2), 99511-67-8; **18** (isomer 1), 99511-56-5; **18** (isomer 2), 99511-68-9; **19**, 99511-57-6; **20**, 96693-32-2; **21**, 96693-33-3; **22**, 99511-58-7; **23**, 99511-59-8; **24**, 99511-61-2; **25**, 99511-62-3; **26**, 99511-63-4; **27**, 99511-64-5; **28**, 99511-65-6; **29** (isomer 1), 99511-66-7; **29** (isomer 2), 99511-69-0; $(PhP)_5$, 3376-52-1; PhC≡CMe, 673-32-5; PhC≡CSiMe$_3$, 2170-06-1; PhC≡CBu-*t*, 4250-82-2; MeC≡CBu-*t*, 999-78-0; PhC≡CH, 536-74-3; benzyl chloride, 100-44-7; 1-bromo-3-chloropropane, 109-70-6; 1-bromo-4-chlorobutane, 6940-78-9; 1-bromo-5-chloropentane, 54512-75-3.

Supplementary Material Available: Tables of hydrogen atoms coordinates (Table V), temperature factors (Table VI), distances from mean least-squares plane P_1, P_2, C_{13}, C_{14} (Table VII), and observed and calculated structure factors (Table VIII) (14 pages). Ordering information is given on any current masthead page.

Synthesis of a (Chloromethyl)cobalt(III) Carbonyl Complex, $Co(\eta^5\text{-}C_5Me_5)(CO)(CH_2Cl)Cl$, from Dichloromethane by a Photoassisted, Oxidative-Addition Reaction with $Co(\eta^5\text{-}C_5Me_5)(CO)_2$

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Presented herein are the preparation and structural characterization of $Co(\eta^5\text{-}C_5Me_5)(CO)(CH_2Cl)Cl$ which represents the first example of an isolable dichloromethane oxidative-addition product from a non-porphyrin cobalt(I) species. This (chloromethyl)cobalt(III) compound was prepared in ca. 60% yield by the photolytic reaction of $Co(\eta^5\text{-}C_5Me_5)(CO)_2$ with CH_2Cl_2 in diisopropyl ether. Its composition was deduced from IR, ^1H and ^{13}C NMR, and mass spectral analysis and confirmed from an X-ray crystallographic study. The molecular configuration expectedly conforms to the well-known three-leg piano-stool geometry with normal Co–CH$_2$Cl and Co–CO bond lengths of 1.991 (8) and 1.775 (10) Å, respectively. Of interest is that the ring carbon atoms of the pentamethylcyclopentadienyl ring exhibit a small but systematic distortion from a regular pentagonal geometry toward an "allyl–ene" geometry; the resulting C–C bond length pattern and slight ring puckering are virtually identical with those found in both $Co(\eta^5\text{-}C_5Me_5)(CO)_2$ and $Rh(\eta^5\text{-}C_5Me_5)(CO)_2$. The physical–chemical properties of this red, reasonably air-stable crystalline compound are reported together with its possible role as precursor for the synthesis of a variety of organocobalt compounds. $Co(\eta^5\text{-}C_5Me_5)(CO)(CH_2Cl)Cl$: $M_r = 307.17$; triclinic; $P\bar{1}$; $a = 7.973$ (4) Å, $b = 13.860$ (7) Å, $c = 6.767$ (3) Å, $\alpha = 95.70$ (2)°, $\beta = 110.43$ (2)°, $\gamma = 81.06$ (2)°, $V = 691.46$ at $T = 295$ K; $d_{calcd} = 1.47$ g/cm^3 for $Z = 2$. The crystal structure was solved via direct methods followed by successive Fourier syntheses and anisotropically refined by least squares (RAELS) to $R_1 = 4.05\%$ for 907 independent diffractometry data with $|F_o| > 2.5\sigma(F_o)$.

Introduction

Metal–carbon bond formation by oxidative addition of organic halides to transition-metal complexes has played a central role in many organic reactions.[1] Studies of electrophilic alkylations of low-valent cobalt complexes have attracted considerable interest, due in part to the desire to find low-cost alternatives to rhodium-based catalytic processes. While many products have been isolated from oxidative-addition reactions of iodo- and diiodoalkanes with nucleophilic cyclopentadienylcobalt(I) complexes,[2-6] relatively few species have been reported from oxidative-addition reactions of chloro- and dichloroalkanes. In particular, the synthesis of stable (chloromethyl)cobalt(III) complexes from dichloromethane reactions has been heretofore accomplished only in reactions of CH_2Cl_2 with reduced vitamin B_{12} and reduced cobalamin model compounds.[7]

In an effort to prepare (chloromethyl)cobalt(III) complexes, Hofmann and Werner[8] found that the low-temperature reaction (−50 °C) of chloroiodomethane and $Co(\eta^5\text{-}C_5H_5)(PMe_3)(CO)$ gives a mixture of $Co(\eta^5\text{-}C_5H_5)(PMe_3)(CH_2Cl)I$ and $Co(\eta^5\text{-}C_5H_5)(PMe_3)(Cl)I$ which can be separated via solubility differences. Although stable in the solid state upon being crystallized at −78 °C, the former (chloromethyl)cobalt(III) complex eliminates CH_2 in solution above −30 °C to form the latter complex. Hofmann and Werner[8] also found that the addition of an equimolar quantity of a two-electron donor (where L =

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PMe_3, $P(OMe)_3$, CNMe) to Co(η^5-C_5H_5)(PMe_3)(CH_2Cl)I produced the corresponding [Co(η^5-C_5H_5)(PMe_3)(L)(CH_2Cl)]$^+$ monocations; these cationic (chloromethyl)cobalt(III) complexes reacted at room temperature with trimethylphosphine to produce the ylidic [Co(η^5-C_5H_5)(PMe_3)(L)(CH_2PMe_3)]$^{2+}$ dications. Similarly, Klein and Hammer[9] obtained cobalt-coordinated ylidic alkylidenetrimethylphosphorane ligands by the oxidative additions of 1,1-dichloroalkanes (including CH_2Cl_2) with Co(PMe_3)$_4$. They proposed that the formation of these complexes involved hypothetical (chloroalkane)cobalt intermediates. Werner and co-workers[10-12] also prepared analogous (halogenomethyl)rhodium(III) complexes, Rh(η^5-C_5H_5)(PMe)(CH_2X)X′ (where X = X′ = Br, I; X = Cl, X′ = I); the diverse substitution chemistry found for the (iodomethyl)rhodium(III) complex illustrates how attractive such complexes are as chemical precursors for the synthesis of a large variety of organometallic compounds.

During our continuing studies of the reactivity of the (Co–Co) double-bonded Co_2(η^5-C_5Me_5)$_2$(μ_2-CO)$_2$ molecule[13] with electronically deficient metal fragments,[14] the accidental inclusion of dichloromethane in a diisopropyl ether solution of Co(η^5-C_5Me_5)$_2$(μ_2-CO)$_2$ which was photolyzed in an attempt to prepare the cobalt dimer led instead to the unexpected synthesis of Co(η^5-C_5Me_5)(CO)(CH_2Cl)Cl (1). This compound, which was characterized by IR, ^1H and ^{13}C NMR, mass spectroscopy, and an X-ray diffraction analysis, is (to our knowledge) the first example of a (chloromethyl)cobalt(III) species isolated from the oxidative addition of dichloromethane to a non-porphyrin cobalt complex.

Experimental Section

All reactions and crystallizations were performed under a nitrogen atmosphere either via standard Schlenk techniques or with a Vacuum Atmospheres glovebox. The following reagent grade solvents were dried and distilled immediately before use: CH_2Cl_2 (P_2O_5), hexane (CaH_2), tetrahydrofuran (potassium benzophenone ketyl), diisopropyl ether (potassium). The Co(η^5-C_5Me_5)(CO)$_2$ monomer was prepared as described by Rausch and Genetti[15] for a variety of mono(ring-substituted cyclopentadienyl)cobalt dicarbonyl compounds. Pentamethylcyclopentadiene was made by a published procedure.[16] All other reagents were purchased from major chemical suppliers and were used without further purification.

Preparation and Characterization of Co(η^5-C_5Me_5)(CO)(CH_2Cl)Cl (1). In a typical reaction, 2.0 g (8 mmol) of Co(η^5-C_5Me_5)(CO)$_2$ and 1.5 mL (24 mmol) of dichloromethane were added to 100 mL of diisopropyl ether in a water-cooled Pyrex photolysis vessel. Nitrogen was slowly bubbled through the solution during the reaction to facilitate removal of carbon monoxide and enhance isolation of the product.

Irradiation of the reactants for 8–12 h with a 450-W Hanovia medium-pressure Hg vapor lamp produced product 1 as a microcrystalline red solid in diisopropyl ether. After decantation of the diisopropyl ether, the red precipitate was extracted with benzene and filtered; removal of the solvent under vacuum gave 1 in ca. 60% yield. With extended photolysis the product decomposes into an insoluble green precipitate.

A ^1H NMR spectrum (benzene-d_6) of 1 obtained on a Bruker WP-270 spectrometer gave resonances at δ 1.13 (s, 15 H), and 4.62, 4.86 (2d, 1 H, diastereotopic, J = 4.6 Hz). A $^{13}C\{^1H\}$ NMR spectrum (benzene-d_6) performed on a JEOL FX-200 spectrometer exhibited three sharp resonances at δ 8.7 (s, 5 C), 42.6 (s, 1 C), and 101.4 (s, 5 C). The resonance at δ 42.6 is assigned to the methylene carbon. The failure to observe the carbonyl ligand ^{13}C NMR resonance (over a 300 ppm range) is attributed in part to quadrupolar broadening effects of the ^{59}Co nucleus ($I = {}^7/_2$).[17]

A solid-state (KBr) infrared spectrum (Beckman IR 4240 spectrophotometer) revealed a strong terminal carbonyl band at 2030 cm^{-1}. The presence of chlorine was established from an X-ray fluorescence spectrum (Applied Research Labs—SEMQ) of single crystals. The composition of 1 was deduced from its mass spectrum (AEI MS 902-C spectrometer; electron impact at 30 eV), which exhibited the parent ion peak at m/e 306, and subsequently confirmed from an X-ray crystallographic determination.

Crystal Structure of Co(η^5-C_5Me_5)(CO)(CH_2Cl)Cl (1). Suitable red-orange crystals were obtained directly from the photolytic reaction vessel. A parallelepiped-shaped needle crystal (of approximate dimensions 0.5 × 0.2 × 0.2 mm) was mounted under argon in a Lindemann glass capillary (which was flame-sealed) with the long dimension parallel with the phi axis of the goniometer. A Syntex (Nicolet) P$\bar{1}$ diffractometer with graphite-monochromatized Mo Kα radiation was utilized to obtain X-ray data at ambient temperature (23 °C). Details of crystal alignment, data collection parameters, and a listing of the crystallographic programs used are given elsewhere.[18] Axial photographs disclosed no mirror plane symmetry. A triclinic unit cell was selected with dimensions a = 7.973 (4) Å, b = 13.860 (7) Å, c = 6.767 (3) Å, α = 95.70 (2)°, β = 110.43 (2)°, and γ = 81.06 (2)°, which were derived from least-squares analysis of 15 well-centered reflections with $15 \le 2\theta \le 25°$. On the basis of V = 691.46 Å^3 and M_r = 307 for $C_{12}H_{17}CoCl_2O$, the calculated density is 1.47 g/cm^3 for Z = 2. The choice of $P\bar{1}$ was made on the basis of the centrosymmetric distributions of the normalized structure factors and was substantiated by the successful refinement of the structure; the crystallographically independent unit consists of one molecule.

Intensities were measured by the θ–2θ scan mode for four octants ($+h,\pm k,\pm l$) over a 2θ range of 3.0–40.0° with variable scan speeds of 4–24°/min and scan widths of 1.0° below $2\theta(K\alpha_1)$ to 1.0° above $2\theta(K\alpha_2)$. Three standard reflections, which were recollected after every 50 measured intensities, showed virtually no variations in their intensities (less than 2%) over the course of data acquisition. Correction of the observed data for absorption effects was not performed due to the relatively small linear absorption coefficient (μ = 15.2 cm^{-1} for Mo Kα radiation) and uniform crystal dimensions around the phi axis of the goniostat. Data reduction of the 1176 collected reflections gave 907 independent reflections with $F_o > 2.5\sigma(F_o)$.

The crystal structure was solved via MULTAN[19] followed by successive Fourier syntheses which yielded the positions of all non-hydrogen atoms. Full-matrix least-squares refinement with RAELS[20] was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Since reliable coordinates for the methyl and methylene hydrogen atoms were not revealed from difference maps, idealized hydrogen positions were calculated from MIRAGE[21] and included in the refinement via the following model. Each hydrogen atom was arbitrarily assigned an identical isotropic temperature factor which was not varied. Likewise, the idealized tetrahedral positions of the two methylene hydrogen atoms were fixed. For each methyl substituent an idealized sixfold set of half-weighted hydrogen positions along the C(ring)–CH_3 line (corresponding to two twofold-related orientations of idealized

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Table I. Positional Parameters for $Co(\eta^5-C_5Me_5)(CH_2Cl)(CO)Cl$

atom	*x*	*y*	*z*
Co1	0.12205 (12)	0.25988 (7)	0.03835 (15)
Cl1	−0.12833 (24)	0.33005 (14)	0.10352 (33)
Cl2	0.32322 (36)	0.07128 (19)	0.31047 (41)
O1	0.3688 (9)	0.33935 (58)	0.4220 (11)
C1	0.2736 (11)	0.30746 (67)	0.2753 (14)
C11	0.2976 (9)	0.21918 (54)	0.1250 (11)
C12	0.1482 (9)	0.16557 (53)	0.2165 (10)
C13	0.0080 (9)	0.23442 (57)	0.2868 (11)
C14	0.0453 (9)	0.33141 (54)	0.2513 (11)
C15	0.2325 (9)	0.32183 (54)	0.1536 (11)
C21	0.4914 (9)	0.17462 (57)	0.0438 (12)
C22	0.1591 (10)	0.05715 (59)	0.2412 (13)
C23	0.1958 (9)	0.21068 (62)	0.3954 (13)
C24	0.0797 (10)	0.42305 (57)	0.3133 (12)
C25	0.3483 (10)	0.40324 (57)	0.0945 (13)
C2	0.1123 (10)	0.14733 (62)	0.1936 (12)

Table II. Selected Interatomic Distances and Angles for $C(\eta^5-C_5Me_5)(CH_2Cl)(CO)Cl$ (1)

Co–C11	2.053 (7)	C11–C12	1.422 (9)
Co–C12	2.109 (7)	C12–C13	1.413 (9)
Co–C13	2.100 (7)	C13–C14	1.445 (10)
Co–C14	2.135 (7)	C14–C15	1.396 (9)
Co–C15	2.111 (7)	C15–C11	1.444 (9)
	2.102 (av)		1.424 (av)
Co–ring (centroid)	1.71	C11–C21	1.499 (9)
Co–C1	1.775 (10)	C12–C22	1.488 (10)
Co–C2	1.991 (8)	C13–C23	1.492 (10)
Co–Cl1	2.248 (2)	C14–C24	1.484 (10)
C1–O1	1.117 (9)	C15–C25	1.504 (10)
C2–Cl2	1.803 (8)		1.493 (av)
B. Intramolecular Angles (deg)			
Co–C2–Cl2	116.3 (4)	Cl1–Co–C2	86.4 (2)
Co–C1–O1	178.3 (8)	Cl1–Co–C1	94.9 (3)
		C1–Co–C2	89.3 (4)
C11–C12–C13	107.2 (6)	C15–C11–C21	126.3 (6)
C12–C13–C14	108.8 (6)	C11–C12–C22	125.5 (7)
C13–C14–C15	107.6 (6)	C12–C13–C23	125.7 (7)
C14–C15–C11	108.1 (6)	C13–C14–C24	125.0 (7)
C15–C11–C12	108.2 (6)	C14–C15–C25	126.4 (7)
	107.9 (av)		125.8 (av)

hydrogen coordinates) was obtained and held constant. In order to permit the refinement of the twofold-related orientations, the occupancy factors (initially 0.5) for the 30 methyl hydrogen positions were coupled with slack constraints involving equal and opposite change cards. This allowed the least-squares refinement to determine which of the twofold-related methyl hydrogen orientations was preferred. Full-matrix least-squares refinement of the least-squares model converged at $R_1(F) = 4.05\%$ and $R_2(F^2) = 4.98\%$[22-24] with no parameter shift-to-esd ratio being greater than 0.01. The standard goodness-of-fit was 1.33, while the data-to-parameter ratio was 907/150 = 6/1. Since the refined occupancy factors for the ten sets of methyl hydrogen positions converged to values of range 0.4–0.6, the refinement indicated no preferred orientation of the methyl hydrogen atoms in the independent pentamethylcyclopentadienyl ring. A final difference electron density map exhibited no unusual features. Atomic coordinates from the last cycle of least-squares refinement are given for the non-hydrogen atoms in Table I, while selected interatomic distances and bond angles are given in Table II. The positional parameters for the hydrogen atoms, the thermal parameters for all atoms, and a listing of observed and calculated structure factor amplitudes are available as supplementary material.

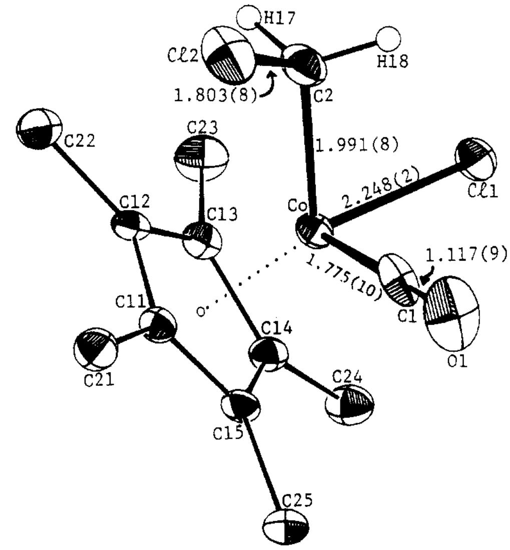

Figure 1. Configuration of the $Co(\eta^5-C_5Me_5)(CO)(CH_2Cl)Cl$ molecule of crystallographic C_1—1 site symmetry. Thermal ellipsoids are scaled to represent 20% probability surfaces.

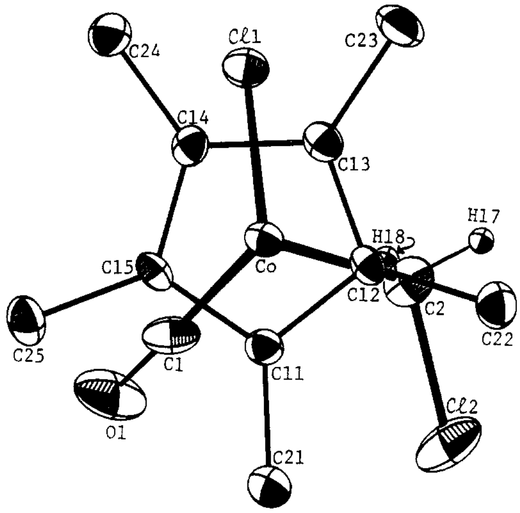

Figure 2. View of the $Co(\eta^5-C_5Me_5)(CO)(CH_2Cl)Cl$ molecule perpendicular to the mean plane of the C_5Me_5 ring showing its orientation relative to $Co(CO)(CH_2Cl)Cl$ fragment.

Results and Discussion

Crystal and Molecular Structure of $Co(\eta^5-C_5Me_5)(CO)(CH_2Cl)Cl$ (1). (a) Overall Description. The crystal structure of 1 consists of discrete molecules well separated from one another; the shortest intermolecular contacts exceed the sums of appropriate van der Waals atomic radii. Figure 1 shows that the molecular configuration expectedly conforms to the well-known three-leg piano-stool $M(\eta^5-C_5R_5)L_3$ type of complex, as exemplified by $Mn(\eta^5-C_5H_5)(CO)_3$[25] and $Rh(\eta^5-C_5H_5)(CO)(CF_2CF_3)I$.[26] The formally tridentate C_5Me_5 ligand and other three monodentate ligands occupy an octahe-

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[22] The unweighted and weighted discrepancy factors used are $R_1(F) = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100$ and $R_2(F^2) = [\sum w_i||F_o|^2 - |F_c|^2|^2/\sum w_i|F_o|^4]^{1/2} \times 100$. All least-squares refinements were based on the minimization of $\sum w_i||F_o|^2 - |F_c|^2|^2$ with individual weights of $w_i = 1/\sigma^2(F_o)$ assigned on the basis of the estimated standard deviations of the observed structure factors. The standard deviation of an observation of unit weight "goodness-of-fit") is defined by $[\sum w_i||F_o| - |F_c||^2/(m - n)]^{1/2}$.

[23] The scattering factor tables used are those of Cromer and Mann[24a] for the hydrogen atoms and those of Stewart et al.[24b] for the hydrogen atoms. Real and imaginary corrections for anomalous dispersion[24c] were included in the structure factor calculations.

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dral-like arrangement about the resulting chiral d^6 Co(III) center. The centrosymmetric symmetry necessitates a racemic mixture in the solid state.

(b) The Pentamethylcyclopentadienyl Ligand. The reasonably small thermal ellipsoids of both the ring carbon and methyl carbon atoms (Figure 2) are presumed to be due to the marked damping effect of the methyl substituents on the librational motion of the ring carbon atoms. The C_5Me_5 ligand is symmetrically disposed relative to the Co(CO)(CH$_2$Cl)Cl fragment such that one ring carbon C12 and its attached CH_3 substituent C22 lie directly above the methylene carbon C2. A pseudo mirror plane passing through the cobalt and these three carbon atoms bisects the other four ring carbon atoms to give C11 and C13 as one mirror-related pair and C14 and C15 as the other pair.

An examination of the C(ring)–C(ring) bond-length pattern and the perpendicular displacements of the ring carbon atoms from their mean plane reveals a small, but yet systematic variation of the ring from a regular pentagonal geometry toward an "allyl–ene" geometry with a slight bending distortion about the two terminal allylic ring carbon atoms (C11 and C13) away from the cobalt atom. Although on the borderline of statistical significance, the observed ring deformation in 1 is remarkably similar to that found for the ring carbons in Co(η^5-C$_5$Me$_5$)(CO)$_2$[18] (2), in which an electronically induced distortion of the cyclopentadienyl ring toward an "allyl–ene" geometry was ascribed to its coordination with a metal atom which has a noncylindrically symmetric distribution of bonding orbitals.[18] The observed pattern of C(ring)–C(ring) distances in 1 (with the corresponding distances in 2 given in parentheses) is attributed to two adjacent "allylic" C11–C12 and C12–C13 bonds of intermediate lengths 1.422 (9) and 1.413 (9) Å (vs. 1.407 (6) and 1.414 (6) Å in 2) separated from the "ethylenic" C14–C15 bond of shortest length 1.396 (9) Å (vs. 1.392 (6) Å in 2) by two longer C11–C15 and C13–C14 bonds of lengths 1.444 (9) and 1.445 (10) Å (vs. 1.445 (6) and 1.447 (6) Å in 2). Evidence for an analogous slight symmetrical puckering of the ring carbons in 1 and 2 from planarity is given by the equivalent C11 and C13 atoms in 1 deviating from the mean ring plane by 0.020 and 0.016 Å (vs. 0.016 and 0.017 Å in 2) toward the cobalt atom in contrast to the unique C12 atom deviating by 0.022 Å (vs. 0.021 Å in 2) and the equivalent C14 and C15 atoms deviating by 0.004 and 0.010 Å (vs. 0.006 and 0.007 in 2) away from the cobalt atom. A virtually identical distortion (including a similar ring puckering) in the pentamethylcyclopentadienyl ring of Ru(η^5-C$_5$Me$_5$)(CO)$_2$ was recently reported by Lichtenberger et al.[27] As originally presented for 2, the slight ring puckering and small systematic variation of the C(ring)–C(ring) bond lengths in 1 from fivefold symmetry toward a localized "allyl–ene" configuration are likewise ascribed to an electronic effect involving its noncylindrical bonding interaction with the asymmetrical Co(CO)(CH$_2$Cl)Cl fragment by which the doubly degenerate e_1 orbitals become nonequivalent in energy. A qualitative description of the net structure-bonding consequences of this removal of degeneracy of the e_1 orbitals in Co(η^5-C$_5$H$_5$)(CO)$_2$ was presented by Byers and Dahl.[18] Their interpretation is in general agreement with a detailed electronic analysis of M(η^5-C$_5$R$_5$)(CO)$_2$ type complexes (M = Co, Rh; R = H, Me) put forth later by Lichtenberger et al.[27] from their use of the nonparameterized Fenske–Hall MO model[28] on an idealized Rh(η^5-C$_5$H$_5$)(CO)$_2$ molecule.[29,30]

As in the case of Co(η^5-C$_5$Me$_5$)(CO)$_2$ (2), the five methyl carbon substituents in 1 are all bent back from the mean inner-ring plane away from the cobalt atom. The observed variations in the vertical displacements from the mean plane for 1 are not unlike the corresponding ones (whose values are enclosed in parentheses) found in 2–viz., 0.15 Å for C22 (vs. 0.13 Å in 2), 0.03 and 0.08 Å for C24 and C25 (vs. 0.09 Å for both carbon atoms in 2), and 0.02 and 0.09 Å for C23 and C21 (vs. 0.07 and 0.09 Å in 2). In 2, this small but definite bending back of the methyl substituents was attributed (in the presumed absence of steric effects) "to a partial breakdown of the bonding orthogonality of the ring carbon atoms upon interaction of the Co(CO)$_2$ fragment with the charge density on only one side of the ring".[18] In 1 intramolecular steric interactions between the CH$_2$Cl ligand and the methyl C21 and C22 atoms may contribute significantly to their out-of-plane displacements. A similar deformation pattern of the methyl carbon atoms was found[27] in Rh(η^5-C$_5$Me$_5$)(CO)$_2$ and was interpreted[27] from electronic considerations to indicate the extent of rehybridization of the different ring carbon atoms. Considerably larger methyl carbon deformations observed in pentamethylcyclopentadienyl ligands of other transition-metal complexes were readily attributed to intramolecular steric crowding.[31]

In contrast to 2, the Co–C(ring) distances in 1 do not significantly reflect the C_5Me_5 ring deformation. This is not surprising in light of the expected different bonding influence of the asymmetrical Co(CO)(CH$_2$Cl)Cl fragment compared to that of the Co(CO)$_2$ fragment. Four of the five Co–C(ring) distances in 1 vary between 2.100 (7) and 2.135 (7) Å with the other Co–C(ring) distance involving the C11 atom trans to the Co–Cl bond having a smaller value of 2.053 (7) Å. These values and the Co–ring(centroid) distance of 1.71 Å are in good agreement with the Co–C(ring) distances determined in Co(η^5-C$_5$Me$_5$)(CO)$_2$[18] (of range 2.062 (4)–2.105 (4) Å; Co–ring(centroid) = 1.70 Å) and in Co$_2$(η^5-C$_5$Me$_5$)$_2$(μ_2-CO)$_2$[13] (of range 2.046 (11)–2.126 (11) Å; Co–ring(centroid) = 1.70 Å).

(c) The Co(CO)(CH$_2$Cl)Cl Fragment. The Co–C2 bond length of 1.991 (8) Å for the chloromethyl ligand is within the expected range found for Co–C(alkyl) bonds in other cobalt complexes—e.g., Co$_2$(η^5-C$_5$H$_5$)$_2$(μ_2-CO)$_2$(μ_2-C$_3$H$_6$)[32] (2.038 (4) and 2.044 (4) Å), Co(PMe$_3$)$_2$(CH$_3$)$_2$(CH$_2$P(Me)$_2$CH$_2$)[33] (2.050 Å for the two mirror-related Co–CH$_3$ bonds and 2.061 Å for the two independent Co–CH$_2$ bonds of the chelating dimethylphosphoniumbis(methylide) ligand), and Co(3-F-Salen)(OH$_2$)(CH$_2$C(O)Me)[34] (2.01 (1) Å).

The Co–CO bond length of 1.775 (10) Å is 0.22 Å shorter than the Co–CH$_2$Cl bond length. Although it is significantly longer than the Co–CO bond lengths of 1.724 (5) and 1.732 (5) Å in Co(η^5-C$_5$Me$_5$)(CO)$_2$, its value is com-

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[29] A comprehensive investigation of the core and valence ionizations of the M(η^5-C$_5$R$_5$)(CO)$_2$ molecules (M = Co, Rh; R = H, Me) was also carried out by Lichtenberger and co-workers[30] in order to reveal the important electronic interactions in these complexes. The data, which exhibit major differences between the valence ionizations of these d^8 Co(I) and Rh(I) complexes, were interpreted in terms of excited-state effects in the positive ions; resulting implications for the comparative stability and chemical behavior of the cobalt and rhodium complexes were discussed.

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parable to those found in a number of other cobalt carbonyl complexes. The C–O distance of 1.117 (9) Å is on the short side of the expected bond length range for terminal carbonyl ligands. The infrared carbonyl stretching frequency of 2030 cm^{-1}, which is unusually high for a carbonyl ligand terminally bound to a cobalt atom, is rationalized in terms of a relatively small $d\pi$[Co(III)] to π^*(CO) back-bonding interaction.

The Co–Cl and C–Cl bond lengths of 2.248 (2) and 1.803 (8) Å, respectively, are also normal. The three angles between the carbonyl, chloride, and chloromethyl ligands are all within 5° of a regular value of 90°.

Discussion of Synthesis, Overall Significance, and Physical Properties of Co(η^5-C$_5$Me$_5$)(CH$_2$Cl)(CO)Cl (1). The markedly different reactivities exhibited by the basic d^8 Co(I) Co(η^5-C$_5$R$_5$)LL′ complexes (where L and L′ denote two-electron donors or an equivalent chelating ligand) with electrophilic organic halides demonstrate the subtle steric and electronic interrelationships that govern oxidative-addition chemistry.[6,10–12] For example, the exchange of a PMe$_3$ ligand for a carbonyl ligand in Co(η^5-C$_5$H$_5$)(CO)$_2$ dramatically alters the reactivity of this molecule toward methyl iodide.[6] Replacement of both carbonyl ligands with the strongly donating PMe$_3$ ligands results in a complex which is unstable in dichloromethane.[6]

While a number of stable complexes of transition metals containing M′–CH$_2$Cl bonds (where M′ denotes Mo(η^5-C$_5$H$_5$)(CO)$_3$, W(η^5-C$_5$H$_5$)(CO)$_3$, or Fe(η^5-C$_5$H$_5$)(CO)$_2$[35,36]) are known, there are relatively few cobalt complexes containing Co–CH$_2$Cl bonds.[6–8] To our knowledge, 1 is the first example of a dichloromethane oxidative-addition product isolated from a non-porphyrin cobalt(I) complex. Produced by the photolytic reaction of CH$_2$Cl$_2$ with Co(η^5-C$_5$Me$_5$)(CO)$_2$ in diisopropyl ether, 1 is obtained (in good yield) as a pure red crystalline solid which precipitates directly from the diisopropyl ether. The success of this preparation was found to be critically dependent upon the solvent choice. Attempts to prepare the complex in alternative solvents (such as THF and CH$_2$Cl$_2$) were unsuccessful. The insolubility of 1 in diisopropyl ether apparently prevents its photodegradation. When extended photolysis times were used, the red crystalline solid gradually decomposed to a green insoluble precipitate.[37,38] Although the mechanism of this reaction is not known, it is presumed that the oxidative addition could likely proceed by a free radial pathway with diisopropyl ether implicated in a radical chain reaction.

Reasonably air-stable as a dry crystalline solid, solutions of 1 decomposed when brought in contact with moist air. Although reasonably stable in ordinary organic solvents (CH$_2$Cl$_2$, benzene), solutions of 1 in acetonitrile displayed a variety of colors with eventual deposition of a precipitate occurring over several days. Sequential ^{1}H NMR spectra of 1 in acetonitrile-d_3 changed from the initially simple spectrum analogous to that observed for 1 in benzene-d_6 (vide supra) to one of extreme complexity within a matter of minutes.

While the instability of 1 in such a polar solvent is not unusual,[38] the facile reactivity of 1 with acetonitrile as a nucleophile may involve three potentially labile substitution sites on 1—viz., the carbonyl ligand, the cobalt-attached chlorine atom, and the methyl-attached chlorine atom. Extensive studies by Werner and co-workers[6,10,11] on the closely related Rh(η^5-C$_5$H$_5$)(PMe$_3$)(CH$_2$I)I demonstrated that nucleophilic substitution of the iodomethyl iodine atom can selectively occur to give stable ylidic [Rh(η^5-C$_5$H$_5$)(PMe$_3$)(CH$_2$L)I]$^+$ monocations (where L = PPh$_3$, AsPh$_3$, P(i-Pr$_3$), SMe$_2$, NEt$_3$). In reactions with methoxide or methyl mercaptide anions, the isolated products were the neutral monosubstituted Rh(η^5-C$_5$H$_5$)(PMe$_3$)(CH$_2$OMe)I or the disubstituted Rh(η^5-C$_5$H$_5$)(PMe$_3$)(CH$_2$SMe)(SMe), respectively.

Of particular interest is the dramatic difference between the stability in solution of the Co–CH$_2$Cl bond in Co(η^5-C$_5$Me$_5$)(CO)(CH$_2$Cl)Cl (1) and that in Co(η^5-C$_5$H$_5$)(PMe$_3$)(CH$_2$Cl)I. Whereas the latter complex, prepared by reaction of Co(η^5-C$_5$H$_5$)(PMe$_3$)(CO) with CH$_2$ClI, is stable in crystalline form but only observed in solution at temperatures below −30 °C (above which elimination of CH$_2$ occurred to give Co(η^5-C$_5$H$_5$)(PMe$_3$)(Cl)I), the former complex 1 is not only relatively air stable as a microcrystalline solid but also stable at room temperature in noncoordinating solvents (vide supra). This marked difference in stability emphasizes the considerable increase in electron-donating ability of a C$_5$Me$_5$ ligand vs. that of a C$_5$H$_5$ ligand and the important influence that such an exchange can have with respect to the Co(III)–CH$_2$Cl interaction in 1.

In addition to exploring the chemical reactivity of the above-mentioned three possible substitution sites on 1 by carrying out reactions similar to those performed by Werner and co-workers[6,10,11] on Rh(η^5-C$_5$H$_5$)(PMe$_3$)(CH$_2$I)I, other potentially intriguing options include possible nucleophilic chloride substitution with organometallic anions which may provide a direct route to methylene-bridged heterometallic complexes and possible abstraction of chloride (or hydride) to yield a cobalt–carbene complex. The reaction chemistry of 1 has been briefly examined. In a room-temperature photolytic reaction of 1 with PMe$_3$ in toluene, the two isolated products were formulated to be Co(η^5-C$_5$Me$_5$)(PMe$_3$)(CH$_2$Cl)Cl and Co(η^5-C$_5$Me$_5$)(PMe$_3$)Cl$_2$ from ^{1}NMR and IR spectra. Analogues of these (pentamethylcyclopentadienyl)cobalt compounds have been previously isolated by Werner et al.;[39] these included the [Co(η^5-C$_5$Me$_5$)(PMe$_3$)$_2$I]$^+$ monocation (obtained as the [PF$_6$]$^-$ salt) and Co(η^5-C$_5$Me$_5$)(PMe$_3$)(COMe)I which were prepared by reactions of methyl iodide with Co(η^5-C$_5$Me$_5$)(PMe$_3$)$_2$ and Co(η^5-C$_5$Me$_5$)(PMe$_3$)(CO), respectively. Efforts to obtain a cobalt–carbene complex by reactions of both 1 and Co(η^5-C$_5$Me$_5$)(PMe$_3$)(CH$_2$Cl)Cl with silver salts were unsuccessful.

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Registry No. 1, 99828-84-9; Co(η^5-C$_5$Me$_5$)(CO)$_2$, 12129-77-0; CH$_2$Cl$_2$, 75-09-2; Co(η^5-C$_5$Me$_5$)(PMe$_3$)(CH$_2$Cl)Cl, 99828-85-0; Co(η^5-C$_5$Me$_5$)(PMe$_3$)Cl$_2$, 99828-86-1.

Supplementary Material Available: Tables listing the anisotropic thermal parameters for the non-hydrogen atoms, atomic parameters for the hydrogen atoms, and observed and calculated structure factor amplitudes for Co(η^5-C$_5$Me$_5$)(CO)(CH$_2$Cl)Cl (8 pages). Ordering information is given on any current masthead page.

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