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Syntheses and Crystal Structures at −35 °C of Bis(η³-2-allyl)-1,2-ethanobis(tricarbonylcobalt) and Bis(η³-2-allyl)-1,3-propanonobis((trimethyl phosphite)dicarbonylcobalt)

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The two η³-allyl complexes {(CO)₃Co[(CH₂)₂CCH₂]}₂ and {(CO)₃Co[(CH₂)₂CCH₂]}₂CO have been prepared by reaction of (chloromethyl)allyl chloride and NaCo(CO)₄ in refluxing THF. Both species are formed during this reaction and may be converted to the trimethyl phosphite derivatives by replacement of one CO ligand per Co atom. The structures of {(CO)₃Co[(CH₂)₂CCH₂]}₂ and {[(CH₃O)₃P](CO)₂Co[(CH₂)₂CCH₂]}₂CO have been determined by single-crystal x-ray diffraction techniques with three-dimensional data gathered at −35 °C by counter methods. Bulky yellow crystals of {(CO)₃Co[(CH₂)₂CCH₂]}₂ form in monoclinic space group $C2/m$, with unit cell constants (at −35 °C) $a = 11.570$ (3) Å, $b = 10.910$ (2) Å, $c = 6.568$ (1) Å, and $\beta = 99.95$ (1)°. The calculated density of 1.583 g cm⁻³, assuming two molecules of {(CO)₃Co[(CH₂)₂CCH₂]}₂ per unit cell, agrees with the measured value of 1.57 g cm⁻³. {[(CH₃O)₃P](CO)₂Co[(CH₂)₂CCH₂]}₂CO crystallizes as thin yellow prisms in orthorhombic space group $P2_12_12$, with unit cell constants (at −35 °C) $a = 19.688$ (4), $b = 20.843$ (10), and $c = 6.532$ (2) Å. The calculated density of 1.528 g cm⁻³ for four molecules of phosphite complex per unit cell agrees with the measured value of 1.50 g cm⁻³. Full-matrix least-squares refinements of the structures have converged with R indices (on $|F|$) of 0.021 and 0.062 for the {(CO)₃Co[(CH₂)₂CCH₂]}₂ and {[(CH₃O)₃P](CO)₂Co[(CH₂)₂CCH₂]}₂CO complexes, respectively, using the 1168 and 2134 symmetry-independent reflections with $I_0 > 2.0\sigma(I_0)$. Molecules of {(CO)₃Co[(CH₂)₂CCH₂]}₂ possess rigorous C_{2h} symmetry and display the significant differences in Co–C(carbonyl) distances which have previously been attributed to the nature of the Co–η³-allyl interaction. Although molecules of {[(CH₃O)₃P](CO)₂Co[(CH₂)₂CCH₂]}₂CO have no rigorous crystallographic symmetry, they do exhibit approximate-C_2 symmetry. In addition to the Co–C(carbonyl) bond asymmetry noted in {(CO)₃Co[(CH₂)₂CCH₂]}₂, the substitution of P(OCH₃)₃ for CO has produced differences in the Co–C(allyl, terminal) bond lengths of {[(CH₃O)₃-P](CO)₂Co[(CH₂)₂CCH₂]}₂CO.

Introduction

In 1960, Heck and Breslow reported the synthesis of the π-allylcobalt complex (η³-C₃H₅)Co(CO)₃, formed from the reaction of NaCo(CO)₄ and allyl bromide in ether at 25 °C.[1] To date, this remains the best method for the preparation of complexes of this kind. We have employed a similar procedure in our attempts to synthesize a precursor of a cobalt–tri-methylenemethane complex; viz., NaCo(CO)₄ (1) and

(chloromethyl)allyl chloride (2) were refluxed in dry THF for 20 min. However, the products which were obtained were neither the mono-π-allylcobalt tricarbonyl of Heck and Breslow nor a desired precursor of a cobalt–trimethylene-methane complex but were, as subsequently determined, the two unexpected compounds 3 and 4.

The molecular structures of unknown compounds 3 and 4 were established by crystal structure analysis: 3 directly by
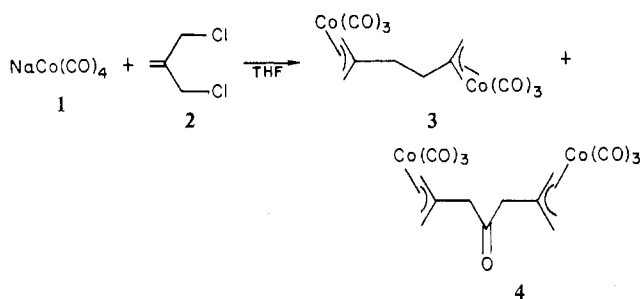
single-crystal x-ray diffraction techniques and **4**, because of thermal instability, by determination of the crystal structure of its bis(trimethyl phosphite) derivative. The infrared, ^{1}H NMR and ^{13}C NMR spectra of **3** and **4** (and its phosphite derivative) are consistent with the structures reported herein.

Experimental Section

All reactions were carried out in an argon atmosphere. THF was distilled from lithium aluminum hydride prior to use. ^{1}H NMR spectra were obtained with a Perkin-Elmer R-12 spectrometer. ^{13}C NMR spectra are proton decoupled and were recorded with a Bruker WH90 spectrometer. NMR data are reported with respect to an internal Me$_4$Si standard. Infrared spectra were obtained with a Perkin-Elmer Model 257 grating spectrometer. Melting points were measured with a Fisher-Johns melting point apparatus and are uncorrected for stem exposure.

Preparation of {(CO)$_3$Co[(CH$_2$)$_2$CCH$_2$]}$_2$ (3) and {(CO)$_3$Co-[(CH$_2$)$_2$CCH$_2$]}CO (4). To a sodium–mercury amalgam consisting of 2 g of sodium dissolved in 20 mL of distilled mercury was added 2 g (5.9 mmol) of Co$_2$(CO)$_8$ dissolved in 40 mL of THF. The mixture was mechanically stirred for 2 h. The resulting pale yellow solution was decanted into an inert atmosphere filter funnel and filtered through Celite under argon. To the filtrate was added 0.75 g (6.0 mmol) of **2**[2] dissolved in 3 mL of THF. The solution was refluxed for 20 min, cooled, and filtered through Celite and alumina. After the solvent was removed under reduced pressure, the residue was chromatographed over an alumina column, eluting first with a 3:1 hexane/benzene solution. A yellow band which passed down the column divided into two yellow bands; the more rapidly moving band was collected under argon. The elutent ratio was then changed to 1:1, and the second band was collected. Solvents were removed from both solutions under reduced pressure and the residues were dried for several hours at 0.3 mm pressure. Both **3** and **4** were recrystallized from hexane.

{(CO)$_3$Co[(CH$_2$)$_2$CCH$_2$]}$_2$ (**3**): mp 80 °C dec; yield 0.55 g (46%); infrared spectrum (cm^{-1}, hexane) 1992 (s), 1996 (s), 2020 (m), 2072 (m); ^{1}H NMR spectrum (δ, acetone-d_6) 2.43 (s, 2H), 2.51 (s, 2H), 3.38 (s, 2H); ^{13}C NMR spectrum (ppm, benzene-d_6, 10 °C) 41.6, 52.6, 102.7.

{(CO)$_3$Co[(CH$_2$)$_2$CCH$_2$]}$_2$CO (**4**): mp 70–71 °C; yield 0.25 g (20%); infrared spectrum (cm^{-1}, hexane) 1725 (w), 1992 (m), 1997 (s), 2018 (s), 2075 (m); ^{1}H NMR spectrum (δ, acetone-d_6) 2.62 (s, 2H), 3.39 (s, 2H), 3.50 (s, 2H); ^{13}C NMR spectrum (ppm, benzene-d_6, 10 °C) 50.9, 53.4, 95.7, 201.6.

General (Trimethyl phosphite)(dicarbonyl) Preparation (5 and 6). To 5 mmol of **3** or **4** dissolved in benzene was added 10 mmol of trimethyl phosphite in benzene. The mixture was stirred for 15 min and the solvent was removed under reduced pressure. The bis-[(trimethyl phosphite)(dicarbonyl)] derivatives **5** and **6** were recrystallized from hexane.

{[(CH$_3$O)$_3$P](CO)$_2$Co[(CH$_2$)$_2$CCH$_2$]}$_2$ (**5**): mp 98–99 °C dec; infrared spectrum (cm^{-1}, chloroform) 1928 (s), 1988 (m); ^{1}H NMR spectrum (δ, acetone-d_6) 2.2 (d, 2H),[3] 2.4 (s, 2H), 2.9 (d, 2H), 3.6 (d, 9H); ^{13}C NMR spectrum (ppm, benzene-d_6, 10 °C) 42.9, 48.3, 51.3, 102.2.

{[(CH$_3$O)$_3$P](CO)$_2$Co[(CH$_2$)$_2$CCH$_2$]}$_2$(CO) (**6**): mp 85–87 °C dec; infrared spectrum (cm^{-1}, chloroform) 1710 (w), 1940 (s), 1995 (m); ^{1}H NMR spectrum (δ, acetone-d_6) 2.2 (d, 2H), 2.8 (d, 2H), 3.3 (s, 2H), 3.6 (d, 9H); ^{13}C NMR spectrum (ppm, nitromethane-d_3, 0 °C) 49.6, 52.5, 96.5, 208.1.

Crystallographic Analyses

{(CO)$_3$Co[(CH$_2$)$_2$CCH$_2$]}$_2$ (**3**). Bulky, multifaceted yellow crystals of this moderately air-sensitive compound were grown slowly by vacuum thermal gradient sublimation. A suitable single crystal so obtained was affixed to a glass fiber and quickly transferred to a Syntex P2$_1$ diffractometer, where it was maintained in a stream of cold (−35 °C), dry nitrogen during the course of the diffraction experiments; as shown in Table I the crystal was stable under these conditions. Preliminary examination of the crystal indicated monoclinic symmetry consistent with space groups C2 (No. 5), Cm (No. 8), or C2/m (No. 12). Crystal data and data collection details are summarized in Table I. The measured intensities were reduced, corrected for absorption, and assigned standard deviations (with $p = 0.02$) as described elsewhere.[4]

{[(CH$_3$O)$_3$P](CO)$_2$Co[(CH$_2$)$_2$CCH$_2$]}$_2$CO (**6**). Yellow crystals of this compound grew as very thin, elongated prisms from a hot, concentrated ether solution which was allowed to cool slowly to room temperature. Examination of a single crystal with the diffractometer indicated the orthorhombic symmetry of space group P2$_1$2$_1$2 (No. 18); other crystal data and data collection details are presented in Table I. The diffraction data were treated in the same manner as outlined in the preceding paragraph.

Solution and Refinement of the Structures

Both structures were solved by standard heavy-atom procedures and then refined by full-matrix least-squares methods.[5] Since refinement of the structure of **3** in centrosymmetric space group C2/m was satisfactory, refinements in the alternative noncentrosymmetric space groups were not conducted. The function minimized in refinement is $\sum w(|F_o| - |F_c|)^2$, where the weight w is $\sigma(|F_o|)^{-2}$, the reciprocal square of the standard deviation of each observation, $|F_o|$. Neutral atom scattering factors for Co, P, O, C,[6] and H[7] were used in these calculations, and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections[6] for anomalous scattering were applied to the Co and P scattering curves.

{(CO)$_3$Co[(CH$_2$)$_2$CCH$_2$]}$_2$ (**3**). Least-squares convergence was attained using only those 1168 data with $I_o/\sigma(I_o) > 2.0$ for a model in which nonhydrogen atoms were refined anisotropically and hydrogen atoms isotropically, with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.021$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.027$ and a standard deviation of an observation of unit weight = $[\sum w(||F_o| - |F_c||)^2/(m - s)]^{1/2} = 1.89$, for $m = 1168$ observations and $s = 71$ variables. Since inspection of the data had suggested that the low-order reflections were systematically affected by secondary extinction, Zachariasen's correction[8] for this effect was included in the concluding cycles of refinement. The final value of the extinction coefficient is 3.2 (2) × 10^{-5} e^{-2}. A structure factor calculation with all 1254 reflections measured during data collection gave R and R_w values of 0.023 and 0.027, respectively.

In the final cycle of refinement all parameter shifts were less than 3% of a corresponding estimated standard deviation (esd). No peak on a final difference Fourier electron density map exceeded 0.2 e Å^{-3}. From previous Fourier maps the carbon atoms at general crystallographic positions exhibited heights of 6.0 e Å^{-3}, and the hydrogen atoms heights of 0.4–0.5 e Å^{-3}.

{[(CH$_3$O)$_3$P](CO)$_2$Co[(CH$_2$)$_2$CCH$_2$]}$_2$CO (**6**). Due to the large number of atomic parameters and the relatively small number of observations (2134 reflections with $I_o/\sigma(I_o) > 2.0$), full anisotropic refinement of this structure was not carried out. Thus, in the final cycles of refinement the oxygen and carbon atoms of the phosphite groups were refined isotropically, the other nonhydrogen atoms were refined anisotropically, and all hydrogen atoms were placed at idealized positions[9] with thermal parameters of 4.0 or 5.0 Å^2 for allyl or methyl hydrogen atoms, respectively. At least-squares convergence, $R = 0.062$, $R_w = 0.053$, and the standard deviation of an observation of unit weight is 1.98 for $m = 2134$ observations and $s = 253$ variables. One of the methyl carbon atoms (C(16), see below) was found to be disordered about two sites, with refined atomic occupancy parameters of 0.60 (4) and 0.42 (4). The second value was reduced to 0.40, and these two positions (now with fixed occupancy parameters) were included in the final cycles of refinement. There was no indication of secondary extinction in this data set. A structure factor calculation with all 2716 reflections gathered during data collection gave R and R_w values of 0.086 and 0.054, respectively.

To determine whether the proper enantiomorph (for the data crystal) had been selected as this model, least-squares refinement of the structure was carried out, beginning with the atomic parameters obtained prior to the inclusion of the imaginary corrections ($\Delta f''$) to the Co and P scattering curves, but now with the signs for these corrections reversed—the computational equivalent of refinement of the opposite enantiomorph. At convergence, $R = 0.062$ and $R_w =$

Table I. Crystallographic Summary

	$\{(CO)_3Co[(CH_2)_2CCH_2]\}_2$	$\{[(CH_3O)_3P](CO)_2Co[(CH_2)_2-CCH_2]\}_2CO$
	Crystal Data at $-35\,°C^a$	
a, Å	11.570 (3)	19.688 (4)
b, Å	10.910 (2)	20.843 (10)
c, Å	6.568 (1)	6.532 (2)
α, deg	90	90
β, deg	99.95 (1)	90
γ, deg	90	90
V, Å^3	816.6 (5)	2680 (4)
d_{measd}, g cm^{-3} (19 °C) (flotation, aqueous ZnCl$_2$)	1.57	1.50
d_{calcd}, g cm^{-3} (-35 °C)	1.583	1.528
Systematic absences	$hkl, h + k = 2n + 1$	$h00, h = 2n + 1$
		$0k0, k = 2n + 1$
Crystal system	Monoclinic	Orthorhombic
Space group	$C2$ (No. 5), Cm (No. 8) or $C2/m$ (No. 12)^b	$P2_12_12$ (No. 18)
Z	2	4
$F(000)$, electrons	192	316
Formula wt	388.06	614.29
Molecular formula	$C_{14}H_{12}Co_2O_6$	$C_{19}H_{30}Co_2O_{11}P_2$
	Data Collection at $-35\,°C^c$	
Radiation (Mo Kα), Å	0.710 69	0.710 69
Mode	ω scan	ω scan
Scan range	Symmetrically over 1.2° about Kα$_{1,2}$ maximum	Symmetrically over 1.0° about Kα$_{1,2}$ maximum
Background	Offset 1.0 and $-1.0°$ in ω from Kα$_{1,2}$ maximum	
Scan rate, deg min^{-1}	Variable, 1.5–5.0	Variable, 2.0–5.0
Check reflections	4 remeasured after every 96 reflections; analyses^d of these data indicated only random fluctuation in intensity for both crystals with all correction factors less than 0.2σ	
2θ range, deg	4.0–60.0	4.0–50.0
Total reflections measd	1254	2716
Data crystal dimensions, mm	0.35 × 0.48 × 0.49	0.11 × 0.15 × 0.68
Data crystal volume, mm^3	0.060	0.014
Data crystal faces	(100), ($\bar{1}$00), (010), (0$\bar{1}$0), (001)$_2$ (00$\bar{1}$)$_2$ ($\bar{1}$10), ($\bar{1}\bar{1}$0), (110), (1$\bar{1}$0), (11$\bar{1}$), (1$\bar{1}$1), ($\bar{1}\bar{1}$1), ($\bar{2}$01)	(110), (1$\bar{1}$0), ($\bar{1}$10), ($\bar{1}\bar{1}$0), ($\bar{1}$01), ($\bar{1}$0$\bar{1}$)
Absorption coeff, μ(Mo Kα), cm^{-1}	21.1	14.6
Transmission factor range	0.43–0.56	0.78–0.84

^{a} Unit cell parameters were obtained by least-squares refinement of the setting angles of 45 reflections with $26 < 2\theta < 30°$ for $\{(CO)_3Co[(CH_2)_2CCH_2]\}_2$, and 18 reflections with $17 < 2\theta < 23°$ for $\{[(CH_3O)_3P](CO)_2Co[(CH_2)_2CCH_2]\}_2CO$. ^{b} Shown by successful refinement to be $C2/m$ (see text). ^{c} Syntex $P2_1$ autodiffractometer equipped with a graphite monochromator and a Syntex LT-1 inert gas low temperature delivery system. ^{d} W. H. Henslee and R. E. Davis, *Acta Crystallogr., Sect B*, 31, 1511 (1975).

Table II. Fractional Coordinates and Anisotropic (×10⁴) and Isotropic Thermal Parameters for Atoms of $\{(CO)_3Co[(CH_2)_2CCH_2]\}_2{}^a$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co^b	0.21938 (2)	0	0.13007 (3)	2790 (13)	3814 (14)	3192 (13)	0	310 (8)	0
O(1)	0.1189 (2)	0	-0.3134 (3)	795 (14)	1860 (30)	379 (9)	0	-64 (9)	0
O(2)	0.1099 (2)	0.2004 (1)	0.3166 (3)	1035 (11)	536 (7)	1117 (12)	274 (8)	434 (9)	-38 (7)
C(1)	0.1596 (2)	0	-0.1442 (3)	436 (10)	929 (17)	413 (10)	0	34 (8)	0
C(2)	0.1518 (1)	0.1214 (1)	0.2440 (2)	515 (7)	433 (7)	604 (8)	80 (6)	154 (6)	70 (6)
C(3)	0.3685 (1)	0.1086 (2)	0.1287 (3)	388 (7)	620 (9)	582 (8)	-100 (6)	26 (6)	203 (7)
C(4)	0.3921 (1)	0	0.2442 (3)	271 (7)	452 (8)	387 (8)	0	37 (6)	0
C(5)	0.4325 (1)	0	0.4740 (3)	321 (7)	428 (8)	384 (8)	0	10 (6)	0

Atom^c	x	y	z	U, Å^2	Atom^c	x	y	z	U, Å^2
H(3,1)	0.381 (2)	0.110 (2)	-0.018 (3)	0.07 (1)	H(5)	0.405 (1)	0.073 (1)	0.543 (3)	0.05 (0)
H(3,2)	0.374 (1)	0.192 (2)	0.204 (3)	0.05 (0)					

^{a} See Figure 1 for identity of the atoms. Numbers in parentheses throughout the table are the estimated standard deviations in the units of the last significant digits for the corresponding parameter. The U_{ij} are the mean-square amplitudes of vibration in Å^2 from the general temperature factor expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. ^{b} For Co the anisotropic thermal parameters are given ×10⁵. ^{c} The sequence number of a hydrogen atom corresponds to that of the carbon atom to which it is bound.

0.054, values which are essentially the same as those obtained with the former model. Since the bond lengths and angles of chemically equivalent portions of the structure obtained with the first model (i.e., $\Delta f''$) are in somewhat better agreement than those obtained with the second model (i.e., $-\Delta f''$), the atomic parameters listed in Table III are those of the first model.

In the final cycle of refinement all shifts in atomic parameters were less than 16% of a corresponding esd, except those of the x and B variables of the disordered methyl carbon atom C(16B), which were

30 and 38%, respectively. A final difference Fourier map showed several peaks with heights of 0.5–1.0 e Å^{-3}; all of these were close to either a Co atom or a phosphite oxygen atom (all of which were refined isotropically). For comparison, carbon atoms from the heavy-atom map exhibited densities of 2.7–4.2 e Å^{-3}.

Table II presents atomic positional and thermal parameters with corresponding esd's as estimated from the least-squares inverse matrix for the structure of **3**, while Table III contains the corresponding information for the structure of **6**. Tabulations of observed and
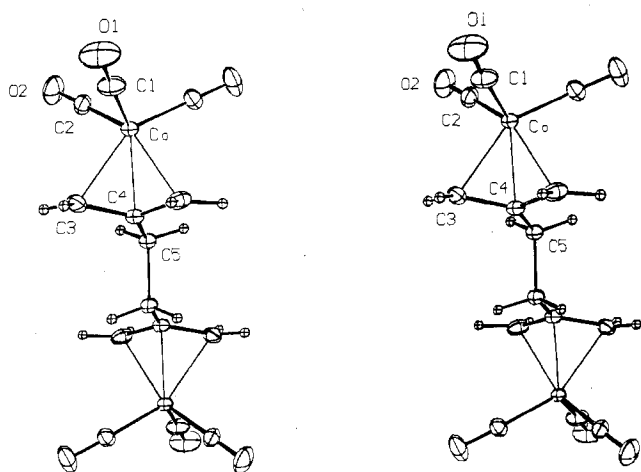
Figure 1. Stereoview of the {(CO)$_3$Co[(CH$_2$)$_2$CCH$_2$]}$_2$ molecule, illustrating the atom numbering scheme. Nonhydrogen atoms are shown as ellipsoids of 20% probability and hydrogen atoms as spheres of radius 0.1 Å.

calculated structure factor amplitudes are available for both crystal structures.[11]

Description of the Structures

The crystal structures of **3** and **6** consist of discrete molecules with no unusual intermolecular contacts. In both species the Co atoms of the CoL$_2$L' (L = L' = CO or L = CO and L' = P(OCH$_3$)$_3$) groups are π bonded to the allylic portions of extended organic ligands. Whereas **3** has rigorous C_{2h} crystallographic symmetry, **6** has only approximate C_2 symmetry. Figures 1 and 2 offer stereoviews of **3** and **6**, respectively, and indicate the atom numbering scheme used herein. Tables IV and V present selected interatomic distances and angles for **3** and **6**.

{(CO)$_3$Co[(CH$_2$)$_2$CCH$_2$]}$_2$ (3). The bonding in complexes of the form (η^3-(CH$_2$)$_2$CR)ML$_n$, where R = H or alkyl, M = a transition metal, and L$_n$ = a suitable complement of ligands has been the subject of considerable theoretical investigation.[12-14] Hence, the details of the molecular geometry of the (η^3-(CH$_2$)$_2$CCH$_2$)Co(CO)$_3$ moiety of **3** are of particular interest. While the variation in M–C(allyl) distances in **3** is the same as established previously in numerous structures of metal-η^3-allyl complexes (i.e., M–C(terminal) > M–C-(central)), the values for **3** are quite well determined: Co–C(terminal) (C(3), C(3)') = 2.095 (1) Å, Co–C(central)

(C(4)) = 2.010 (2) Å. Because the central allylic carbon atom C(4) lies in a crystallographic mirror plane, the two allylic C–C bonds are equal, 1.409 (2) Å, and in agreement with values recently reported for the structures of {[η^3-(H$_3$C)C$_3$H$_3$-(CHCH$_3$C(O)CH$_3$)]Fe(CO)$_3$}$^+$ (1.384 (15), 1.404 (16) Å),[15] [(C$_2$H$_5$)$_2$B(C$_3$N$_2$H$_3$)$_2$](η^3-C$_3$H$_5$)(C$_3$N$_2$H$_4$)(CO)$_2$Mo (1.387 (6), 1.412 (6) Å),[16] and [(C$_2$H$_5$)$_2$B(C$_3$N$_2$H$_3$)$_2$][η^3-CH$_2$C-(C$_6$H$_5$)CH$_2$](CO)$_2$Mo (1.393 (10), 1.411 (10) Å).[17]

The Co–C(carbonyl) bond lengths in **3** differ substantially, Co–C(1) = 1.815 (2) Å and Co–C(2) = 1.769 (1) Å. Examination of the molecular orbital diagram for this kind of complex (in particular, (η^3-C$_3$H$_5$)Co(CO)$_3$) has shown this Co–C(carbonyl) bond length asymmetry to be a consequence of the π bonding between metal and allyl moiety.[12-14] In contrast, the Co–C(carbonyl) distances in (η^4-C$_4$H$_4$)Co$_2$(CO)$_6$ range from 1.778 (3) to 1.793 (2) Å.[18] (The C–O bond lengths of **3** are normal and in agreement with those of (C$_4$H$_4$)-Co$_2$(CO)$_6$.)

As in most 2-substituted η^3-allyl metal complexes,[12] methylene carbon C(5) lies out of the plane of the η^3-allyl ligand toward the metal (Co) atom (see Table VI). In addition, the hydrogen atoms of the terminal methylene carbon atoms are situated on opposite sides of this plane, probably the result of rotations of these carbon atoms to increase the overlap between the ligand π_2 orbitals (essentially carbon p$_z$ orbitals) and the Co d$_{xz}$ orbital.[13] Similar small rotations about the terminal C–C bonds of the butadiene residues of metal–butadiene complexes have been ascribed[19] to enhanced metal–butadiene orbital overlap. Since the distance between the syn hydrogen atoms (H(3,1) and H(3,1)') of the allyl ligand of 2.40 (3) Å is considerably greater than that of the van der Waals H···H contact distance of ~2.0 Å,[20] these rotations are probably more important in improving metal–allyl orbital overlap than in diminishing intramolecular H···H repulsions.

There are two dihedral angles of some interest in this structure—that between the η^3-allyl plane and the carbonyl carbon plane and that between the η^3-allyl plane and the C(3)–Co–C(3)' plane. In **3**, these angles are 22.7 and 77.8°, respectively, while from a gas-phase electron diffraction study[21] of (η^3-C$_3$H$_5$)Co(CO)$_3$ the corresponding values are 36 and 105°. Other structural features of **3** are compared to (η_3-C$_3$H$_5$)Co(CO)$_3$, {η^3-[(C$_6$H$_5$)C]$_3$CO}Co(CO)$_3$,[22] and **6** in Table VII.

{[(CH$_3$O)$_3$P](CO)$_2$Co[(CH$_2$)$_2$CCH$_2$]}$_2$CO (6). The most interesting aspects of the structure of **6** are the effects of the substitution of the P(OCH$_3$)$_3$ ligand for the CO molecule upon

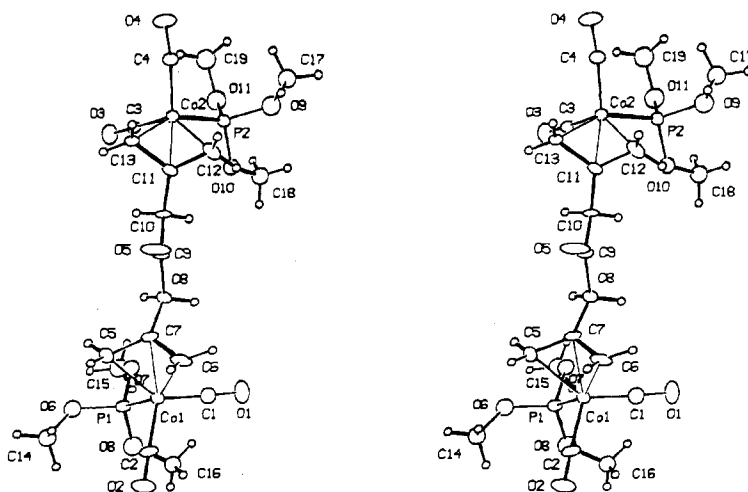**Figure 2.** Stereoview of the {[(CH$_3$O)$_3$P](CO)$_2$Co[(CH$_2$)$_2$CCH$_2$]}$_2$CO molecule, illustrating the atom numbering scheme. Nonhydrogen atoms are shown as ellipsoids of 20% probability and hydrogen atoms as spheres of radius 0.1 Å.

Table III. Fractional Coordinates and Anisotropic ($\times 10^3$) and Isotropic Thermal Parameters for Atoms of {[(CH₃O)₃P](CO)₂Co[(CH₂)₂CCH₂]}₂Co^a

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)^b	0.19762 (6)	0.02506 (6)	0.23725 (23)	318 (7)	257 (6)	393 (8)	0 (6)	−2 (8)	−45 (8)
Co(2)^b	0.03830 (6)	0.32337 (6)	1.01280 (22)	316 (7)	313 (7)	343 (8)	30 (7)	−12 (8)	−39 (8)
P(1)	0.1544 (1)	−0.0544 (1)	0.3938 (5)	48 (2)	29 (1)	44 (2)	−5 (1)	5 (2)	−7 (2)
P(2)	−0.0606 (1)	0.3236 (1)	0.8808 (4)	34 (1)	35 (1)	38 (2)	5 (1)	−1 (1)	−3 (2)
O(1)	0.0774 (4)	0.0506 (4)	−0.0040 (17)	89 (7)	87 (7)	93 (8)	11 (6)	−51 (7)	12 (7)
O(2)	0.3070 (4)	−0.0302 (4)	−0.0044 (15)	75 (6)	63 (5)	88 (7)	7 (5)	41 (7)	−15 (6)
O(3)	0.0056 (4)	0.2198 (4)	1.2889 (15)	85 (6)	61 (6)	72 (7)	−6 (5)	−16 (6)	22 (6)
O(4)	0.0521 (4)	0.4426 (3)	1.2492 (15)	86 (6)	52 (5)	77 (6)	−13 (5)	12 (6)	−33 (6)
O(5)	0.2083 (4)	0.2236 (3)	0.5958 (15)	51 (5)	50 (5)	137 (9)	−26 (4)	48 (6)	−53 (6)
C(1)	0.1254 (6)	0.0392 (5)	0.0904 (20)	63 (8)	32 (7)	60 (9)	−7 (6)	−1 (8)	5 (6)
C(2)	0.2651 (6)	−0.0090 (4)	0.0904 (18)	58 (8)	27 (6)	52 (8)	−2 (5)	13 (7)	−20 (6)
C(3)	0.0178 (5)	0.2605 (5)	1.1776 (17)	37 (6)	39 (6)	29 (7)	4 (5)	2 (5)	−3 (6)
C(4)	0.0457 (5)	0.3975 (5)	1.1466 (17)	34 (6)	54 (7)	43 (7)	9 (6)	8 (6)	−1 (6)
C(5)	0.2430 (5)	0.0554 (5)	0.5085 (24)	35 (6)	46 (6)	77 (9)	6 (5)	−20 (7)	−11 (8)
C(6)	0.2272 (5)	0.1192 (4)	0.2163 (22)	55 (7)	24 (5)	81 (11)	−3 (5)	28 (8)	−13 (7)
C(7)	0.2065 (5)	0.1035 (5)	0.4153 (17)	27 (5)	36 (6)	46 (7)	−4 (5)	1 (6)	−24 (6)
C(8)	0.1427 (5)	0.1322 (4)	0.5041 (19)	41 (6)	25 (5)	48 (7)	−2 (5)	0 (7)	−6 (6)
C(9)	0.1559 (5)	0.1941 (4)	0.6172 (18)	39 (6)	29 (6)	55 (7)	0 (5)	6 (6)	−13 (6)
C(10)	0.0995 (5)	0.2172 (4)	0.7569 (18)	36 (5)	28 (5)	41 (6)	3 (4)	11 (6)	−20 (6)
C(11)	0.1081 (5)	0.2855 (4)	0.8277 (17)	24 (5)	26 (6)	48 (8)	2 (5)	4 (5)	−4 (5)
C(12)	0.0800 (5)	0.3364 (5)	0.7241 (22)	33 (6)	44 (6)	76 (9)	13 (5)	29 (7)	13 (7)
C(13)	0.1398 (5)	0.3007 (4)	1.0159 (19)	33 (6)	33 (5)	49 (7)	0 (4)	−7 (6)	−19 (6)

Atom	x	y	z	U, Å²	Atom	x	y	z	U, Å²
					Oxygen and Carbon Atoms of the Trimethyl Phosphite Ligands				
O(6)	0.1954 (4)	−0.0905 (4)	0.5677 (13)	0.067 (2)	C(15)	0.0434 (7)	−0.0798 (6)	0.6109 (24)	0.083 (4)
O(7)	0.0880 (3)	−0.0361 (3)	0.5188 (13)	0.058 (2)	C(16A)^c	0.1059 (10)	−0.1137 (9)	0.0765 (34)	0.076 (7)
O(8)	0.1325 (4)	−0.1161 (4)	0.2670 (14)	0.082 (2)	C(16B)^c	0.1571 (12)	−0.1414 (11)	0.0986 (34)	0.048 (6)
O(9)	−0.0860 (4)	0.3790 (4)	0.7371 (17)	0.080 (3)	C(17)	−0.0567 (6)	0.4393 (6)	0.7098 (21)	0.066 (4)
O(10)	−0.0763 (3)	0.2626 (3)	0.7478 (15)	0.055 (2)	C(18)	−0.1413 (6)	0.2510 (5)	0.6572 (21)	0.066 (4)
O(11)	−0.1245 (4)	0.3161 (4)	1.0297 (16)	0.086 (3)	C(19)	−0.1339 (7)	0.3559 (7)	1.1906 (25)	0.088 (5)
C(14)	0.2630 (6)	−0.1115 (5)	0.5392 (21)	0.063 (4)					

				Hydrogen Atoms^{d,e}				
H(5,1)	0.224	0.039	0.631	0.051	H(15,3)	0.067	−0.105	0.710	0.063
H(5,2)	0.291	0.060	0.506	0.051	H(16A,1)	0.096	−0.156	0.029	0.063
H(6,1)	0.274	0.126	0.198	0.051	H(16A,2)	0.065	−0.089	0.078	0.063
H(6,2)	0.198	0.147	0.142	0.051	H(16A,3)	0.137	−0.094	−0.014	0.063
H(8,1)	0.126	0.102	0.601	0.051	H(16B,1)	0.132	−0.179	0.062	0.063
H(8,2)	0.114	0.142	0.393	0.051	H(16B,2)	0.155	−0.111	−0.010	0.063
H(10,1)	0.059	0.216	0.680	0.051	H(16B,3)	0.204	−0.153	0.119	0.063
H(10,2)	0.101	0.191	0.876	0.051	H(17,1)	−0.083	0.463	0.614	0.063
H(12,1)	0.052	0.326	0.611	0.051	H(17,2)	−0.056	0.461	0.837	0.063
H(12,2)	0.108	0.373	0.707	0.051	H(17,3)	−0.012	0.434	0.660	0.063
H(13,1)	0.171	0.336	1.014	0.051	H(18,1)	−0.140	0.212	0.583	0.063
H(13,2)	0.153	0.265	1.099	0.051	H(18,2)	−0.175	0.248	0.761	0.063
H(14,1)	0.279	−0.132	0.660	0.063	H(18,3)	−0.152	0.285	0.566	0.063
H(14,2)	0.265	−0.141	0.428	0.063	H(19,1)	−0.174	0.344	1.261	0.063
H(14,3)	0.291	−0.076	0.510	0.063	H(19,2)	−0.096	0.353	1.281	0.063
H(15,1)	0.008	−0.057	0.676	0.063	H(19,3)	−0.138	0.399	1.143	0.063
H(15,2)	0.025	−0.107	0.509	0.063					

^{a} See Figure 2 for identity of the atoms. Numbers in parentheses are the estimated standard deviations in the units of the last significant digits for the corresponding parameter. The U_{ij} parameters are defined in Table II. ^{b} For the Co atoms the anisotropic thermal parameters are given $\times 10^4$. ^{c} Refined atomic occupancy parameters for disordered methyl carbon C(16) are 0.60 (4) and 0.42 (4) for C(16A) and C(16B), respectively. ^{d} As stated in the text, the hydrogen atoms were placed at idealized positions. ^{e} The sequence number of a hydrogen atom corresponds to that of the carbon or oxygen atom to which it is bound. The occupancy parameters for the hydrogen atoms of C(16A) and C(16B) were adjusted in accordance with the values assigned to C(16A) and C(16B) (see text).

its molecular structure. The resulting molecular asymmetry is apparent from an examination of the metal–carbon distances of Tables IV and V and is illustrated in Figure 3. Although the same asymmetry in Co–C(carbonyl) bonding as noted in **3** (due to metal–η^3-allyl bonding[12,13]) is evident in **6**, additional asymmetry, now in the Co–allyl bonding, has been introduced by Co–P coordination. As shown in Figure 3, C(6) and C(13), which are approximately trans to P(1) and P(2), respectively (C–Co–P = 153°), are apparently more strongly bonded to Co than C(5) and C(12). In addition, bonds C(6)–C(7) and C(11)–C(13) appear to be longer than bonds C(5)–C(7) and C(11)–C(12). This implies greater Co→allyl back-bonding in the C(6)–C(7) and C(11)–C(13) portions of the ligand, an effect which is consistent with the shorter Co(1)–C(6) and Co(2)–C(13) distances.

This difference in Co–C(allyl) bond length is more emphatically demonstrated by comparing the Co–C(terminal) distances in **3** to those in **6**. In **3**, the Co–C(terminal) distances are equal (by symmetry) and apparently significantly longer than those Co–C(terminal) distances in **6** which are trans to P (2.095 (1) vs. 2.05 (1) Å). This appreciable difference is undoubtedly due to an increase in electron density at the Co atoms of **6**, compared to that of **3**, which results from the substitution of a strongly electron-donating and weakly electron-withdrawing phosphorus-containing ligand for the weakly electron-donating and strongly electron-withdrawing CO ligand. As a consequence of this increase in electron density on the Co atoms of **6**, these metal atoms are able to supply additional electron density to their respective allyl ligands. However, because terminal carbon atoms C(5) and
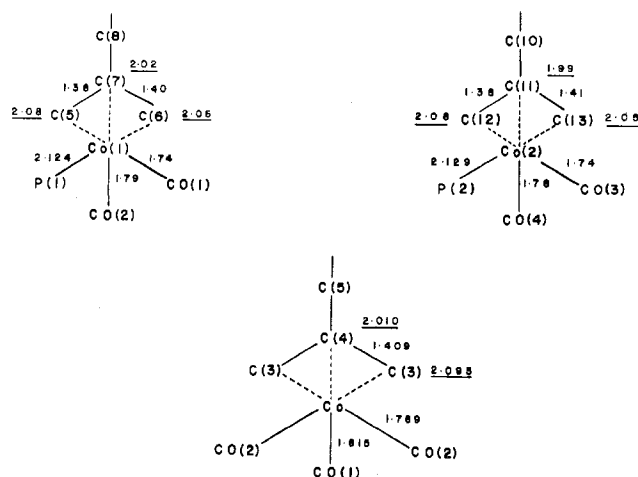
Figure 3. Selected interatomic distances in **3** (bottom) and **6** (top). Underlined values are Co–C(allyl) distances.

Table IV. Interatomic Distances (Å) and Angles (deg) for $\{(CO)_3Co[(CH_2)_2CCH_2]\}_2{}^a$

Co–C(1)	1.815 (2)	C(3)–C(4)	1.409 (2)
Co–C(2)	1.769 (1)	C(4)–C(5)	1.501 (2)
Co–C(3)	2.095 (1)	C(5)–C(5)'	1.540 (2)
Co–C(4)	2.010 (2)	C(3)–H(3,1)	1.00 (1)
Co–C(5)	3.043 (2)	C(3)–H(3,2)	1.03 (2)
C(1)–O(1)	1.130 (3)	C(5)–H(5)	0.99 (2)
C(2)–O(2)	1.134 (2)		

C(1)–Co–C(2)	107.4 (1)	C(3)–C(4)–C(3)'	114.6 (2)
C(2)–Co–C(2)'	97.0 (1)	C(3)–C(4)–C(5)	122.6 (1)
Co–C(1)–O(1)	177.9 (1)	C(4)–C(5)–C(5)'	110.5 (1)
Co–C(2)–O(2)	178.9 (1)	H(5)–C(5)–C(4)	113 (1)
H(3,1)–C(3)–C(4)	119 (1)	H(5)–C(5)–C(5)'	107 (1)
H(3,2)–C(3)–C(4)	120 (1)	H(5)–C(5)–H(5)'	106 (1)
H(3,1)–C(3)–H(3,2)	116 (2)		

^{a} Numbers in parentheses are the estimated standard deviations in the last significant digit. See Figure 1 for identity of the atoms. Coordinates of primed atoms are related to the coordinates of the corresponding unprimed atoms in Table II by symmetry.

C(12) must compete for this excess electronic charge with CO ligands in approximately trans positions (C(terminal)–Co–CO = 139, 140°), the effects of this greater metal→allyl donation in **6** are more pronounced at those terminal carbon atoms which are "trans" to the P(OCH₃)₃ ligands (see Figure 3).

Although the P(OCH₃)₃ ligand contains the electronegative CH₃O groups and accordingly is less electron releasing and

more electron withdrawing than PR₃ molecules with less electronegative substituents,[23] the P(OR)₃ ligand is, as indicated here and elsewhere,[24] considerably less electron withdrawing than the CO ligand. Unfortunately, the large errors associated with the bond lengths and angles of **6** preclude more definitive assessments of these structural parameters.

Deviations of selected atoms from the η^3-allyl planes of **6** are given in Table VI. The methylene carbon substituents C(8) and C(10) lie further from their respective planes than does the corresponding substituent atom C(5) from the η^3-allyl plane in **3**. Furthermore, the cobalt atoms of **6** are decidedly closer to their η^3-allyl residues than is the cobalt atom of **3** to its allyl group. Both effects are probably due to the replacement of CO by P(OCH₃)₃.

Aside from the effects of the disordered methyl group C(16) (discussed above), the dimensions of the trimethyl phosphite ligands (see Table V) compare favorably with values determined previously. For example, in {NiBr[P(OCH₃)₃]₄}BF₄ the mean P–O and O–C bond lengths are 1.579 (7) and 1.45 (2) Å, and the mean P–O–C and O–P–O angles are 124.9 (7) and 103.2 (4)°.[25]

Results

Both **3** and **4** are formed within 20 min in refluxing THF, as indicated by the disappearance of the IR absorptions of the cobaltate (**1**) carbonyl ligands below 1900 cm⁻¹ and by the appearance of an absorption at 2000 cm⁻¹ which can be attributed to the neutral carbonyl complexes. Reaction at room temperature is complete after 30 h; however, thermal decomposition at ambient temperature diminishes the yields appreciably. By monitoring the consumption of **2** by gas chromatographic analysis, it was noted that a minimum of 1.5 mol of **1** is needed to consume 1 mol of **2**. Optimal yields of **3** and **4** were obtained with a 2:1 molar ratio of **1** to **2**. When 3–5:1 molar ratios of **1** to **2** were employed, a decrease in the yield of **4** was observed.

Conversion of **3** and **4** to their respective bis[(trimethyl phosphite)(dicarbonyl)] derivatives occurs rapidly at ambient temperature upon addition of 2 equiv of (CH₃O)₃P and is accompanied by the evolution of 80% of the theoretical yield of CO.[2] Since the phosphite derivatives of **3** and **4** are more thermally stable than the parent compounds, 1 mol of (CH₃O)₃P/mol of **2** was added to the reaction mixture in hopes of generating **5** and **6** in situ. Unfortunately, this greatly inhibited the rate of reaction and yielded a red (cobalt) complex containing phosphite and CO ligands, but as indicated by its ¹³C NMR spectrum, no organic moiety.

Table V. Interatomic Distances (Å) and Angles (deg) for $\{[(CH_3O)_3P](CO)_2Co[(CH_2)_2CCH_2]\}_2CO{}^a$

Co(1)–P(1)	2.124 (3)	Co(2)–C(10)	3.02 (1)	C(7)–C(8)	1.51 (1)	P(2)–O(9)	1.571 (9)
Co(1)–C(1)	1.74 (1)	Co(2)–C(11)	1.99 (1)	C(8)–C(9)	1.51 (1)	P(2)–O(10)	1.570 (8)
Co(1)–C(2)	1.79 (1)	Co(2)–C(12)	2.08 (1)	C(9)–O(5)	1.21 (1)	P(2)–O(11)	1.600 (10)
Co(1)–C(5)	2.08 (1)	Co(2)–C(13)	2.05 (1)	C(9)–C(10)	1.52 (1)	O(6)–C(14)	1.41 (1)
Co(1)–C(6)	2.05 (1)	C(1)–O(1)	1.15 (2)	C(10)–C(11)	1.51 (1)	O(7)–C(15)	1.40 (2)
Co(1)–C(7)	2.02 (1)	C(2)–O(2)	1.12 (1)	C(11)–C(12)	1.38 (1)	O(8)–C(16A)	1.35 (2)
Co(1)–C(8)	3.03 (1)	C(3)–O(3)	1.14 (1)	C(11)–C(13)	1.41 (2)	O(8)–C(16B)	1.31 (2)
Co(2)–P(2)	2.129 (3)	C(4)–O(4)	1.16 (1)	P(1)–O(6)	1.584 (9)	O(9)–C(17)	1.39 (1)
Co(2)–C(3)	1.74 (1)	C(5)–C(7)	1.38 (1)	P(1)–O(7)	1.589 (8)	O(10)–C(18)	1.43 (1)
Co(2)–C(4)	1.78 (1)	C(6)–C(7)	1.40 (2)	P(1)–O(8)	1.591 (8)	O(11)–C(19)	1.35 (2)

C(1)–Co(1)–P(1)	94.0 (4)	C(4)–Co(2)–C(11)	125.8 (4)	C(10)–C(9)–O(5)	122.3 (9)
C(1)–Co(1)–C(2)	112.3 (6)	P(2)–Co(2)–C(11)	112.7 (3)	C(10)–C(11)–C(12)	122.2 (9)
C(1)–Co(1)–C(7)	104.6 (5)	P(2)–Co(2)–C(4)	105.8 (3)	C(10)–C(11)–C(13)	121.8 (8)
C(2)–Co(1)–C(7)	124.6 (4)	C(5)–C(7)–C(6)	115.4 (10)	C(12)–C(11)–C(13)	115.7 (9)
P(1)–Co(1)–C(7)	112.9 (3)	C(5)–C(7)–C(8)	123.7 (10)	Co–C–O(CO)	174 (1)–179 (1)
P(1)–Co(1)–C(2)	104.3 (3)	C(6)–C(7)–C(8)	120.5 (9)	Co–P–O(OCH₃)	113.0 (3)–122.3 (3)
C(3)–Co(2)–P(2)	92.3 (3)	C(7)–C(8)–C(9)	112.7 (8)	P–O–C(CH₃)	121.4 (8)–131.3 (12)
C(3)–Co(2)–C(4)	111.6 (5)	C(8)–C(9)–C(10)	116.2 (8)	O–P–O	95.8 (4)–103.7 (4)
C(3)–Co(2)–C(11)	103.7 (4)	C(8)–C(9)–O(5)	121.6 (9)		

^{a} Numbers in parentheses are the estimated standard deviations in the last significant digit. See Figure 2 for identity of the atoms.

Table VI. π-Allyl Planes[a]

Atoms	Dev (A) from plane[c]	Atoms	Dev (A) from plane[c]
\{(CO)₃Co[(CH₂)₂CCH₂]\}₂			
$0.9824X - 0.1869Z - 3.8894 = 0$[b]			
C(5)	-0.075 (2)	H(3,2)	-0.11 (2)
H(3,1)	0.48 (2)	Co	-1.698 (1)
\{[(CH₃O)₃P](CO)₂Co[(CH₂)₂CCH₂]\}₂CO			
C(5), C(6), C(7) Plane			
$-0.6347X - 0.6787Y - 0.3696Z + 5.0471 = 0$			
C(8)	0.176 (9)	H(6,1)*	-0.65
H(5,1)*	0.18	H(6,2)*	0.16
H(5,2)*	-0.66	Co(1)	1.650 (1)
C(11), C(12), C(13) Plane			
$0.8662X + 0.1483Y - 0.4771Z - 0.1468 = 0$			
C(10)	-0.137 (10)	H(13,1)*	0.64
H(12,1)*	-0.16	H(13,2)*	-0.15
H(12,2)*	0.65	Co(2)	-1.651 (1)

[a] Orthornormal coordinate system with axes X, Y, and Z parallel to unit cell vectors a, b, and c^* (or c, in the orthorhombic structure), respectively. A negative deviation from the plane indicates that the atom with coordinates given in Table II or III lies between the plane and the origin. See Figures 1 and 2 for identity of the atoms. Coordinates of atoms marked with * represent idealized positions (see text). [b] Since this plane is strictly parallel to the b axis, its Y component is zero. [c] Numbers in parentheses are estimated standard deviations in the last significant digits.

Complexes **3** and **4** were separated on an alumina column, eluted with a hexane–benzene mixture. Both complexes decompose slowly at –30 °C, even when stored under CO. However, **5** and **6** are thermally stable and can be maintained indefinitely under argon.

Attempts to isolate reaction intermediates by lowering reaction temperatures, altering reactant ratios, or varying the method of addition of starting materials were unsuccessful. For example, when a twofold excess of **2** was used per mole of **1**, no intermediates, such as a (monochloromethyl)-π-allyl complex (**8**, see below), were detected, and only products **3** and **4** were observed. Furthermore, when the reaction was carried out under slight CO pressure (2–3 atm), the yields of **3** and **4** were negligible.

Discussion

At least two mechanistic routes, Schemes I and II, can account for the formation of **3** and **4**, and because of the versatility of the tetracarbonylcobaltate ion either route may be reasonably evoked.

In Scheme I, the cobaltate anion (**1**) reacts with **2** to produce the σ-allylcobalt tetracarbonyl species **7**,[26] which upon loss of
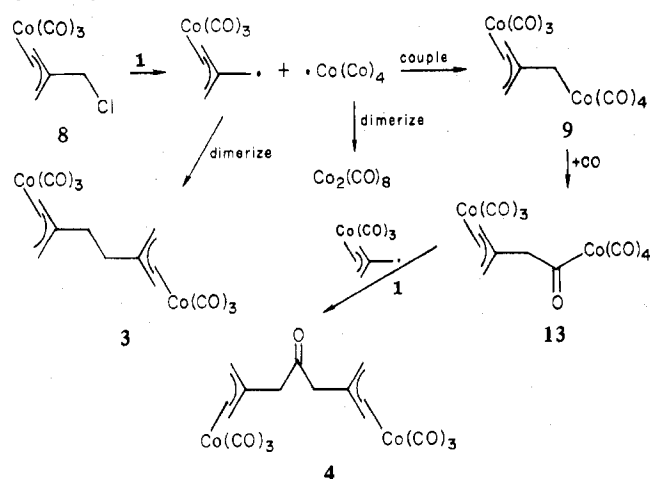
Scheme I
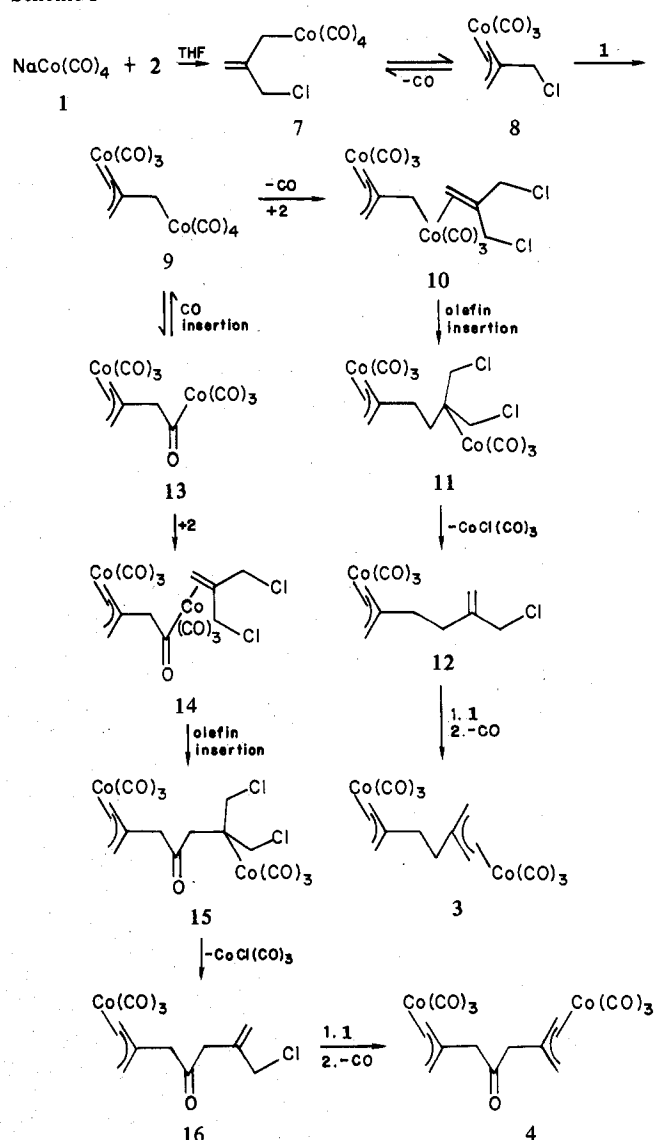
CO immediately forms (2-chloromethyl)allylcobalt tricarbonyl (**8**).[1] As stated above, we were unable to isolate intermediate **8**, and thus suspect that it again reacts with **1** to give dicobalt complex **9**. Thermal loss of CO by **9** then affords a coordinately unsaturated complex which can combine with the olefinic portion of another molecule of **2** to yield **10**. With insertion of the coordinated olefin in the least sterically

Table VII. Selected Distances (A) and Angles (deg) of Some Cobalt η^3-Allyl Complexes[a]

Compd	Co–C(CO)	Co–C(allyl) Terminal	Co–C(allyl) Central	C–C(allyl)	C–Co–C(CO)	C–C–C(allyl)	Ref
\{(CO)₃Co[(CH₂)₂CCH₂]\}₂	1.769 (1)	2.095 (1)	2.010 (2)	1.409 (2)	97.0 (1)	114.6 (2)	This work
	1.815 (2)				107.4 (1)		
(C₃H₅)Co(CO)₃	1.804 (3)	2.101 (6)	1.985 (16)	1.391 (9)	101 (1)	123 (3)	21[c]
					109 (2)		
\{[(C₆H₅)C]₃CO\}Co(CO)₃	1.83[b]	2.121	2.017	1.45		89	22
(2 crystallographically		2.135	1.981	1.48		88	
independent molecules/		2.113		1.48			
unit cell)		2.074		1.48			
\{[(CH₃O)₃P](CO)₂Co-	1.74 (1)	2.051 (9)	1.994 (10)	1.38 (1)	112.3 (6)	115 (1)	This work
[(CH₂)₂CCH₂]\}₂CO	1.78 (1)	2.083 (13)	2.015 (10)	1.40 (2)	111.6 (5)	116 (1)	
	1.74 (1)	2.054 (9)		1.38 (1)			
	1.79 (1)	2.075 (13)		1.41 (2)			

[a] Numbers in parentheses are the estimated standard deviations, if available, in the last significant digits. [b] Only the mean Co–C(carbonyl) distance was reported. [c] Electron diffraction.

Scheme II

hindered manner into the cobalt–carbon σ bond, a new carbon–carbon bond is made (**11**), and following elimination of CoCl(CO)₃ by unsaturated complex **11**, allyl halide **12** is produced. Now if the first two steps of this scheme are repeated, the second π-allylcobalt complex (**3**) is formed.

An alternative to loss of CO from **9** is insertion of CO to afford the unsaturated acylcobalt complex **13**. Insertion of CO into cobalt–carbon σ bonds is known to occur at room temperature.[27] Unsaturated species **13** may now coordinate with **2** and, by insertion of olefin into the acylcobalt σ bond, produce **15**, which upon elimination of CoCl(CO)₃ forms allyl halide complex **16**. This complex can now be converted to product **4** as illustrated by the final steps in this sequence. It has been shown by Heck[28] that insertion of an olefin into a cobalt–acyl carbon bond may also occur intramolecularly to effect, after elimination, a cyclic eneone.

Seyferth and Spohn have shown that benzyl bromide and sodium tetracarbonylcobaltate (**1**) in THF form dibenzyl ketone (major product) and 1,2-diphenylethane (yield, 10%).[29] To account for the coupling of the organic fragments, they have proposed a free radical mechanism in which the benzyl radical is formed by the transfer of an electron from the cobaltate anion. An analogous mechanism (Scheme II) might be appropriate here.

If it is assumed that undetected intermediate **8** is formed, it could then be converted to a π-allyl stabilized radical, Cl⁻, and the monomeric cobalt tetracarbonyl radical by electron transfer from **1**. This allyl radical could then combine with another π-allyl stabilized radical to give **3**, or it could couple with the cobalt tetracarbonyl radical to form **9**. Insertion of CO into the cobalt–carbon bond, followed by the addition of another CO molecule, would effect the acyl complex shown. Disproportionation of the acyl complex either by electron transfer (again) or by homologous cleavage of the cobalt–acyl carbon bond and subsequent combination with the π-allyl-stabilized radical would afford complex **4**. Although identification of Co₂(CO)₈ as a by-product of this reaction (see Scheme II) would offer some support for a free radical mechanism, it was not observed.

It is noteworthy that when 2 equiv of **1** was added to 1 mol of 1,4-dibromo-2-butene, an immediate, rapid evolution of butadiene was noted. This suggests that **1** may be acting as an electron-transfer agent because the displacement of Br⁻ followed by the 1,4-elimination of CoBr(CO)₄ would not be expected to occur so readily.

Support for either of these mechanisms is presently unavailable. Seyferth suggests that to achieve high yields of dimeric products a very stable free radical is necessary (e.g., the *gem*-diphenyl radical).[30] The stability of the π-allylcobalt tricarbonyl radical is an important question here. If dimerization is not the first step in the reaction, then the existence of long-lived free radicals seems essential, because this would allow the radicals to diffuse through solvent cages and then to couple to form the ethano-bridged product **3**. Finally, the possibility of the occurrence of both reaction pathways cannot be ruled out; with a maximum combined yield of **3** and **4** of 66% (see Experimental Section) other unidentified organocobalt species might be participating in the reaction also.

Registry No. **1**, 14878-28-5; **2**, 1871-57-4; **3**, 65890-25-7; **4**, 65890-24-6; **5**, 65915-83-5; **6**, 65890-23-5.

Supplementary Material Available: Listings of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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