monitoring indicated a 1:4 ratio of $(PMePh_2)_2(CO)_2CoCOCH_3$ (7) and $(PMePh_2)(CO)_3CoCOCH_3$ (6).

Preparation and Carbonylation of $(PMePh_2)_2(CO)_2CoCH_2OCH_3$ (10). An orange THF solution (40 mL) containing $[(PMePh_2)_2(CO)_2Co]_2Hg$ (1.00 g, 0.81 mmol) was reduced with excess Na(Hg) to a golden yellow solution (4 h) containing $(PMePh_2)_2(CO)_2Co^-Na^+$. This was transferred, cooled to −78 °C, and treated with $ClCH_2OCH_3$ (0.13 mL, 1.6 mmol). After being warmed to room temperature (1 h), the light yellow suspension was filtered through Celite and evaporated, and the resulting yellow residue was chromatographed on alumina–CH_2Cl_2. The yellow band that cleanly separated left a golden yellow gum after vacuum drying (0.78 g). ^1H NMR spectra are consistent with this gum being at least 87% $(PMePh_2)_2(CO)_2CoCH_2OCH_3$ (10) (calculated yield 76%), whereas the ^{31}P NMR spectrum contained in addition to the assigned resonance of 10 at δ 30.2 two other absorptions at δ 44.4 (36%) and 26.10 (21% relative intensity).

Into a CH_2Cl_2 solution (60 mL) of the above gum (600 mg) was bubbled carbon monoxide, and over 1-, 2-, and 3-h intervals 20-mL portions were removed, evaporated, and chromatographed (15 g of alumina) with CH_2Cl_2. The distribution of each component—$(PMePh_2)_2(CO)_2CoCH_2OMe$ (10), $(PMePh_2)_2(CO)_2CoCOCH_2OMe$ (11), and $(PMePh_2)(CO)_3CoCOCH_2OMe$ (9)—was assessed via ^1H NMR spectroscopy, using the relative integration ratios for the OCH_3 absorptions at δ 3.22 (10), 3.11 (11), and 3.43 (9). Table I records these results, no other organometallic product being detected. In a separate experiment, it was determined that this carbonylation quantitatively afforded $(PMePh_2)(CO)_3CoCOCH_2OMe$ (9) over 12 h.

Preparation and Carbonylation of $(PMePh_2)_2(CO)_2CoCOCH_2OCH_3$ (11). Methyldiphenylphosphine (0.49 mL, 2.2 mmol) was added to a CH_2Cl_2 solution (40 mL) of $(PMePh_2)(CO)_3CoCH_2OCH_3$ (8) (1.02 g, 2.62 mmol). An IR spectrum recorded after 0.5 h of the yellow solution indicated that 8 had converted to $(PMePh_2)_2(CO)_2CoCOCH_2OCH_3$ (11). After concentrating and chromatographing (alumina–CH_2Cl_2) the product, a golden yellow gum, remained; it was crystallized from ether–pentane as a light yellow solid, mp 105–106 °C; 1.44 g (93%).

Anal. Calcd for $C_{31}H_{31}O_4P_2Co$: C, 63.23; H, 5.27. Found: C, 63.05; H, 5.27.

The ^1H NMR spectra ($CDCl_3$) of 11, indicated a 1:1 ratio of 11 vs. 8, as deduced from integration ratios of the OCH_3 absorptions for each component. Adding excess (50% stoichiometric) phosphine to these solutions, however, increased the ratio to >15:1. In contrast, CH_2Cl_2 solutions containing 11 and CH_3I (1.5 equiv) completely regenerated 8 (2 h), as determined by IR spectral monitoring. Although ^{31}P NMR spectra of 11 in CH_2Cl_2 afforded several resonances (as observed for 7), addition of excess $MePh_2P$ to these solutions then gave only two signals, δ 26.0 (for 11) and −26.8 (for free phosphine).

A CH_2Cl_2 solution (4 mL) containing $(MePh_2P)_2(CO)_2CoCOCH_2OCH_3$ (11) (0.15 g, 0.26 mmol) was treated with CO (1 atm) for 1 h. The gas dispersion frit then was removed, and IR spectra of the yellow solution indicated a 1:1 mixture of 11 and $(PMePh_2)(CO)_3CoCOCH_2OCH_3$ (9).

Reaction of $(PMePh)(CO)_3Co^-Na^+$ with Ethyl Malonyl Chloride. A THF solution (60 mL) containing 1.46 mmol of $(PMePh_2)(CO)_3Co^-Na^+$ was prepared by Na(Hg) cleavage of $[(PMePh_2)(CO)_3Co]_2$ (1.50 g, 0.73 mmol). The yellow green solution then was transferred via a stainless-steel double-ended needle, cooled to −78 °C, and treated dropwise with $ClCOCH_2CO_2CH_2CH_3$ (0.19 mL, 1.46 mmol). This instantaneously generated a red solution. Its IR spectrum indicated two medium intensity ligand ν(CO) at 1740 (ester) and at 1668 cm^{-1} (acyl), which are consistent with the presence of $(PMePh_2)(CO)_3CoCOCH_2CO_2CH_2CH_3$ (13). The terminal CO absorption region, however, shows a poorly resolved broad peak (1950–1980 cm^{-1}) due to the presence of $[(PMePh_2)(CO)_3Co]_2$ [ν(CO) 1973 (sh), 1953 (vs) cm^{-1}]. The ^{31}P NMR spectrum of the same sample (after stripping and redissolving in $CDCl_3$) likewise contained absorptions for 13 (δ 34.5) and for the above dimer (δ 50.9) in 2:1 intensity ratio.

The original reaction mixture (at −78 °C) was filtered quickly through Celite (maintained at −78 °C) and was passed through an alumina column (100 g). Quick passage of the mixture through the alumina (cold) did not separate 13 from dimer; extended contact with alumina (or Florosil) decomposed the mixture to dimer. As the result of rapid chromatography on a cold column, a 2:1 mixture of $(PMePh_2)(CO)_3CoCOCH_2CO_2CH_2CH_3$ (13) and $[(PMePh_2)(CO)_3Co]_2$ was obtained as a dark red-brown syrup (0.611 g). No other organometallic products were detected by ^{31}P or ^1H NMR spectroscopy, although residual THF (ca. 10%) was evident. The 2:1 quantification (55% yield of 13) was determined by integrating the P–CH_3 absorptions in the ^1H NMR spectra.

Reaction of $(CO)_4CoCH_2CO_2CH_2CH_3$ (14) and Methyldiphenylphosphine. To a cold (+5 °C) CH_2Cl_2 solution (54 mL) containing $(CO)_4CoCH_2CO_2CH_2CH_3$ (14) (2.23 g, 8.6 mmol) was added $PMePh_2$ (1.61 mL, 8.6 mmol), and the dark red-brown solution was stirred (0.5 h). IR spectral examination then indicated that 15 [ν(CO) 1695 cm^{-1} (ester)] had quantitatively converted to $(PMePh_2)(CO)_3CoCOCH_2CO_2CH_2CH_3$ (13). The solution was concentrated (to 25 mL), quickly filtered through 20 g of alumina with additional CH_2Cl_2 and evaporated. A dark brown syrup remained, 3.61 g after vacuum drying at 10^{-2} mm/+5 °C/0.5 h, which contained a 9:1 mixture of $(PMePh_2)(CO)_3CoCOCH_2CO_2CH_2CH_3$ (13) (83% yield) and $(PMePh_2)(CO)_3CoCH_2CO_2CH_2CH_3$ (12) as the only organometallics detected by ^1H NMR spectroscopy. This spectral data was collected at −50 °C, and the quantification was done by integrating the P–Me doublets centered at δ 2.11 (12) (which also contained the $CoCH_2$ resonance) and at δ 2.02 (13). When this product was stored for 12 h at 0 °C, the product ratio was redetermined as 5.3:1 (13:12).

The deinsertion of 13 to 12 in CH_2Cl_2 solution at room temperature was examined under 1 atm of N_2 and of CO. Thus, 0.31 g of 91% pure $(PMePh_2)(CO)_3CoCOCH_2CO_2CH_2CH_3$ (13) (0.60 mmol), having $(PMePh_2)(CO)_3CoCH_2CO_2CH_2CH_3$ (12) as the impurity, was dissolved in 16 mL of CH_2Cl_2 under N_2, and the dark brown solution was monitored by IR spectroscopy. Over 13 h, the acyl ν(CO) for 13 (1732, 1668 cm^{-1}) diminished in intensity as that for 12 (1684 cm^{-1}) grew in; the half-life for this transformation is 9 h. After 13 h, the remaining solution was evaporated, and the ^1H NMR spectrum was recorded (−50 °C): a 2.8/1 mixture of 12 to 13—the only products detected—was established. Identical results obtained for a parallel reaction that was conducted under 1 atm of CO.

Results and Discussion

I. Preparation of Cobalt Alkyl Compounds $(PMePh_2)(CO)_3Co$–R [R = CH_3 (5), CH_2OCH_3 (8), $CH_2CO_2CH_2CH_3$ (12)] and $(PMePh_2)_2(CO)_2Co$–CH_2OCH_3 (10). Mono(phosphine)-substituted cobalt alkyls $(PMePh_2)(CO)_3Co$–R [R = CH_3 (5), CH_2OCH_3 (8), $CH_2CO_2CH_2CH_3$ (12)] are generated readily via the standard procedure[9,14] of alkylating the $(PMePh_2)(CO)_3Co^-Na^+$ nucleophile (eq 4). The methyl complex 5

$$[(PMePh_2)(CO)_3Co]_2 \xrightarrow[THF]{Na(Hg)} 2(PMePh_2)(CO)_3Co^-Na^+ \xrightarrow{2RX} (PMePh_2)(CO)_3Co\text{–}R \quad (4)$$

5, R = CH_3
8, R = CH_2OCH_3
12, R = $CH_2CO_2CH_2CH_3$

was isolated as a yellow powder, in agreement with Martin and Baird,[10] whereas methoxymethyl 8 and carbometh-

oxymethyl **12** were obtained only as yellow gums (in 90% yields after chromatography). All three slowly decompose upon storage (even at −10 °C); chromatography on alumina, however, subsequently elutes the purified alkyl complex (yellow band) from the uncharacterized green residue. Methylene chloride solutions of **5**, **8**, and **12**, in contrast, are stable (at or below room temperature only) for at least several hours.

These cobalt alkyl complexes are characterized unambiguously in solution by their IR and ^1H, ^{13}C, and ^{31}P NMR spectral data (Table II). The spectroscopically pure products obtained are free of solvent and other organic residues; they are free of organometallic contaminants; they obviously have similar structures in solution. For example, the methylene groups attached to the Co center in the new complexes **8** and **12** afford ^1H and ^{13}C NMR spectral absorptions exhibiting coupling to one phosphorous. The IR spectra, with a pattern of one weak and two strong $\nu(C{\equiv}O)$ [or one weak and one broad, strong $\nu(CO)$], closely resemble those reported for other mono(phosphine) (usually PPh_3) cobalt alkyl and acyl compounds, $L(CO)_3Co–R$.[10,13,15] Trigonal-bipyramidal structures with the organic and phosphine ligands in axial (trans) positions, moreover, have been assigned to this class of molecules, on the basis of IR spectral data (which are consistent with pseudo-C_3 local symmetry) and on several X-ray crystallographic structural determinations.[13,15d,f] We accordingly assign trigonal-bipyramidal structures to **8** and **12** (and **10**) that contain axial phosphine and alkyl ligands and three equatorial carbonyls.[9,10]

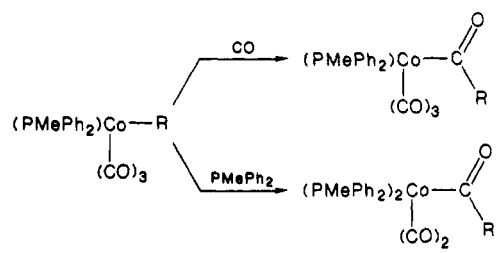
Phosphorus-31 NMR spectroscopy serves as a sensitive spectral probe for both the purity of $(PMePh_2)(CO)_3Co$ alkyl and acyl complexes, as well as for the structural type. Thus, the presence of even small amounts of free phosphine (δ −26.8) or of starting dimer (δ +50.7) is readily apparent. The four structural types encountered in this study likewise absorb in distinctive regions: $(PMePh_2)(CO)_3Co–R$ (δ >+40), $(PMePh_2)(CO)_3Co–COR$ (δ 33), $(PMePh_2)_2(CO)_2Co–R$ (δ 30), $(PMePh_2)_2(CO)_2Co–COR$ (δ 26), although more data will be required in order to establish this correlation.

The bis(phosphine)-substituted methoxymethyl complex $(PMePh_2)_2(CO)_2Co–CH_2OCH_3$ (**10**) also is prepared by alkylating a Co(I−) nucleophile (eq 5). This new intermediate, in turn, results from sodium amalgam reduction of the readily available $[(PMePh_2)_2(CO)_2Co]_2Hg$.[16] (The analogous triphenylphosphine system had been generated by cleaving $(PPh_3)_2(CO)_2Co–I$ with Na(Hg).[15b,17]) Treating our Co(I−) nucleophile with chloromethyl methyl ether and working up by column chromatography affords **10** in 76% yield as a yellow gum. This complex, however, is unstable, and in contrast to its monophosphine analogue **8**, **10** degrades even in CH_2Cl_2 solution to several unidentified species. IR and ^1H NMR spectral data (collected quickly on samples of **10** immediately after chromatography) nevertheless are consistent with the trigonal-bipyramidal $(PMePh_2)_2(CO)_2Co–R$ structure having diaxial (trans) phosphines. The methylene resonance in the ^1H NMR spectrum clearly shows spin–spin coupling to two equivalent phosphines, and the two IR spectral $\nu(CO)$ of unequal intensities are consistent with the cis-diequatorial array of carbonyls.[18] This marked instability of **10** undoubtedly arises from the lability of one of the ligated phosphines (vide infra).

$$[(PMePh_2)_2(CO)_2Co]_2Hg \xrightarrow[THF]{Na(Hg)} (PMePh_2)_2(CO)_2Co^-Na^+ \xrightarrow{CH_3OCH_2Cl} (PMePh_2)_2(CO)_2Co–CH_2OCH_3 \quad (5)$$
10

Examples of other methyl, methoxymethyl, and carbalkoxymethyl complexes $L(CO)_3Co–R$ have been reported previously. All three have been generated with L = CO,[9] but only the $(CO)_4Co$(carbalkoxymethyl) complexes are sufficiently stable for isolation and for NMR and other spectral analysis.[13] With L = PPh_3, the more stable methyl[14a] and several carbalkoxymethyl compounds have been fully characterized; in particular our ^{13}C NMR spectral data for **12** is in rather close agreement with that of $(PPh_3)(CO)_3Co–CH_2CO_2CH_2Ph$.[13] The structure of the latter—containing diaxial carbobenzoxymethyl and PPh_3 ligands—also was established by a single-crystal X-ray diffraction study.[13] Only one example of a bis(phosphine) complexes $L_2(CO)_2CoR$, $(PPh_3)_2(CO)_2Co–CH_3$, has been previously characterized, albeit without benefit of NMR spectral data.[17a]

We adopted $PMePh_2$ in preference to PPh_3 in this study for three reasons. First, as a matter of convenience, the starting dimer $[(PMePh_2)(CO)_3Co]_2$ is a soluble compound that is readily purified and used in subsequent reductive chemistry, in contrast to its insoluble PPh_3 analogue.[10] Second, the presence of the $P–CH_3$ doublet in the ^1H NMR spectra of the Co alkyl and acyl complexes offers a useful analytical probe. Finally, with $PMePh_2$, we retain the option of promoting CO insertion (eq 6) with excess phosphine as well as with CO. Such a phosphine-facilitated alkyl migration evidently does not occur upon reacting PPh_3 and $(PPh_3)(CO)_3CoCH_3$.[3b]



(6)

The disadvantage to working with these $PMePh_2$-substituted cobalt complexes, however, is that they generally form gums. Any solids that do precipitate at −80 °C from ether–pentane solutions inevitably melt well below 0 °C. These gums in turn are unstable; we could neither store these cobalt alkyl and acyl complexes, nor could we routinely obtain acceptable elemental analyses. Of the seven new compounds reported in Table II, only **11** and **12** analyzed properly, although **8** and **9** are obtained spectroscopically pure.[19] Four of these new compounds owe their

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(16) Reducing Hg(II) bis(carbonylmetalate) with Na(Hg) often is a cleaner source of its carbonylmetalate anion than is similar cleavage of either the carbonylmetalate dimer or the carbonylmetalate halide derivative. Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852.

(17) (a) Hieber, W.; Duchatsch, H. *Chem. Ber.* **1965**, *98*, 2933. (b) Hieber, W.; Beck, W.; Lindner, E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1961**, *16B*, 229. (c) Booth, B. L.; Hasyeldine, R. N.; Perkins, I. *J. Chem. Soc., Dalton Trans.* **1975**, 1843.

(18) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks-Cole: Monterey, CA, 1985; p 79.

(19) Insubsequent, unrelated studies we found that use of triphenylphosphine generally leads to stable cobalt alkyl and acyl complexes $(PPh_3)(CO)_3Co–R$, which are generally crystalline, easily purified, and readily dissolved in most organic solvents. These complexes, moreover, routinely produce acceptable elemental analyses.

Table II. Spectroscopic Characterization of Cobalt Complexes

complex	IR (CH_2Cl_2), cm^{-1}	^1H NMR ($CDCl_3$), δ	$^{13}C\{^1H\}$ NMR ($CDCl_3$), ppm	^{31}P NMR ($CDCl_3$), ppm
$(PMePh_2)(CO)_3Co-CH_2OCH_3$ (8)	2034 (w), 1959 (br, vs)	5.18 (d, J_{PH} = 2.2 Hz) $CoCH_2$ 3.42 (s) OCH_3 2.06 (d, J_{PH} = 8.5 Hz) PCH_3[a]	200.6 (br) CO 68.3 (d, J = 26 Hz) $CoCH_2$[c] 59.6 OCH_3 19.1 (d, J = 29 Hz) PCH_3[b]	40.0
$(PMePh_2)(CO)_3Co-CH_2CO_2CH_2CH_3$ (12)[d]	2050 (vw), 1974 (br, vs) (C≡O) 1685 (m) (C=O)	4.11 (quart, J = 7.1 Hz) OCH_2 2.14–2.08 (m) $CoCH_2$ + PCH_3[a] 1.25 (t, J = 7.1 Hz) OCH_2CH_3	198.4 (d, J = 21 Hz) CO 181.1 (s) CO_2 59.3 (s) OCH_2 19.4 (d, J = 33 Hz) PCH_3[b] 14.0 OCH_2CH_3 4.6 (d, J = 16 Hz) $CoCH_2$[e]	45.6
$(PMePh_2)(CO)_3Co-COCH_3$ (6)	2048 (w), 1976 (vs) (C≡O) 1957 (vs) 1666 (m) (C=O)		238.6 (d, J_{PC} = 33 Hz) $CoCOCH_3$ 198.8 (br) CO 49.9 (d, J_{PC} = 25 Hz) $CoCOCH_3$ 18.0 (d, J_{PC} = 29 Hz) PCH_3[b]	33.4
$(PMePh_2)(CO)_3Co-COCH_2OCH_3$ (9)	2048 (w), 1982 (vs) (C≡O) 1961 (vs) 1672 (w) (C=O)	4.33 (s) $COCH_2$ 3.43 (s) OCH_3 2.02 (d, J = 8.5 Hz) PCH_3[a]	239.0 (d, J = 31 Hz) $CoCOCH_3$ 198.4 (br d, J = 21 Hz) CO 89.4 (d, J = 28 Hz) CH_2O 59.0 (s) OCH_3 18.0 (d, J = 29 Hz) PCH_3[b]	33.4
$(PMePh_2)(CO)_3Co-COCH_2CO_2CH_2CH_3$ (13)	2055 (w), 1985 (vs) (C≡O) 1966 (vs) 1732 (m), 1668 (m) (C=O)	4.16 (quart, J = 7.1 Hz) OCH_2 4.04 (s) $COCH_2$ 2.02 (d, J = 8.6 Hz) PCH_3[a] 1.25 (t, J = 7.1 Hz) CH_3	233.5 (d, J = 33 Hz) $CoCOCH_2$ 196.5 (d, J = 22 Hz) CoCO 165.3 (s) CO_2 66.7 (d, J = 23 Hz) $COCH_2CO_2$ 59.7 (s) CO_2CH_2 17.1 (d, J = 30 Hz) PCH_3[b] 12.8 (s) CH_3	34.5
$(PMePh_2)_2(CO)_2Co-CH_2OCH_3$ (10)	1964 (m), 1901 (s) (C≡O)	4.36 (t, J = 5.4 Hz) $CoCH_2$ 3.22 (s) OCH_3 1.56 (br s) PCH_3[f]		30.2
$(PMePh_2)_2(CO)_2Co-COCH_3$ (7)	1969 (s), 1908 (vs) (C≡O) 1653 (m) (C=O)	2.58 (s) $COCH_3$ 1.55 (br s) PCH_3[f]	249.1 (t, J = 12 Hz) $CoCOCH_3$ 203.1 (br s) CoCO 49.3 (t, J = 11 Hz) CH_3 16.0 (t, J = 13 Hz) PCH_3[g]	26.5
$(PMePh_2)_2(CO)_2Co-COCH_2OCH_3$ (11)	1971 (s), 1908 (vs) (C≡O) 1647 (m) (C=O)	4.27 (s) $COCH_2$ 3.11 (s) OCH_3 1.57 (virt t, J = 3.5 Hz) PCH_3[f]	248.4 (t, J = 10 Hz) $CoCOCH_2$ 203.8 (br s) CoCO 88.7 (t, J = 11 Hz) CH_2 58.4 (s) OCH_3 15.9 (t, J = 13 Hz) PCH_3[g]	26.0

[a] Phenyl absorptions: δ 7.5 (m). [b] Phenyl absorptions: δ 135–128, as a doublet (C-ipso, J_{PC} = 42–47 Hz), doublet (C-ortho, J_{PC} = 11 Hz), singlet (C-para), doublet (C-meta, J_{PC} = 10–11 Hz) pattern. [c] J_{CH}^1 = 141 Hz. [d] $(CO)_4CoCH_2CO_2CH_2CH_3$, ^{13}C NMR ($CDCl_3$) δ 195.7 (CO), 163.7 (CO_2), 59.6 (OCH_2), 13.2 (CH_3), 6.8 ($CoCH_2$); IR (CH_2Cl_2) 2110, 2020 (C≡O) cm^{-1}, 1695 (C=O) cm^{-1}. [e] J_{CH}^1 = 143 Hz. [f] Phenyl absorptions: δ 7.4 (m). [g] Phenyl absorptions: δ 137–127 as a virtual triplet (C-ipso, J = 20 Hz), virtual triplet (C-ortho, J = 5 Hz), singlet (C-para), and a virtual triplet (C-meta, J = 5 Hz).

solution instability either to lability of coordinated phosphine (**7**, **10**, and **11**) or of ligated CO (**13**) (vide infra). All seven cobalt alkyl and acyl complexes, however, are characterized in solution through analysis of their IR and ^1H, ^{13}C, ^{31}P NMR spectral data.

II. Cobalt Methyl/Acetyl and Methoxymethyl/Methoxyacetyl Transformations. Scheme I depicts our results for alkyl–CO migration reactions of cobalt methyl and methoxymethyl complexes. Both $(PMePh_2)(CO)_3CoCH_2OCH_3$ (**8**) and as previously reported[10] $(PMePh_2)(CO)_3CoCH_3$ thus quantitatively add CO (1 atm; 2 h in THF solution) and give their acyl complexes **9** and **6**, respectively. IR spectral ν(CO) for the acyl ligand (1678 cm^{-1} for **9** in THF) proved especially diagnositic in monitoring these reactions, since no other physical changes of the starting solution (of **8**) were apparent.

Workup of these reactions affords $(PMePh_2)(CO)_3CoCOCH_3$ (**6**) as a yellow solid and $(PMePh_2)(CO)_3CoCOCH_2OCH_3$ (**9**) as a yellow gum (92% yield), even after column chromatography and repeated attempts at low-temperature crystallization. Spectral data for **9** both demonstrate the absence of organic and organometallic contaminants and resemble that of **6** (Table II). Their IR spectra, as noted, are consistent with trigonal-bipyramidal structures having trans disposition of the acyl and phosphine ligands. The PPh_3 analogue of **9** $(PPh_3)(CO)_3CoCOCH_2OCH_3$ had been previously prepared (but without supporting spectral data) through the reaction of PPh_3 with $(CO)_4CoCH_2OCH_3$.[3a]

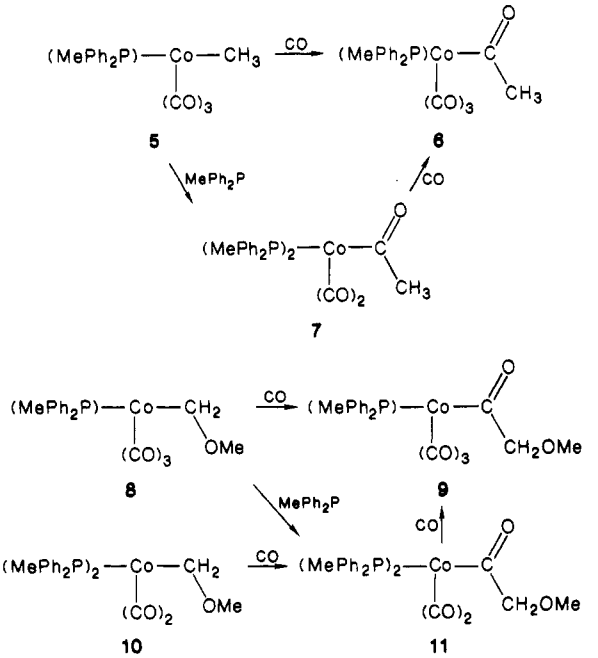
Both acyl complexes **6** and **9** are stable as CH_2Cl_2 solutions and under a N_2 atmosphere for at least 24 h. Neither deinserted CO and regenerated its starting alkyl compound: ^{31}P NMR spectral thus exhibited only one singlet (δ 33.4 for either **6** or **9**) for these solutions.

The carbonylation step that produces **6** and **9** presumably entails an alkyl–CO migratory insertion, analogous to that established for carbonylating $(CO)_5Mn(alkyl)$ complexes.[20] Results of a previous study by Nagy-Magos, Bor, and Marko[21] on carbonylating $(PPh_3)(CO)_3CoCH_2Ph$ are in accordance with this mechanism. They found that ^{13}CO (1 atm) regiospecifically converts this benzyl complex to the labeled phenylacetyl compound $(PPh_3)(CO)_2(^{13}CO)CoCOCH_2Ph$.

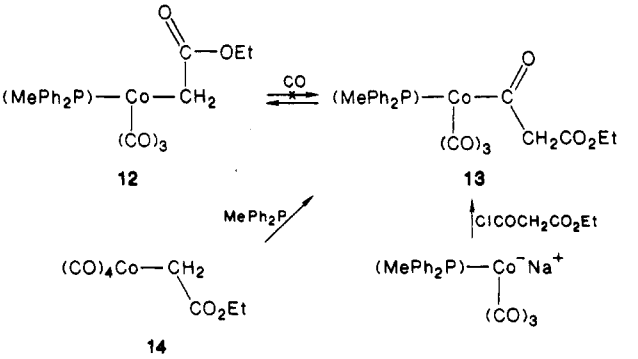
Methyldiphenylphosphine also intercepts alkyl migration reactions on the cobalt methyl and methoxymethyl (**8**) complexes (Scheme I). With **8**, for example, 1 equiv of $PMePh_2$ in CH_2Cl_2 solution quantitatively generates

(20) Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410.
(21) Nagy-Magos, Z.; Bor, G.; Marko, L. *J. Organomet. Chem.* **1968**, *14*, 205.

Scheme I

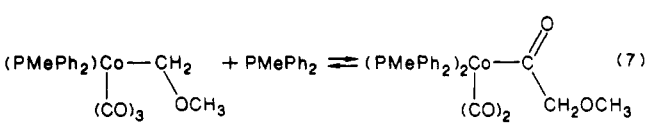


Scheme II



$(PMePh_2)_2(CO)_2CoCOCH_2OCH_3$ (**11**) over 0.5 h, as evidenced by the changes in the IR spectra (Table II). Chromatographic workup produces **11** as an analytically pure, light yellow solid in 93% yield. A similar reaction and workup with **5** gave the acetyl analogue $(PMePh_2)_2(CO)_2CoCOCH_3$ (**7**) as a yellow gum (79%). Both acyl complexes **7** and **11**, however, are unstable in solution.

This solution instability derives from the presence of highly labile phosphine that is coordinated on **7** and on **11**. NMR spectra (^1H, ^{13}C, and ^{31}P) of **11** inevitably indicated the presence of varying amounts of **8**, which increased by sequestering the $PMePh_2$ released and thus shifting the equilibrium (eq 7) to the left. When excess

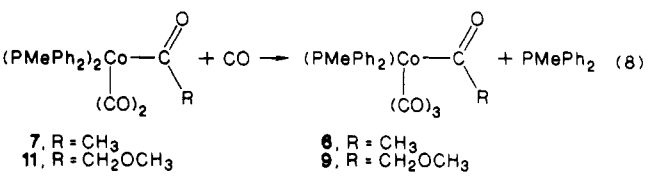


(7)

methyl iodide was added to a CH_2Cl_2 solution of **11**, for example, **8** was completely regenerated. Gradual loss of phosphine from **11** (or **7**) in solution additionally initiates other decomposition pathways, as evident by the presence of at least five signals for ligated phosphine in the ^{31}P NMR spectra. Adding excess phosphine, however, suppresses this phosphine dissociation, and ^{31}P NMR spectra now contain only one signal for ligated phosphine on **11** (δ 26.0) and another for excess $PMePh_2$ (δ −26.8).

Structural assignment for **7** and **11** possessing trans-axial phosphines reasonably follows from analysis of their NMR and IR spectral data (Table II). The ^1H NMR of **11** clearly has a virtual triplet[22] at δ 1.57 for the phosphine–methyl absorption. ^{13}C NMR spectra of both **7** and **11** also indicate that their acyl carbonyl and adjacent methyl (**7**) or methylene (**11**) carbons couple to two equivalent phosphines. These phosphines evidently are stereochemically nonrigid for at least **11**; its ^{31}P NMR spectrum (δ 26.8 in toluene-d_8) remains a sharp singlet between −50 and +22 °C. Finally, the two IR ν(CO) for the terminal carbonyls, of unequal intensities, are consonant with a cis-diequatorial geometry of these ligands.[18]

Observations on **7** and **11** readily dissociating phosphine in solution are consistent with the results of their reactions with carbon monoxide. Both bis(phosphine) acyl complexes accordingly form 1:1 mixtures (1 h) with their mono(phosphine) acyl derivatives **6** and **9**, respectively, under 1 atm of CO (eq 8). The latter reaction presumably



(8)

occurs also during the carbonylation of $(PMePh_2)_2(CO)_2CoCH_2OCH_3$ (**10**) (Scheme I). As indicated by the data in Table I, **10** adds CO (at 1 atm) to give initially **11**, which subsequently forms **9**. We, however, do not distinguish between two plausible reaction sequences: (1) **7**/**11** could dissociate $PMePh_2$, deinsert CO from the acyl ligand, and then add and insert CO on the alkyl complex $(PMePh_2)(CO)_3CoR$; (2) the coordinatively unsaturated acyl compound $(PMePh_2)(CO)_2CoCOR$, resulting from phosphine dissociation, could directly add CO and give **6** or **9**.

Precedent for this phosphine lability from [bis(phosphine)]$(CO)_2Co$(acyl) complexes is available from the work of Donaldson and Hughes.[23] They found that a cobalt η^1-2-cyclopropene-1-carbonyl intermediate $(PPh_3)_2(CO)_2Co{-}CO{-}\overline{CHC(Ph)=C(Ph)}$, available by alkylating the requisite Co(I−) anion with 2,3-diphenyl-2-cyclopropene-1-carbonyl chloride, preferentially extrudes phosphine in forming its η^3-oxocyclobutenyl derivative $(PPh_3)(CO)_2Co{-}[\eta^3{-}\overline{CHC(Ph)=C(Ph)CO}]$.

Related cobalt acetyl complexes $(L_1)(L_2)(CO)_2CoCOCH_3$, with $L_1 = PPh_3$, L_2 = phosphite or L_1, L_2 = phosphite, have been prepared by reacting phosphite with the requisite $(L_1)(CO)_3CoCH_3$ complex.[3b] The solution behavior of the resulting acetyl complexes, e.g., NMR spectra, was not recorded for most. More recently, Atwood[24] has used $[P(OMe)_3]_2(CO)_2CoCOCH_3$ as an olefin hydrogenation catalyst, with its activity apparently depending on preferential dissociation of carbon monoxide.

III. Cobalt Carbethoxymethyl and Carbethoxyacetyl Complexes. The carbethoxymethyl complex $(PMePh_2)(CO)_3CoCH_2CO_2CH_2CH_3$ (**12**) does not add CO

(22) (a) Verkade, J. G.; McCarley, R. E.; Hendricker, D. G.; King, R. W. *Inorg. Chem.* **1965**, *4*, 228. (b) Jenkens, J. M.; Shaw, B. L. *J. Chem. Soc. A* **1966**, *770*, 1407. (c) Fackler, J. P.; Fetchin, J. A.; Mayhew, J.; Siedel, W. C.; Swift, T. J.; Weeks, M. *J. Am. Chem. Soc.* **1969**, *91*, 1941.

(23) Donaldson, W. A.; Hughes, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 4846.

(24) Janik, T. S.; Pyszczek, M. F.; Atwood, J. D. *J. Mol. Catal.* **1981**, *11*, 33. Atwood, J. D.; Janik, T. S.; Pyszczek, M. F.; Sullivan, P. S. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 259.

(even at 70 psig) in CH_2Cl_2 solution over 8 h (Scheme II). Instead, starting **12** is recovered quantitatively, and none of the anticipated carbethoxyacetyl compound $(PMePh_2)(CO)_3CoCOCH_2CO_2CH_2CH_3$ (**13**) is detected by IR spectroscopy. We did however independently synthesize **13** by two alternative synthetic routes.

These two syntheses (Scheme II) consist of acylating nucleophilic $(PMePh_2)(CO)_3Co^-Na^+$ with ethyl malonyl chloride and treating $(CO)_4CoCH_2CO_2CH_2CH_3$ (**14**) with $PMePh_2$. The former reaction afforded a 2:1 mixture of **13** and starting dimer $[(PMePh_2)(CO)_3Co]_2$, which did not separate upon column chromatography. We believe that the dimer originates from the unstable hydride $(PMePh_2)(CO)_3CoH$,[10] which in turn derives from the Co(I–) anion deprotonating the ethyl malonyl chloride. A similar reaction occurred upon reacting $Cp(CO)_2Fe^-Na^+$ with $ClCOCH_2CO_2CH_2CH_3$; the entire organometallic fraction consisted of $Cp(CO)_2FeH$ and $[Cp(CO)_2Fe]_2$.[8d]

In the second synthetic procedure, $PMePh_2$ quantitatively transforms $(CO)_4CoCH_2CO_2CH_2CH_3$ (**14**) in CH_2Cl_2 solution to a 9:1 mixture of **13** and its deinsertion product $(PMePh_2)(CO)_3CoCH_2CO_2CH_2CH_3$ (**12**). Chromatography gave a brown gum that contained **13** (83% yield) plus **12**. ^1H and ^{13}C NMR spectra are especially diagnostic for **13** (Table II), although these data must be recorded at low temperatures in order to slow down subsequent deinsertion of **13** to **12**. As with other cobalt acyl complexes in this study, all ^{13}C resonances for **13** were assigned. Those for the acyl and β-methylene carbons, for example, appear as doublets due to coupling to phosphorus.

Carbethoxyacetyl **13**, generated by either synthetic route, readily deinserts CO and gives **12** at room temperature. IR spectra monitoring of this reaction is particularly convenient: the ester ν(CO) for **12** (1685 cm^{-1}) slowly grows in as the acyl and ester ν(CO) for **13** (1668 and 1732 cm^{-1}, respectively) diminish in intensity. Results of both IR and ^1H NMR spectral studies, furthermore, support **13** cleanly degrading to **12** with a half-life of 9 h, which is independent of N_2 or CO serving as the inert atmosphere.

Independent support for our assignment of **13** as a carbethoxyacetyl complex rests with previously reported work on the triphenylphosphine analogues $(PPh_3)(CO)_3CoCOCH_2CO_2R$. Heck and Breslow[3a] isolated the carbomethoxyacetyl derivative as an analytically pure yellow solid, but no spectral data are available. Separate studies, however, have focused on a similar reaction of PPh_3 and $(CO)_4CoCH_2CO_2CH_2CH_3$ (**14**). In ether solutions, **14** apparently formed an unstable and uncharacterized carbethoxyacetyl intermediate that degraded to $(PPh_3)(CO)_3CoCH_2CO_2CH_2CH_3$,[13] whereas in heptane solution a similar reaction gave only the phosphine-substituted carbethoxymethyl $(PPh_3)(CO)_3CoCH_2CO_2CH_2CH_3$.[25]

Conclusions

In summary, this study has accomplished three objectives. First, a cobalt methoxymethyl complex $(PMePh_2)(CO)_3CoCH_2OCH_3$ (**8**) carbonylates under extremely mild conditions (1 atm CO; room temperature) and gives its methoxyacetyl derivative **9**. This acyl is stable in solution, with no evidence of CO or phosphine dissociating in solution. Second, the bis(phosphine) methoxyacetyl complex $(PMePh_2)_2(CO)_2CoCOCH_2OCH_3$ (**11**), which is available by reacting $PMePh_2$ with **8**, is unstable in solution due to its rapid phosphine dissociation. In the presence of CO, **11** accordingly affords **9**. Thus, carbonylating $(PMePh_2)_2(CO)_2CoCH_2OCH_3$ (**10**) (1 atm of CO) gives first **11** and then **9**. These methoxyacetyl complexes **9** and **11** closely resemble their analogous acetyl analogues both in the preparative chemistry and in the subsequent reactions. Third, the carbethoxymethyl complex $(PMePh_2)(CO)_3CoCH_2CO_2CH_2CH_3$ (**12**) is inert to CO (1–5 atm). The anticipated carbethoxyacetyl compound **13** is independently available by either reacting $(PMePh_2)(CO)_3Co^-Na^+$ and ethyl malonyl chloride or treating $(CO)_4CoCH_2CO_2CH_2CH_3$ (**14**) with $PMePh_2$. The product **13** subsequently deinserts CO—even in the presence of 1 atm of CO—and generates **12**. The half-life of this deinsertion (9 h at room temperature), however, is sufficiently slow that any **13** forming in appreciable concentration during carbonylation attempts on **12** (typically 1–2 h in duration) easily would have been detected. This inertness of the carbalkoxymethyl ligand on a labile organometallic system toward carbon monoxide therefore contrasts the much higher reactivity of the alkoxymethyl ligand.

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Registry No. **5**, 86196-53-4; **6**, 86177-65-3; **7**, 103384-22-1; **8**, 103384-19-6; **9**, 103384-20-9; **10**, 103384-23-2; **11**, 103384-26-5; **12**, 103384-21-0; **13**, 103384-27-6; **14**, 79170-75-5; $(PMePh_2)(CO)_3Co^-Na^+$, 55888-64-7; $[(PMePh_2)(CO_3Co]_2$, 31224-11-0; $[(PMePh_2)_2(CO)_2Co]_2Hg$, 103384-24-3; $(PMePh_2)_2(CO)_2Co^-Na^+$, 103384-25-4; $ClCH_2OCH_3$, 107-30-2; $BrCH_2CO_2CH_2CH_3$, 105-36-2; $ClCOCH_2CO_2CH_2CH_3$, 36239-09-5.

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