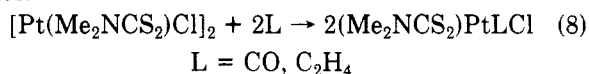


proven useful for the preparation of alkylplatinum complexes.



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## Syntheses and NMR Spectra of Co<sub>3</sub>(CO)<sub>9</sub>[μ<sub>3</sub>-CCHAr<sub>2</sub>] Clusters Derived from DDT and Related Molecules: X-ray Crystal Structures of [[Bis(4-chlorophenyl)methyl]carbynyl]tricobalt Nonacarbonyl and of Its Bis(4-chloronaphthyl) Analogue

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The reaction of Co<sub>2</sub>(CO)<sub>8</sub> with a series of 1,1,1-trichloro-2,2-bis(aryl)ethanes yields the corresponding Co<sub>3</sub>(CO)<sub>9</sub>[μ<sub>3</sub>-CCHAr<sub>2</sub>] tetrahedral clusters, where Ar = 4-chlorophenyl (3), 4-methoxyphenyl (4), or 4-chloronaphthyl (6). Co<sub>3</sub>(CO)<sub>9</sub>[μ<sub>3</sub>-CCH(*p*-C<sub>6</sub>H<sub>4</sub>Cl)<sub>2</sub>] (3) crystallizes in the monoclinic space group *P*2<sub>1</sub>/*n* with *a* = 13.0834 (27) Å, *b* = 14.2224 (16) Å, *c* = 14.1649 (24) Å, β = 95.871 (15)°, *V* = 2621.9 (8) Å<sup>3</sup>, and *Z* = 4; treatment of all 3434 unique data led to final values of *R*<sub>F</sub> = 3.7% and *R*<sub>wF</sub> = 3.3%. (*R*<sub>F</sub> = 2.5% and *R*<sub>wF</sub> = 3.0% for those 2781 data with |*F*<sub>o</sub>| > 6σ(|*F*<sub>o</sub>|).) The chloronaphthyl cluster of Co<sub>3</sub>(CO)<sub>9</sub>[μ<sub>3</sub>-CCH(C<sub>10</sub>H<sub>6</sub>Cl)<sub>2</sub>] (6) crystallizes in the triclinic space group *P*1 with *a* = 8.839 (3) Å, *b* = 12.156 (4) Å, *c* = 16.513 (5) Å, α = 105.974 (25)°, β = 92.280 (25)°, γ = 115.512 (22)°, *V* = 1513.57 (84) Å<sup>3</sup>, and *Z* = 2; treatment of the 3620 unique data led to final values of *R*<sub>F</sub> = 4.8% and *R*<sub>wF</sub> = 5.3%. At -120 °C, the cobalt carbonyl ligands of the phenyl clusters 3 and 4 exhibit a 6:3 splitting in their <sup>13</sup>C NMR spectra; however, the naphthyl cluster 6 does not show this effect. These data are discussed in terms of the ability of the aryl groups to obstruct the fluxionality of the cobalt carbonyl ligands.

### Introduction

The observed tendency of the carbynyl-tricobalt nonacarbonyl group to stabilize a positive charge in the α-position, as in the cluster [(OC)<sub>9</sub>Co<sub>3</sub>(μ<sub>3</sub>-C=CR<sub>2</sub>)]<sup>+</sup>, has been attributed to its ability to delocalize the charge onto the carbonyl ligands via the cobalts.<sup>1</sup> In order to compare the relative charge-stabilizing abilities of a C<sub>6</sub>H<sub>5</sub> unit and a (OC)<sub>9</sub>Co<sub>3</sub>(μ<sub>3</sub>-C) moiety, one needs to construct a molecule in which a phenyl ring and a carbynyl-nonacarbonyl-tricobalt unit are both attached to the same electron-deficient or electron-rich center. Therefore, it seemed a viable proposal to construct molecules in which one or more phenyl groups were bonded to a methynyl group situated in a position α to the nonacarbonyl-tricobalt moiety. By this means, one could remove the α-hydrogen either as a proton or as a hydride to prepare a cluster-stabilized anion or cation, respectively, and then determine the barrier to phenyl rotation in each case by variable-temperature NMR measurements. However, one needs a general route to

clusters containing such arylmethyl- or diarylmethyl-capping functionalities. Nonacarbonyl-tricobalt clusters are most easily synthesized via the direct reaction of dicobalt octacarbonyl with an appropriate trichloromethyl-containing precursor. The acid-catalyzed reaction of arenes with trichloroacetaldehyde (chloral) is a very well-established process that leads to molecules of the type Ar<sub>2</sub>CH-CCl<sub>3</sub>.<sup>2</sup> Indeed, this is a general route to commercial pesticides such as 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT) 1 or the corresponding 4-methoxyphenyl compound (Methoxychlor) 2, which is also readily available. Thus, we here describe the syntheses and characterizations of several clusters derived by reaction of these molecules with dicobalt octacarbonyl.

### Results and Discussion

The reaction of DDT with Co<sub>2</sub>(CO)<sub>8</sub> proceeds normally in that, upon heating, carbon monoxide is evolved; after the usual purification procedure, a mixture of black and white crystalline products is obtained. However, even after column chromatography and repeated recrystallizations, the black product (which is obtained in only minor yield)

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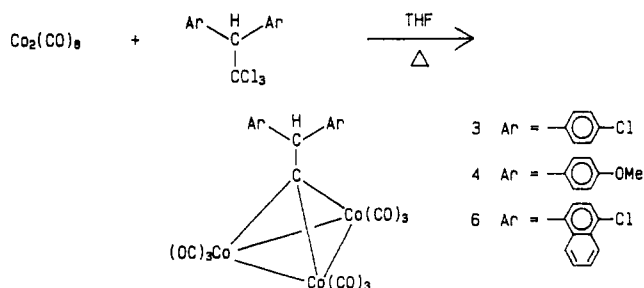
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could not be cleanly separated from the accompanying white material. This separation was finally effected by manually removing the individual crystals under a microscope. The microanalytical data (carbon, hydrogen, and chlorine) on the black crystals were in accord with the expected formula, i.e.,  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(p\text{-C}_6\text{H}_4\text{Cl})_2]$  (**3**). The mass spectrum exhibited peaks with isotopic abundances appropriate for a two-chlorine pattern at  $m/z$  648/650/652, which corresponds to  $[\text{M} - \text{CO}]^+$ , and also a series of ions showing the successive losses of seven more terminal carbonyl ligands.

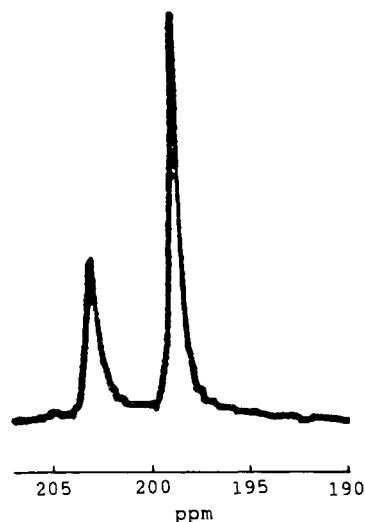
The  $^1\text{H}$  NMR spectrum of the white crystals, i.e., the major product from the reaction of DDT with dicobalt octacarbonyl, shows not only resonances in the aromatic region but also two doublets at  $\delta$  6.8 and 5.5 which are coupled to each other. Correspondingly, the  $^{13}\text{C}$  NMR spectrum of the molecule exhibits resonances at 71 and 64 ppm which are coupled to the above-mentioned protons, thus establishing the presence of a  $>\text{CH}-\text{CH}<$  unit in the molecule. These data were consistent with the assignment of the white crystals as 2,2-bis(4-chlorophenyl)-1,1-dichloroethane (DDD), and this was confirmed by comparison with an authentic sample. The mechanism of the reaction of trichloromethyl units with  $\text{Co}_2(\text{CO})_8$  has never been fully elucidated, but the general view is that the process occurs by radical abstractions. Indeed, Pauson has noted<sup>3</sup> that the reaction of  $\text{C}_6\text{H}_5\text{-CCl}_3$  with  $\text{Co}_2(\text{CO})_8$  yields not only the anticipated phenyl-capped cluster but also  $\text{Ph}(\text{Cl})\text{C}=\text{C}(\text{Cl})\text{Ph}$  and  $\text{PhCl}_2\text{C}-\text{CCl}_2\text{Ph}$ ; these latter products are readily rationalizable as arising from radical intermediates.

Since we wished to gain some insight into the molecular dynamics of the neutral cobalt cluster **3**, its variable-temperature  $^{13}\text{C}$  NMR spectrum was recorded. The room-temperature spectrum exhibited resonances at shifts appropriate for the apical carbon, for the cobalt carbonyls and for the bis(4-chlorophenyl)methyl fragment. We had thought it possible that restricted rotation of the phenyl rings might occur in which case the ortho and meta carbons of the aryl rings would no longer be magnetically equivalent. [This is precisely what happens with diarylmethyl anions or their  $\text{Cr}(\text{CO})_3$  complexes.<sup>4,5</sup>] Experimentally, the  $^{13}\text{C}$  NMR resonances of the ortho, meta, and C-Cl carbons overlap somewhat at low temperature in the freon solvent, thus obscuring any small splittings. Concomitantly however, we observed that the cobalt carbonyls split into a 6:3 pattern at  $-120^\circ\text{C}$ , as shown in Figure 1.

The reaction of Methoxychlor (**2**), with  $\text{Co}_2(\text{CO})_8$  yields the analogous bis(methoxyphenyl) cluster **4**. In this case,

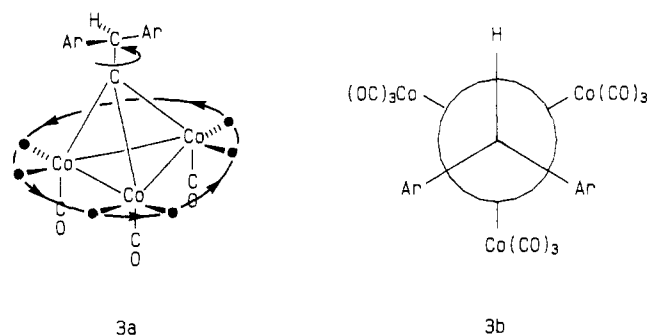


however, the phenyl ring resonances are widely separated, and, by  $-80^\circ\text{C}$ , the ortho and meta carbons are split,



**Figure 1.** Carbonyl region of the 125-MHz  $^{13}\text{C}$  NMR spectrum of  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(\text{C}_6\text{H}_4\text{Cl})_2]$  (**3**) recorded in  $\text{CD}_2\text{Cl}_2/\text{CFCl}_3$  at  $-120^\circ\text{C}$ .

clearly indicating that aryl rotation has slowed on the NMR time scale. Furthermore, this molecule also exhibits the unexpected 6:3  $^{13}\text{CO}$  pattern at  $-120^\circ\text{C}$ . This rather surprising result is amenable to several interpretations; first, one could be stopping axial-equatorial exchange of the cobalt carbonyls on the NMR time scale. Despite numerous attempts this phenomenon has not so far been unequivocally demonstrated.<sup>6,7</sup> Secondly, one could invoke slowed rotation of the diarylmethyl-capping group relative to the cobalt triangle. In the first instance, the molecule would maintain  $\text{C}_{3v}$  symmetry, but the cessation of the localized exchange would lead to a 6:3 pattern. This process could occur even if intermetal exchange were to continue. That is, the six aforementioned carbonyls could execute a merry-go-round process in the equatorial plane while the other three ligands would maintain their axial positions, as in **3a**. The second postulated process would



require that the bulky capping group rotate slowly about the alkylidene carbon- $\alpha$ -carbon bond axis on the NMR time scale presumably such that the predominant rotamer would be the staggered molecule as in **3b**. This situation would not demand the hitherto unknown cessation of localized  $\text{Co}(\text{CO})_3$  rotation but merely the slowing of intermetal exchange—a well-established phenomenon.<sup>6,8</sup> In order to evaluate these possibilities, it was necessary to obtain information on the steric interactions between the

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Table I. Experimental Data for the X-ray Diffraction Studies of  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(\text{p-C}_6\text{H}_4\text{Cl})_2]$  (3) and  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(4\text{-C}_{10}\text{H}_6\text{Cl})_2]$  (6)

3		6	
(A) Unit Cell Data			
$a$ , Å	13.0834 (27)	8.839 (3)	
$b$ , Å	14.2224 (16)	12.156 (4)	
$c$ , Å	14.1649 (24)	16.513 (5)	
$\alpha$ , deg	90	105.974 (25)	
$\beta$ , deg	95.871 (15)	92.280 (25)	
$\gamma$ , deg	90	115.512 (22)	
$V$ , Å <sup>3</sup>	2621.9 (8)	1513.57 (84)	
cryst system	monoclinic	triclinic	
space group	$P2_1/n$	$P\bar{1}$	
$Z$	4	2	
formula	$\text{C}_{23}\text{H}_9\text{O}_9\text{Cl}_2\text{Co}_3$	$\text{C}_{31}\text{H}_{13}\text{O}_9\text{Cl}_2\text{Co}_3$	
mol wt	677.01	777.15	
$D(\text{calcd})$ , g/cm <sup>3</sup>	1.71	1.705	
$T$ , °C	24 (297 K)	22 (295 K)	
(B) Collection of X-ray Diffraction Data			
diffractometer	Syntax P2 <sub>1</sub>	Nicolet P3	
radiatn	Mo $K\alpha$ ( $\lambda = 0.71069$ Å)	Mo $K\alpha$ ( $\lambda = 0.71069$ Å)	
monochromator	highly oriented (pyrolytic) graphite: equatorial mode with $2\theta(m) = 12.160^\circ$ ; assumed to be 50% perfect/50% ideally mosaic for polarization correction		
reflectns measd	$+h, \pm k, \pm l$	$+h, \pm k, \pm l$	
for $2\theta$ , deg	5–45	0–45	
unique data	3434	3620	
scan type	coupled $\theta(\text{crystal})-2\theta(\text{counter})$		
scan width, deg	$[2\theta(K\alpha_1) - 1.0] \rightarrow [2\theta(K\alpha_2) + 1.0]$		
scan speed, deg/min	4.0	5.9	
std reflectns	three mutually orthogonal reflectns collected before each set of 97 data points; no decay observed	two reflectns (1,–4,–5 and 1,3,–8) collected before each set of 48 data points, no significant decay observed	

(diarylmethyl)carbynyl group and the cobalt carbonyl ligands, and so crystals of 3 suitable for an X-ray diffraction study were obtained.

The crystal consists of discrete units of  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(\text{C}_6\text{H}_4\text{Cl})_2]$  which have close to (noncrystallographic)  $C_s$  symmetry excluding rotation of the  $\text{C}_6\text{H}_4\text{Cl}$  groups. There are no abnormally short inter- or intramolecular contacts. The structure and labeling scheme is illustrated in Figure 2. X-ray crystallographic data and interatomic distances and angles are listed in Tables I through III. The tricobalt plane has normal Co–Co bond lengths, with  $\text{Co}(1)\text{--Co}(2) = 2.474(1)$  Å,  $\text{Co}(1)\text{--Co}(3) = 2.471(1)$  Å, and  $\text{Co}(2)\text{--Co}(3) = 2.462(1)$  Å. These values fall within the range reported for previous structures containing the  $\text{Co}_3(\text{CO})_9\text{C}$  fragment, viz., 2.463(5)–2.498(4) Å.<sup>9–15</sup> Although the variation in Co–Co bond lengths is statistically significant, it is of little chemical importance. Similar variations in chemically equivalent Co–Co bond distances have been seen previously and are probably a result of crystal packing forces.<sup>9,10</sup> The methylidyne carbon (C(1)) lies at distances of 1.914(3)–1.921(3) Å from the cobalt atoms. Again, these distances are typical. The *p*-chlorophenyl rings show normal distances and angles. As shown in Figure 3a, the chlorophenyl rings are slightly "twisted" relative to an axis perpendicular to the plane of the three cobalt atoms; the dihedral angles  $\text{C}(1)\text{--C}(2)\text{--C}(41)\text{--C}(42)$  and  $\text{C}(1)\text{--C}(2)\text{--C}(51)\text{--C}(56)$  are  $+83^\circ$  and  $-58^\circ$ , respectively, thus removing the potential  $C_s$  symmetry of the

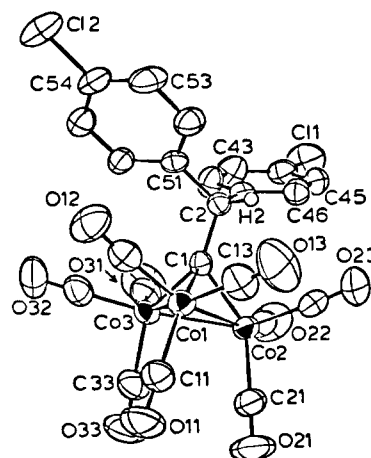


Figure 2. Labeling of the atoms in  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(\text{C}_6\text{H}_4\text{Cl})_2]$  (3).

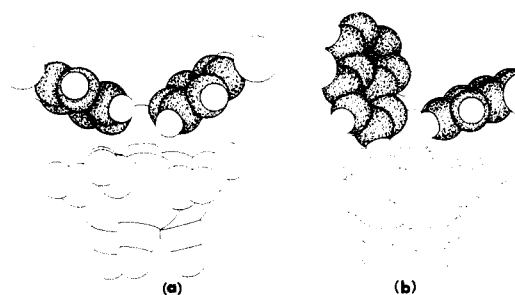


Figure 3. CHEM-X plots illustrating the twisting of (a) the chlorophenyl rings in 3 and (b) the chloronaphthyl rings in 6.

entire molecule 3. (In DDT itself,<sup>16</sup> the corresponding angles are  $+87^\circ$  and  $-47^\circ$ ; in contrast, in a series of porphyrin–iron–carbene complexes derived from DDT, the

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Table II. Final Atomic Parameters for  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(p\text{-C}_6\text{H}_4\text{Cl})_2]^a$ 

atom	x	y	z
Co(1)	0.75321 (3)	0.77559 (3)	0.70445 (3)
Co(2)	0.59813 (3)	0.70589 (3)	0.61694 (3)
Co(3)	0.68006 (3)	0.84406 (3)	0.55199 (3)
Cl(1)	0.61000 (9)	0.46201 (9)	0.17826 (7)
Cl(2)	1.24577 (7)	0.76571 (9)	0.53301 (8)
O(11)	0.66108 (22)	0.91044 (21)	0.83176 (20)
O(12)	0.96941 (22)	0.83611 (21)	0.71574 (19)
O(13)	0.80334 (29)	0.61120 (23)	0.82331 (24)
O(21)	0.44731 (23)	0.78707 (23)	0.73630 (22)
O(22)	0.47157 (23)	0.66702 (26)	0.43873 (21)
O(23)	0.61722 (24)	0.51277 (20)	0.68850 (24)
O(31)	0.62084 (29)	0.84122 (23)	0.34673 (21)
O(32)	0.84784 (25)	0.98068 (20)	0.55602 (21)
O(33)	0.51724 (26)	0.96921 (23)	0.61158 (23)
C(1)	0.73462 (22)	0.72129 (19)	0.58051 (19)
C(2)	0.80144 (23)	0.64770 (19)	0.53883 (20)
C(11)	0.69695 (28)	0.85838 (25)	0.78422 (24)
C(12)	0.88534 (32)	0.81475 (25)	0.70994 (23)
C(13)	0.78228 (32)	0.67503 (29)	0.77816 (25)
C(21)	0.50418 (28)	0.75688 (26)	0.68996 (26)
C(22)	0.52092 (28)	0.68208 (27)	0.50731 (28)
C(23)	0.60880 (26)	0.58784 (28)	0.66209 (27)
C(31)	0.64423 (31)	0.83995 (26)	0.42560 (28)
C(32)	0.78328 (32)	0.92695 (25)	0.55354 (25)
C(33)	0.57991 (32)	0.92276 (27)	0.58873 (27)
C(41)	0.75277 (22)	0.60373 (20)	0.44593 (20)
C(42)	0.75729 (28)	0.64417 (24)	0.35806 (23)
C(43)	0.71385 (30)	0.60128 (29)	0.27562 (24)
C(44)	0.66504 (26)	0.51678 (26)	0.28158 (24)
C(45)	0.65901 (26)	0.47435 (23)	0.36787 (26)
C(46)	0.70297 (26)	0.51793 (22)	0.44923 (22)
C(51)	0.91281 (23)	0.67921 (21)	0.53472 (20)
C(52)	0.99082 (26)	0.62745 (24)	0.58361 (24)
C(53)	1.09336 (26)	0.65381 (28)	0.58385 (26)
C(54)	1.11689 (24)	0.73208 (26)	0.53425 (24)
C(55)	1.04137 (26)	0.78523 (23)	0.48499 (24)
C(56)	0.93999 (24)	0.75867 (22)	0.48652 (22)
H(2)	0.8044	0.5974	0.5841
H(42)	0.7882	0.7050	0.3545
H(43)	0.7126	0.6341	0.2159
H(45)	0.6252	0.4144	0.3703
H(46)	0.7017	0.4871	0.5097
H(52)	0.9743	0.5713	0.6169
H(53)	1.1461	0.6182	0.6195
H(55)	1.0582	0.8414	0.4510
H(56)	0.8874	0.7955	0.4508

<sup>a</sup> All hydrogen atoms were assigned an isotropic thermal parameter of  $B = 4.0 \text{ \AA}^2$ .

chlorophenyl rings of the  $\text{Ar}_2\text{C}=\text{Fe}$  moiety are aligned almost orthogonally to each other.<sup>17,18</sup> The Co-C(1)-C(2) bond angles in **3** are Co(1)-C(1)-C(2) = 127.6 (2)°, Co(2)-C(1)-C(2) = 127.8 (2)°, and Co(3)-C(1)-C(2) = 139.7 (2)°. Since the *p*-chlorophenyl rings are oriented toward Co(3), the increased Co(3)-C(1)-C(2) angle is probably a result of intramolecular steric forces. Axial carbonyl ligands (i.e., those trans to the apical carbon) are associated with somewhat longer cobalt-carbon distances (Co(1)-C(11) = 1.837 (4) Å; Co(2)-C(21) = 1.835 (4) Å; Co(3)-C(33) = 1.839 (4) Å) than are the equatorial carbonyl ligands (Co(1)-C(13) = 1.789 (4) Å to Co(1)-C(12) = 1.810 (4) Å). The corresponding carbon-oxygen distances show little variation: C-O(axial) = 1.129(5) Å (average) and C-O-

Table III. Selected Interatomic Distances (Å) and Angles (deg) for  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(p\text{-C}_6\text{H}_4\text{Cl})_2]$ 

(A) Co-Co and Co-C(methyldiene) Distances			
Co(1)-Co(2)	2.474 (1)	Co(1)-C(1)	1.911 (3)
Co(1)-Co(3)	2.471 (1)	Co(2)-C(1)	1.921 (3)
Co(2)-Co(3)	2.462 (1)	Co(3)-C(1)	1.914 (3)
(B) Co-CO and C-O Distances			
Co(1)-C(11)	1.837 (4)	C(11)-O(11)	1.134 (5)
Co(1)-C(12)	1.810 (4)	C(12)-O(12)	1.136 (5)
Co(1)-C(13)	1.789 (4)	C(13)-O(13)	1.128 (5)
Co(2)-C(21)	1.835 (4)	C(21)-O(21)	1.126 (5)
Co(2)-C(22)	1.796 (4)	C(22)-O(22)	1.131 (5)
Co(2)-C(23)	1.797 (4)	C(23)-O(23)	1.133 (5)
Co(3)-C(31)	1.805 (4)	C(31)-O(31)	1.128 (5)
Co(3)-C(32)	1.791 (4)	C(32)-O(32)	1.137 (5)
Co(3)-C(33)	1.839 (4)	C(33)-O(33)	1.126 (5)
(C) Distances Involving the $\mu_3\text{-C-CH-(C)}_2$ System			
C(1)-C(2)	1.521 (4)	C(2)-C(41)	1.535 (4)
		C(2)-C(51)	1.531 (4)
(D) Angles within the $\text{Co}_3(\mu_3\text{-C})$ Core			
Co(1)-Co(2)-Co(3)	60.08 (2)	Co(1)-C(1)-Co(2)	80.43 (11)
Co(3)-Co(1)-Co(2)	59.71 (2)	Co(1)-C(1)-Co(3)	80.50 (11)
Co(2)-Co(3)-Co(1)	60.21 (2)	Co(2)-C(1)-Co(3)	79.86 (11)
Co(1)-Co(2)-C(1)	49.59 (8)	Co(3)-Co(2)-C(1)	49.93 (8)
Co(1)-Co(3)-C(1)	49.70 (8)	Co(2)-Co(1)-C(1)	49.97 (8)
Co(2)-Co(3)-C(1)	50.20 (8)	Co(3)-Co(1)-C(1)	49.81 (8)

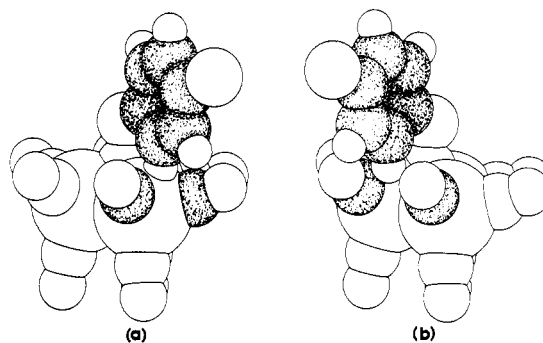


Figure 4. CHEM-X plots of selected conformations (see text) of  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(\text{C}_6\text{H}_4\text{Cl})_2]$  (**3**). For clarity only one chlorophenyl ring is depicted.

(equatorial) = 1.132 (5) Å (average).

To probe the possible steric interactions between the bulky capping group and the terminal carbonyl ligands, the crystallographically derived atomic coordinates were manipulated by using the CHEM-X molecular modelling program.<sup>19</sup> The (diarylmethyl)carbynyl fragment was rotated so as to position a phenyl ring between two metal carbonyl ligands either (a) on the same cobalt atom or (b) on adjacent cobalt atoms. These situations are depicted in Figure 4 and show that, in the most extreme cases, the ortho-hydrogens of the chlorophenyl rings can get uncomfortably close to the metal carbonyls. A similar effect may be responsible for the slowed rotation of the aryl rings in **4** as detected by <sup>13</sup>C NMR.

To gain further data on this problem, we chose to synthesize an even more bulky capping carbynyl substituent. The sulfuric acid catalyzed reaction of trichloroacetaldehyde with 1-chloronaphthalene gave 1,1,1-trichloro-2,2-bis(4-chloronaphthyl)ethane (**5**), which underwent reaction with dicobalt octacarbonyl to yield the bis(naphthyl) cluster **6**. It is noteworthy that this synthesis is exceptionally sensitive to the effects of temperature and reaction time. If kept for several hours at more than 50 °C, the

(17) (a) Chevrier, B.; Weiss, R.; Lange, M.; Chottard, J. C.; Mansuy, D. *J. Am. Chem. Soc.* **1981**, *103*, 2899. (b) Olmstead, M. M.; Cheng, R. J.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 4143. (c) Mansuy, D.; Battioni, J.-P.; Lavalley, D. K.; Fischer, J.; Weiss, R. *Inorg. Chem.* **1988**, *27*, 1052.

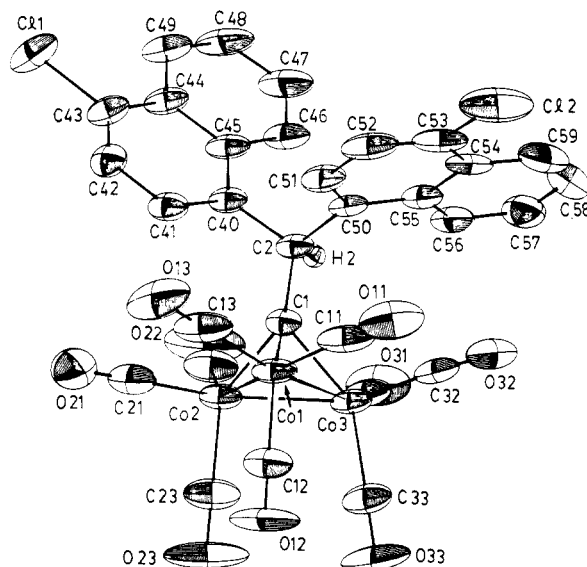
(18) An important factor here must be the relatively wide Ar-C(sp<sup>3</sup>)-Ar angle of ≈120° in the iron-carbene complexes; the aryl rings thus have the freedom to rotate into the most favorable conformation and so minimize steric interactions between the aryl rings. In contrast, the Ar-C(sp<sup>3</sup>)-Ar angle is only ≈110° in DDT.

(19) CHEM-X, July 1986 version, developed and distributed by Chemical Design Ltd., Oxford, England.

**Table IV. Final Atomic Positions and Temperature Factors ( $\text{\AA}^2$ ) for  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(\text{4-C}_{10}\text{H}_6\text{Cl})_2]$** 

atom	x	y	z
Co(1)	0.09551 (8)	0.24094 (6)	0.84170 (4)
Co(2)	0.15933 (8)	0.11416 (5)	0.71507 (4)
Co(3)	0.38948 (7)	0.31142 (6)	0.81761 (3)
Cl(1)	-0.3989 (2)	0.1532 (2)	0.3980 (9)
Cl(2)	0.2028 (3)	0.8467 (2)	0.9443 (1)
O(11)	0.1656 (6)	0.4822 (4)	0.9743 (2)
O(12)	0.1158 (5)	0.0942 (4)	0.9549 (3)
O(13)	-0.2727 (6)	0.1456 (5)	0.7995 (3)
O(21)	-0.1963 (6)	-0.0755 (4)	0.6455 (3)
O(22)	0.2724 (7)	0.1167 (4)	0.5514 (3)
O(23)	0.2529 (7)	-0.0588 (4)	0.7770 (3)
O(31)	0.6185 (5)	0.3423 (4)	0.6940 (3)
O(32)	0.5561 (5)	0.5785 (4)	0.9317 (2)
O(33)	0.5158 (5)	0.2044 (4)	0.9312 (2)
C(1)	0.1899 (5)	0.2865 (4)	0.7462 (2)
C(2)	0.1904 (6)	0.3713 (4)	0.6932 (3)
C(11)	0.1376 (7)	0.3891 (5)	0.9217 (3)
C(12)	0.1065 (6)	0.1493 (5)	0.9124 (3)
C(13)	-0.1295 (8)	0.1815 (6)	0.8151 (3)
C(21)	-0.0573 (8)	0.0004 (5)	0.6740 (3)
C(22)	0.2313 (7)	0.1134 (5)	0.6150 (4)
C(23)	0.2186 (7)	0.0078 (5)	0.7524 (3)
C(31)	0.5296 (6)	0.3287 (5)	0.7426 (3)
C(32)	0.4886 (6)	0.4757 (5)	0.8864 (3)
C(33)	0.4693 (6)	0.2457 (5)	0.8883 (3)
C(40)	0.0470 (5)	0.3109 (4)	0.6153 (2)
C(41)	-0.1136 (6)	0.2208 (5)	0.6159 (3)
C(42)	-0.2501 (6)	0.1728 (5)	0.5480 (3)
C(43)	-0.2241 (6)	0.2118 (5)	0.4794 (3)
C(44)	-0.0623 (6)	0.3018 (4)	0.4721 (3)
C(45)	0.0767 (6)	0.3524 (4)	0.5418 (3)
C(46)	0.2372 (6)	0.4443 (5)	0.5352 (3)
C(47)	0.2611 (8)	0.4846 (6)	0.4645 (3)
C(48)	0.1263 (8)	0.4311 (6)	0.3969 (4)
C(49)	-0.0316 (7)	0.3442 (5)	0.3995 (3)
C(50)	0.2015 (6)	0.4987 (4)	0.7510 (2)
C(51)	0.0554 (7)	0.4977 (5)	0.7778 (3)
C(52)	0.0575 (8)	0.6065 (6)	0.8357 (3)
C(53)	0.2036 (8)	0.7162 (5)	0.8670 (3)
C(54)	0.3571 (7)	0.7271 (4)	0.8407 (3)
C(55)	0.3568 (6)	0.6161 (4)	0.7798 (3)
C(56)	0.5123 (7)	0.6297 (5)	0.7532 (3)
C(57)	0.6582 (8)	0.7431 (7)	0.7842 (5)
C(58)	0.6584 (10)	0.8489 (6)	0.8429 (5)
C(59)	0.5143 (10)	0.8431 (5)	0.8716 (4)
H(2)	0.290 (5)	0.384 (3)	0.671 (2)
H(41)	-0.130 (6)	0.188 (5)	0.662 (3)
H(42)	-0.361 (7)	0.110 (5)	0.551 (3)
H(46)	0.342 (6)	0.479 (5)	0.585 (3)
H(47)	0.378 (6)	0.558 (5)	0.466 (3)
H(48)	0.143 (7)	0.458 (6)	0.354 (4)
H(49)	-0.136 (6)	0.301 (4)	0.353 (3)
H(51)	-0.054 (7)	0.415 (5)	0.753 (3)
H(52)	-0.042 (8)	0.603 (6)	0.847 (4)
H(56)	0.506 (6)	0.549 (5)	0.709 (3)
H(57)	0.749 (7)	0.744 (5)	0.772 (3)
H(58)	0.763 (7)	0.923 (6)	0.873 (3)
H(59)	0.526 (5)	0.922 (4)	0.920 (3)

cluster decomposed; on the other hand, when the reaction was carried out at  $\approx 40^\circ\text{C}$ , the main product was  $\text{Co}_4(\text{C}-\text{O})_{12}$ . The X-ray crystal structure of **6** (see Figure 5 and Tables I, IV, and V) reveals that all the carbonyls are terminally bonded and also that the chloronaphthyl ring planes are again twisted relative to the axis normal to the tricobalt plane; the analogous dihedral angles to those reported above for **3** are  $+78^\circ$  and  $-34^\circ$ . It is apparent that, in the solid state at least, the twist angle between the chloronaphthyl rings in **6** is approximately  $30^\circ$  greater than that for the chlorophenyl rings in **3** (see Figure 3b). We note also that in **6** one of the cobalt tricarbonyl vertices has rotated slightly, presumably to alleviate the steric interactions with the capping group. Comparisons of the bond lengths and angles in **6** with those of **3** naturally show

**Figure 5.** Labeling of the atoms in  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(\text{C}_{10}\text{H}_6\text{Cl})_2]$  (**6**).**Table V. Selected Interatomic Distances ( $\text{\AA}$ ) and Angles ( $\text{deg}$ ) for  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(\text{4-C}_{10}\text{H}_6\text{Cl})_2]$** 

(A) Co-Co and Co-C(methyldiene) Distances			
Co(1)-Co(2)	2.477 (1)	Co(1)-C(1)	1.918 (4)
Co(1)-Co(3)	2.449 (1)	Co(2)-C(1)	1.906 (5)
Co(2)-Co(3)	2.459 (1)	Co(3)-C(1)	1.942 (5)
(B) Co-CO and C-O Distances			
Co(1)-C(11)	1.789 (6)	C(11)-O(11)	1.139 (7)
Co(1)-C(12)	1.848 (7)	C(12)-O(12)	1.117 (9)
Co(1)-C(13)	1.785 (7)	C(13)-O(13)	1.138 (8)
Co(2)-C(21)	1.771 (5)	C(21)-O(21)	1.149 (6)
Co(2)-C(22)	1.794 (6)	C(22)-O(22)	1.129 (8)
Co(2)-C(23)	1.823 (7)	C(23)-O(23)	1.138 (10)
Co(3)-C(31)	1.775 (5)	C(31)-O(31)	1.141 (7)
Co(3)-C(32)	1.792 (5)	C(32)-O(32)	1.133 (6)
Co(3)-C(33)	1.853 (7)	C(33)-O(33)	1.129 (9)
(C) Distances Involving the $\mu_3\text{-C-CH-(C)}_2$ System			
C(1)-C(2)	1.524 (7)	C(2)-C(40)	1.533 (6)
		C(2)-C(50)	1.539 (6)
(D) Angles within the $\text{Co}_3(\mu_3\text{-C})$ Core			
Co(1)-Co(2)-Co(3)	59.49 (2)	Co(1)-C(1)-Co(2)	80.74 (18)
Co(3)-Co(1)-Co(2)	59.88 (2)	Co(1)-C(1)-Co(3)	78.74 (18)
Co(2)-Co(3)-Co(1)	60.63 (2)	Co(2)-C(1)-Co(3)	79.41 (21)
Co(1)-Co(2)-C(1)	49.84 (13)	Co(3)-Co(2)-C(1)	50.94 (13)
Co(1)-Co(3)-C(1)	50.19 (13)	Co(2)-Co(1)-C(1)	49.42 (14)
Co(2)-Co(3)-C(1)	49.65 (13)	Co(3)-Co(1)-C(1)	51.06 (14)

many similar features. Again, twisting of the chloronaphthyl rings of the capping group prevents the molecule from adopting approximate  $C_s$  symmetry.

Interestingly, the low-temperature  $^{13}\text{C}$  NMR spectrum of **6** does not show a 6:3 splitting of the cobalt carbonyl groups. Furthermore, in the  $^{13}\text{C}$  NMR spectrum, the corresponding carbons of the two chloronaphthyl rings are equivalent. Evidently, the naphthyls must have sufficient conformational mobility to generate a molecular mirror plane on the NMR time scale.

It is perhaps surprising that the DDT- and Methoxychlor-derived clusters **3** and **4**, respectively, exhibit a 6:3 pattern in the  $^{13}\text{C}$  NMR spectrum at low temperature while the chloronaphthyl analogue **6** does not. One might have imagined that the bulky naphthyl rings would cause much more steric hindrance to the carbonyls than would the phenyl rings in **3** and **4**. A closer examination of the system reveals that the naphthyl rings are relatively restricted in their movement because of their mutual steric

repulsions. In order to interfere with the movements of the metal carbonyl ligands, which can involve local rotation of a  $\text{Co}(\text{CO})_3$  fragment and/or carbonyl migration between cobalt vertices, the aryl rings have to be able to orient themselves such they are almost orthogonal to the tricobalt plane, as shown for **3** in Figure 4. In contrast to **3** and **4**, molecular modelling studies indicate that such conformations are difficult to achieve in **6**.

Without further labelling studies, it is not yet possible to distinguish unequivocally between the two scenarios outlined above, namely, the cessation of local rotation of the  $\text{Co}(\text{CO})_3$  vertices or slowed rotation of the carbonyl capping group.<sup>20</sup> To resolve the ambiguity as to the origin of the 6:3 splitting of the carbonyl ligands observed in **3** and **4**, it is necessary to construct clusters of potentially lower symmetry which also incorporate other NMR probes. To this end, we have synthesized molecules of the type  $\text{Co}_3(\text{CO})_6(\text{tripod})[\mu_3\text{-CCHAr}_2]$ , where tripod is the tris(diphenylphosphino)methane ligand. The variable-temperature  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra of these clusters together with an X-ray characterization of one such molecule are discussed in an accompanying manuscript.<sup>21</sup>

### Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. All solvents were dried according to standard procedures before use.<sup>22</sup>  $^{13}\text{C}$  NMR spectra were recorded at 125.7 and 62.9 MHz by using Bruker AM500 and WM250 spectrometers, respectively.  $^1\text{H}$  NMR spectra were recorded by using Bruker WM250 and WP80 spectrometers. Chemical shifts reported were referenced to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 283 instrument using KBr solution cells. Mass spectra were obtained on a VG Analytical ZAB-E reversed-geometry double-focussing mass spectrometer with a VG11/250J data system. FAB (positive ion) spectra were obtained by using 3-nitrobenzyl alcohol as the matrix. Microanalytical data are from Guelph Chemical Laboratories, Guelph, Ontario.

$\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(p\text{-C}_6\text{H}_4\text{Cl})_2]$  (**3**). To a solution of  $\text{Co}_2(\text{CO})_8$  (18.70 g, 54.7 mmol) in THF (100  $\text{cm}^3$ ), under an atmosphere of  $\text{N}_2$ , was slowly added by syringe a solution of DDT (10.80 g, 30.5 mmol) dissolved in THF (50  $\text{cm}^3$ ). After the solution was stirred at 50 °C for 2 h, the heat source was removed and the reaction mixture stirred at room temperature overnight. Following filtration under nitrogen pressure (Schlenk tube apparatus) to remove cobalt salts, the solvent was evaporated. The residue was dissolved in hexane and filtered to eliminate any insoluble products. The hexane was then removed by using a rotary evaporator, and the crude material was purified by column chromatography on silica gel (eluent, hexane). The first band that eluted contained the organic starting material DDT. The second band was collected and found to contain the desired product **3** as well as some DDD. Separation of **3** from the DDD was achieved by carrying out repeated recrystallizations in a dichloromethane/hexane medium. The black crystals of **3** were selected with the aid of a microscope after each recrystallization.  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta$  7.15 (d, 4 H), 6.70 (d, 4 H), 5.30 (s, 1 H).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2/\text{CFCl}_3$ ) (room temperature):  $\delta$  305.9 (alkylidyne C), 200.7 (Co-CO's), 145.7 ( $\text{C}_1$ , ipso carbons, C-CH-C), 133.5 ( $\text{C}_4$ , C-Cl), 131.3, 129.4 ( $\text{C}_{2,6}$ ,  $\text{C}_{3,5}$ ), 76.9 (Ar-CH-Ar).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2/\text{CFCl}_3$ ) (-120 °C) (Co-CO's):  $\delta$  202.9 (3 C), 198.5 (6 C). IR ( $\text{CCl}_4$ ):  $\nu_{\text{CO}}$  2092 (m), 2030 (vs), 2010 (s), 1989 (w), 1980 (w)  $\text{cm}^{-1}$ . Mass spectrum (DEL):  $m/z$  (%) 648 (29)  $\text{C}_{22}\text{H}_9\text{Cl}_2\text{Co}_3\text{O}_8$  (M - CO)<sup>+</sup>, 592 (65) (M - 3CO)<sup>+</sup>, 564 (60) (M - 4CO)<sup>+</sup>, 536 (31) (M - 5CO)<sup>+</sup>, 508 (100) (M - 6CO)<sup>+</sup>, 480 (43) (M - 7CO)<sup>+</sup>, 452 (38) (M - 8CO)<sup>+</sup>, 424 (48) (M - 9CO)<sup>+</sup>. Anal. Calcd for  $\text{C}_{22}\text{H}_9\text{Cl}_2\text{Co}_3\text{O}_8$ : C, 40.80; H, 1.34; Cl, 10.47. Found: C, 40.77; H, 1.33; Cl, 10.49.

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$\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(p\text{-C}_6\text{H}_4\text{OCH}_3)_2]$  (**4**). A THF solution (100  $\text{cm}^3$ ) of  $\text{Co}_2(\text{CO})_8$  (10.88 g, 31.8 mmol) and Methoxychlor (6.11 g, 17.7 mmol) was stirred at reflux under an atmosphere of  $\text{N}_2$  for 4 h. The solution was allowed to cool to room temperature and filtered (under  $\text{N}_2$  pressure) to remove any cobalt salts. The solvent was removed under reduced pressure, and the residue was dissolved in hexane. After any insoluble material was filtered off, the hexane solution was evaporated and purification of the resultant solid by flash chromatography on silica gel (eluent, ether/petroleum ether, 5/95) yielded the product **4** as dark purple crystals (1.32 g, 2.0 mmol, 11.2%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.65 (d, 4 H), 6.92 (d, 4 H), 5.95 (s, 1 H), and 3.76 (s, 6 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) (room temperature):  $\delta$  311.1 (alkylidyne C), 199.7 (Co-CO's), 158.9 (MeO-C), 138.9 ( $\text{C}_1$ , ipso carbons, C-CH-C), 129.7 ( $\text{C}_{3,5}$ ), 114.1 ( $\text{C}_{2,6}$ ), 76.8 (Ar-CH-Ar), 55.3 (O-CH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2/\text{CFCl}_3$ ) (-120 °C):  $\delta$  202.3 (3 C), 198.0 (6 C) (Co-CO's), 157.5 (MeO-C), 137.8 ( $\text{C}_1$ , ipso carbons, C-CH-C), 129.3, 128.8 ( $\text{C}_{3,5}$ ), 113.1, 112.7 ( $\text{C}_{2,6}$ ). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}}$  2100 (m), 2050 (vs), 2030 (s), 2010 (sh)  $\text{cm}^{-1}$ . Mass spectrum (FAB):  $m/z$  (%) 668 (3)  $\text{C}_{25}\text{H}_{15}\text{O}_{11}\text{Co}_3$  (M)<sup>+</sup>, 640 (12) (M - CO)<sup>+</sup>, 584 (100) (M - 3CO)<sup>+</sup>, 556 (50) (M - 4CO)<sup>+</sup>, 528 (28) (M - 5CO)<sup>+</sup>, 500 (48) (M - 6CO)<sup>+</sup>, 472 (25) (M - 7CO)<sup>+</sup>, 444 (22) (M - 8CO)<sup>+</sup>, 416 (18) (M - 9CO)<sup>+</sup>. Anal. Calcd for  $\text{C}_{25}\text{H}_{15}\text{O}_{11}\text{Co}_3$ : C, 44.94; H, 2.26. Found: C, 44.69; H, 2.22.

**Synthesis of 1,1,1-Trichloro-2,2-bis(4-chloronaphthyl)ethane (5).** Following the procedure of Haskelberg and Lavie,<sup>23</sup> 4-chloronaphthalene and trichloroacetaldehyde reacted in the presence of concentrated  $\text{H}_2\text{SO}_4$  to yield **5**. The 500-MHz  $^1\text{H}$ - $^1\text{H}$  COSY 2-D NMR experiment (in  $\text{CD}_2\text{Cl}_2$ ) revealed all the expected proton interactions leading to the following assignments:  $\delta$  8.39 (d, 2 H, H<sub>8</sub>), 8.35 (d, 2 H, H<sub>5</sub>), 8.08 (d, 2 H, H<sub>3</sub>), 7.6 (mult, 6 H, H<sub>2</sub>, H<sub>6</sub>, H<sub>7</sub>), and 6.86 (s, 1 H, H<sub>4</sub>).

$\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(\text{C}_{10}\text{H}_6\text{Cl})_2]$  (**6**). A solution of  $\text{Co}_2(\text{CO})_8$  (4.95 g, 14.5 mmol) and  $(\text{C}_{10}\text{H}_6\text{Cl})_2\text{CHCCl}_3$  (**5**) (3.66 g, 8.1 mmol) in THF (75  $\text{cm}^3$ ) was stirred at 45 °C under an atmosphere of  $\text{N}_2$  for 3 h. The solvent was removed by evaporation, and purification of the residue by column chromatography on neutral alumina (eluent, hexane) yielded two products. The major product, present in the first band, was spectroscopically identified as  $\text{Co}_4(\text{CO})_{12}$ . The second band was collected and evaporated to give dark purple crystals of the desired product **6** (0.17 g, 0.2 mmol, 2.6%).  $^{13}\text{C}$  NMR ( $\text{CH}_2\text{Cl}_2$ ) (room temperature):  $\delta$  303.7 (alkylidyne C), 199.8 (Co-CO's), 141.4 ( $\text{C}_1$ , ipso carbons, C-CH-C), 131.0 ( $\text{C}_4$ , C-Cl), 131.8, 127.7, 127.3, 127.0, 126.0, 125.3 ( $\text{C}_{2,3,5,6,7,8}$ ), 122.9, 122.5 ( $\text{C}_{9,10}$ ), 61.7 (Ar-CH-Ar). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}}$  2092 (m), 2038 (s), 2027 (s), 2010 (m)  $\text{cm}^{-1}$ . Mass spectrum (FAB):  $m/z$  (%) 748 (8)  $\text{C}_{30}\text{H}_{13}\text{Cl}_2\text{Co}_3\text{O}_8$  (M - CO)<sup>+</sup>, 720 (17) (M - 2CO)<sup>+</sup>, 692 (88) (M - 3CO)<sup>+</sup>, 664 (100) (M - 4CO)<sup>+</sup>, 636 (77) (M - 5CO)<sup>+</sup>, 608 (32) (M - 6CO)<sup>+</sup>, 580 (32) (M - 7CO)<sup>+</sup>, 552 (17) (M - 8CO)<sup>+</sup>, 524 (70) (M - 9CO)<sup>+</sup>. Anal. Calcd for  $\text{C}_{31}\text{H}_{13}\text{Cl}_2\text{Co}_3\text{O}_9$ : C, 47.91; H, 1.69; Cl 9.12. Found: C, 48.02; H, 1.81; Cl, 9.31.

**Determination of the Structure of  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(p\text{-C}_6\text{H}_4\text{Cl})_2]$  (**3**).** A black crystal of approximate orthogonal dimensions 0.3 × 0.3 × 0.4 mm<sup>3</sup> was mounted along its extended axis in a thin-walled glass capillary and was aligned and centered on a Syntex P<sub>21</sub> automated four-circle diffractometer. Determination of accurate unit-cell dimensions and the crystal's orientation matrix were performed as described previously.<sup>24</sup> This and other details of the data collection are given in Table I.

Examination of the data set revealed the systematic absences  $h0l$  for  $h + l = 2n + 1$  and  $0k0$  for  $k = 2n + 1$ , indicating the centrosymmetric monoclinic space group  $P2_1/n$ . Data were corrected for the effects of absorption (by interpolation, in  $2\theta$  and  $\phi$ , between normalized curves from  $\Psi$ -scans of six close to axial reflections) and for Lorentz and polarization factors. Symmetry equivalent data were averaged, and the resulting unique data set was placed on an approximately absolute scale by means of a Wilson plot.

The positions of the three cobalt atoms were determined by direct methods using the program MULTAN<sup>25</sup> and a subsequent

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"E map". All remaining non-hydrogen atoms were located from difference Fourier maps. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms (with hydrogen atoms included in idealized locations with  $d(\text{C-H}) = 0.95 \text{ \AA}^{26}$ ) led to convergence with<sup>27</sup>  $R_F = 3.7\%$ ,  $R_{wF} = 3.3\%$ , and  $\text{GOF} = 1.37$  for all 3434 unique data; for those 2781 data with  $|F_o| > 6\sigma(|F_o|)$ ,  $R_F = 2.5\%$ , and  $R_{wF} = 3.0\%$ . A final difference Fourier map showed no significant features. Final positional and thermal parameters are listed in Table II.

All calculations were performed on the SUNY—Buffalo modified Syntex XTL system. The function  $\sum w(|F_o| - |F_c|)^2$  was minimized during the least-squares procedure; here  $w^{-1} = [\sigma(|F_o|)]^2 + [0.01|F_o|]^2$ . The analytical forms of the neutral atoms' scattering factors were corrected for both the real ( $\Delta f'$ ) and the imaginary ( $i\Delta f''$ ) components of anomalous dispersion.<sup>28</sup>

**Determination of the Crystal Structure of  $\text{Co}_3(\text{CO})_9[\mu_3\text{-CCH}(\text{C}_{10}\text{H}_6\text{Cl})_2]$  (6).** A black, air-stable crystal of dimensions  $0.16 \times 0.32 \times 0.35 \text{ mm}^3$  was grown from a cooled ether/hexane solution. Precession photographs revealed the crystal was triclinic, and accurate unit cell parameters were determined from a least-squares fit of  $\chi$ ,  $\phi$ , and  $\delta$  for 15 reflections in the range  $21.5^\circ < 2\theta < 27.3^\circ$ . Measurements were made on a Nicolet P3 diffractometer with use of graphite-monochromated  $\text{Mo K}\alpha$  radiation. Crystal data and other numbers related to data collection appear in Table I.

Data collection over  $h$ ,  $\pm k$ , and  $\pm l$  resulted in 3620 unique reflections and 2784 observed reflections with  $I > 3\sigma(I)$ . Data were corrected for Lorentz-polarization effects, but not for absorption ( $\mu(\text{Mo K}\alpha) = 19.22 \text{ cm}^{-1}$ ).

Considering only observed data, heavy-atom positions were found by using the direct methods program SHELXS.<sup>30</sup> Subsequent

Fourier difference maps revealed the positions of all remaining atoms, including the hydrogens.<sup>31</sup> Anisotropic refinements of all non-hydrogen atoms by full-matrix least-squares methods resulted in  $R_F = 4.8\%$  and  $R_{wF} = 5.3\%$ . Final atom positions and thermal parameters appear in Table IV. Computations were carried out on the McMaster VAX 8600 system. The weighting scheme is  $w = [\sigma^2(F) + 0.004F^2]^{-1}$ . Scattering curves from ref 28 were used during refinement of the structure, and anomalous dispersion corrections from ref 29 were applied to the curves for Co and Cl. Geometry calculations were performed by using MOLGEOM.<sup>32</sup>

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**Registry No.** 3, 123882-18-8; 4, 123882-19-9; 5, 123882-17-7; 6, 123882-20-2; DDT, 50-29-3;  $\text{Co}_2(\text{CO})_8$ , 10210-68-1; Methoxychlor, 72-43-5.

**Supplementary Material Available:** Tables of anisotropic thermal parameters and bond distances and angles for molecules 3 and 6 (9 pages); listings of observed and calculated structure factors for molecules 3 and 6 (36 pages). Ordering information is given on any current masthead page.

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## Palladium-Catalyzed Oxidative Carbonylation of Ethylene and Propylene by Butyl Nitrite and Carbon Monoxide

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In the oxidative carbonylation of ethylene by carbon monoxide and butyl nitrite catalyzed by  $\text{PdCl}_2(\text{PhCN})_2$  in the presence of triphenylphosphine, the pentacoordinated tetravalent palladium complex  $\text{PdCl}_2(\text{COOBu})\text{NO}(\text{PPh}_3)$  has been isolated and has proved to be an intermediate in the catalytic cycle.

### Introduction

The catalytic oxidative carbonylation of ethylene to form difunctionalized derivatives (alkyl acrylate, dialkyl succinate, alkyl alkoxypropionate) was first described by Fenton<sup>1</sup> and Medema and van Helden.<sup>2</sup> In their exper-

iments the catalytic system used was derived directly from the Wacker oxidation catalyst, i.e.  $\text{PdCl}_2/\text{CuCl}_2$ .

As demonstrated by Heck,<sup>3</sup> in these reactions the carboalkoxy groups can be transferred to ethylene via the palladium atom by an organometallic derivative, e.g. carboalkoxymercuric chloride (and, as more recently demonstrated, by carboalkoxycopper chloride<sup>4</sup>) or can also be

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