A Sandwich Complex Containing Trimethylenemethane, (η⁴-2-Methylene-1,3-propanediyl)(η⁵-2,4-cyclopentadien-1-yl)-cobalt

R. Scott Lokey and Nancy S. Mills*

Department of Chemistry, Trinity University, San Antonio, Texas

Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, Delaware 19716

(η⁴-2-Methylene-1,3-propanediyl)(η⁵-2,4-cyclopentadien-1-yl)cobalt (TMMCoCp) was prepared by reaction of dilithioisobutylene with (η⁵-2,4-cyclopentadien-1-yl)(triphenylphosphine)cobalt diiodide. TMMCoCp was characterized spectroscopically (^{1}H and ^{13}C NMR, IR, mass, and UV/vis spectroscopy) and by a crystal structure (monoclinic, $P2_1/n$, $a = 6.057$ (2) Å, $b = 7.890$ (1) Å, $c = 8.813$ (2) Å, $\beta = 93.04$ (2)°, $V = 415.3$ (2) Å³, $Z = 2$; for 553 observed reflections, $R_F = 5.27\%$.) The complex, which is isoelectronic with (η⁴-1,3-cyclobutadiene)(η⁵-2,4-cyclopentadien-1-yl)cobalt, is the first neutral trimethylenemethane complex of cobalt and is the simplest trimethylenemethane mixed-sandwich complex reported to date. Cyclic voltammetry of TMMCoCp in acetonitrile showed a single irreversible wave on the anodic scan. Initial examination of its chemistry revealed that metalation with *n*-butyllithium/TMEDA occurred exclusively on the trimethylenemethane ligand.

We have been involved for some time with the question of Y-aromaticity[1] in delocalized dilithiated hydrocarbons.[2] The ease of preparation of many of these species suggested that they might be useful synthetic precursors to novel molecules, and we have been investigating their applicability in the synthesis of organometallic compounds. As shown in Scheme I, we have considered dianions such as the dianion of isobutylene as a 6π-electron donor capable of reaction with metal dihalides to give either metallocyclobutanes or trimethylenemethane compounds, depending on the metal dihalide and its ligands. As further guidance, we considered that cyclobutadiene transition-metal complexes might serve as models for potentially successful syntheses with delocalized cross-conjugated dianions. One might consider those complexes as containing dianionic 6π-electron cyclobutadiene ligands, aromatic in the Hückel sense, which would be isoelectronic with the potentially Y-aromatic 6π-electron dianion of isobutylene.

We now report the successful preparation of (η⁴-2-methylene-1,3-propanediyl)(η⁵-2,4-cyclopentadien-1-yl)-cobalt (TMMCoCp) from reaction of the dianion of isobutylene prepared as previously reported[2] by dimetalation of isobutylene with *n*-butyllithium/*N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA), with 1 molar equiv of (η⁵-2,4-cyclopentadien-1-yl)diiodo(triphenylphosphine)cobalt.[3] This represents the first report of a neutral trimethylenemethane complex of cobalt as well as the preparation of the simplest mixed-sandwich trimethylenemethane complex. The reaction, run in THF at −78 °C, resulted in the formation of TMMCoCp as reddish brown, air-stable crystals in 18% (isolated) yield. The majority of the reaction mixture was pentane-insoluble and contained paramagnetic materials. We believe that reduction via electron transfer from the isobutylene dianion to the cobalt starting material is responsible for the paramagnetic

Scheme I
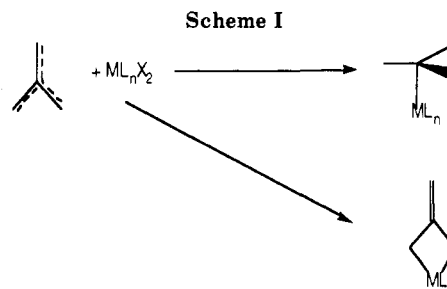
material. We have also reacted the dianion of isobutylene with carbonyl(η⁵-2,4-cyclopentadien-1-yl)diiodocobalt[3] which results in the synthesis of TMMCoCp in similar yield.

TMMCoCp was characterized spectroscopically and its identity confirmed by a crystal structure. The 300-MHz-^{1}H NMR spectrum in C_6D_6 showed two singlets, at 4.73 and 1.79 ppm, with integration respectively of 5:6 protons. The analogous (η⁴-1,3-cyclobutanediene)(η⁵-2,4-cyclopentadien-1-yl)cobalt (CbCoCp) showed a resonance at 4.86 ppm for the cyclopentadienyl protons as well as a resonance at 3.61 ppm for the equivalent cyclobutadiene protons.[4] The ^{13}C NMR spectrum in C_6D_6 of TMMCoCp showed resonances at 81.76 ppm from TMS for the cyclopentadienyl carbons (compared with 83.4 ppm for the cyclopentadienyl carbons of (η⁴-1,2,3,4-tetraphenyl-1,3-cyclobutadiene)(η⁵-2,4-cyclopentadien-1-yl)cobalt[5]), at 44.99 ppm for the trimethylenemethane methylene carbons, and at 112.25 ppm for the central carbon of the trimethylenemethane ligand. GC/mass spectral analysis showed three major fragmentations: m/charge 178 (51% abundance) for the parent ion, 124 (100%) from loss of the TMM ligand, and 59 (70%) from loss of the cyclopentadienyl ligand. This fragmentation may be compared to that of the isoelectronic CbCoCp[4] in which the major

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(6) The UV/vis spectrum in pentane shows maxima at 219, 257, and 440 nm (ε = 17 141, 14 110, and 876). The crystals are thermochromic, turning yellow at −196 °C from their reddish-brown coloration at room temperature.

Table I. Principal Infrared Absorptions of Ferrocene, (Trimethylenemethane)(cyclopentadienyl)cobalt, (Trimethylenemethane)iron Tricarbonyl, and (Cyclobutane)(cyclopentadienyl)cobalt

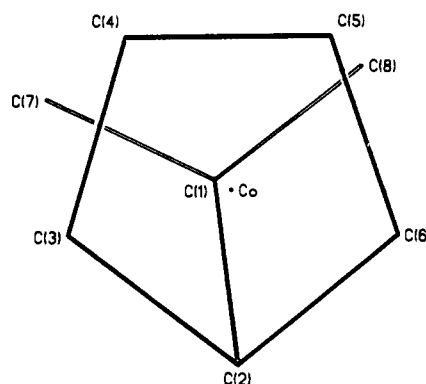|												
$Cp_2Fe^{a,b}$	3084					1407		1101	999			787
$CpCo(TMM)^a$	3113	3067	2997	1477	1442	1415	1385	1107	1000	979	805	784
$(CO)_3FeTMM^c$		3067	3000	1478	1456		1349			989	803	
$CpCoCB^a$	3090	3060				1408		1101	997			

[a] Determined in KBr. [b] Rosenblum, M.; North, B.; Wells, D.; Giering, W. P. *J. Am. Chem. Soc.* **1972**, *94*, 1239. [c] Emerson, G. F.; Ehrlich, K.; Giering, W. P.; Lauterbur, W. P. *J. Am. Chem. Soc.* **1966**, *88*, 3172.
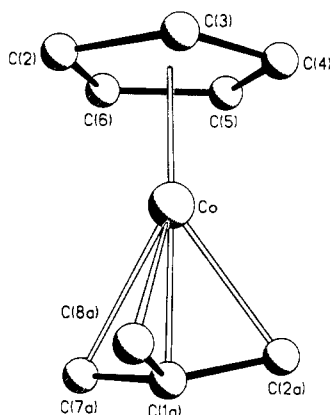
Figure 1. The molecular structure of $CpCo(C_4H_6)$ constructed from an end-for-end inversionally disordered model: Co–Cp(cent), 1.584 (8); Co–C(1), 1.891 (8); Co–C(2), 2.052 (8); Co–C(7) 2.251 (9); Co–C(8), 2.048 (7); C(1)–C(2), 1.325 (11); C(1)–C(7), 1.321 (11); C(1)–C(8), 1.330 (11) Å.

Figure 2. A view of the disorder model used in the refinement of $CpCo(C_4H_6)$ revealing the superimposition of the Cp and C_4H_6 ligands; C(2) is shared by both.

fragmentations, in addition to the parent molecular ion, were those from loss of C_2H_2 and C_4H_4 fragments, presumably from the cyclobutadiene ligand. The infrared spectral data are summarized in Table I; the spectrum of TMMCoCp is therefore very nearly a composite of the spectra of ferrocene and, excluding the carbonyl bands, of tricarbonyl(η^4-2-methylene-1,3-propanediyl)iron ((trimethylenemethane)iron tricarbonyl).[5] The crystal structure of TMMCoCp unambiguously establishes the presence of the TMM ligand despite the presence of end-for-end disorder; the Cp and TMM planes are superimposed by inversion at the Co atom (Figures 1 and 2). The unit-cell is isomorphous with cobaltacene.[7] The TMM ligand is pyramidal with the central carbon atom directed away from the metal atom as has been previously observed in TMM complexes of Cr,[8] Fe,[9] Mo,[10] and Ir.[11]

Because of the physical similarities (solubility in most organic solvents, air stability, high relative volatility)[12] and electronic similarities between CbCoCp and TMMCoCp, we have begun to investigate similarities in reactivity. Oxidation of TMMCoCp by cyclic voltammetry suggested that it should prove to be fairly unstable under the conditions for electrophilic aromatic substitution, as was true for CbCoCp.[12] TMMCoCp in acetonitrile with tetraethylammonium perchlorate as supporting electrolyte exhibited one irreversible one-electron wave on the anodic scan at 564 mV relative to the saturated calomel electrode. Ferrocene exhibits a well-behaved reversible one-electron wave in acetonitrile on the anodic scan at 370 mV relative to the saturated calomel electrode while CbCoCp shows

two irreversible waves, the first of which corresponded to the transfer of two electrons, on the anodic scan, at 790 and 1140 mV.[12] The Friedel–Crafts acylation that proceeds readily with ferrocene gives low (<5%) yields of acylated products with CbCoCp. We have therefore begun the investigation of the reaction chemistry of TMMCoCp by reacting it with n-butyllithium/TMEDA. The metalation was performed by four additions of 0.5 equiv of the metalating system to TMMCoCp in C_6D_6 and was monitored by ¹H NMR spectroscopy. The initial metalation occurred exclusively on the TMM ligand, within the sensitivity of the instrument. With addition of 0.50 equiv of the metalating system, the singlet at 1.79 ppm decreased with respect to the cyclopentadienyl protons. The cyclopentadienyl region was essentially unchanged. Upon addition of the second 0.50 equiv of metalating system, the signal for the unmetalated TMM protons disappeared.

Addition of a third aliquot of base resulted in deterioration of the cyclopentadienyl region of the spectrum. While a singlet still remained at 4.73 ppm in the cyclopentadienyl region, a multiplet centered at 4.95 ppm had begun to appear. Closer examination of the multiplet revealed three poorly resolved triplets, at 5.01, 4.95, and 4.90 ppm. The ratio of the peaks was 1:2:1 and an estimate of the coupling constants gave $J \sim$ 2–3 H. Metalation of the ring would be expected to give two triplets for the two protons adjacent to the lithiated carbon and the two protons further away. The 1:2:1 set of triplets may reflect two different conformations on the dilithiated TMMCoCp. Dilithiated ferrocene shows two triplets (J = 1.25 Hz) at 4.36 and 4.91 ppm, downfield of the unmetalated cyclopentadienyl ring.[13]

Addition of the fourth aliquot of base (2.0 equiv) caused a further increase in the area of the three multiplets at the expense of the Cp singlet. The change in the areas of the two sets of peaks was only slight, showing that the second metalation of TMMCoCp was significantly slower than the first. Because of the complexity of the upfield region of the spectrum which contains peaks for metalating system

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Table II. Crystal Data for TMMCoCp

(a) Crystal Parameters

formula	$C_9H_{10}Co$	V, $Å^3$	415.3 (2)
cryst system	monoclinic	Z	2
space group	$P2_1/n$	D(calcd), g cm^{-3}	1.424
a, Å	6.057 (2)	μ(Mo Kα), cm^{-1}	19.6
b, Å	7.890 (1)	T, K	293
c, Å	8.813 (2)	color	red
β, deg	93.04 (2)	size, mm	0.28 × 0.31 × 0.36

(b) Data Collection

diffractometer	Nicolet R3M	indpdt rflns	952
radiation	Mo Kα (0.710 73 Å)	$R(I)$, %	1.4
monochromator	graphite	obsd rflns ($5\sigma(F_o)$)	553
scan limits, deg	$4 \leq 2\theta \leq 55$	std rflns	3 std/197 rflns
rflns collected	1085	variation in stds, %	±1

(c) Refinement

$R(F)$, %	5.27	$\Delta(\rho)$, e Å^{-3}	0.40
$R(wF)$, %	6.31	Δ/σ (final)	0.188
GOF	1.957	N_0/N_v	7.0

as well as its hexane solvent, we cannot assign peaks to the metalated TMM ligand.

We are continuing to probe the chemistry of TMMCoCp as well as to explore the analogous reaction of the dianion of isobutylene with other members of the cobalt triad, such as (η^5-1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)di-iodo(triphenylphosphine)rhodium.

Experimental Section

NMR spectra (chemical shifts in parts per million from internal Me$_4$Si for ^{1}H and ^{13}C) were recorded on a Varian VXR-300 NMR spectrometer. Mass spectra were obtained on a Hewlett-Packard 5995C GC/MS. All reactions were carried out under argon by using standard Schlenk and vacuum-line techniques. Tetrahydrofuran, N,N,N',N'-tetramethylethylenediamine (TMEDA), and benzene were distilled from the benzophenone ketyl under argon. Pentane was distilled frm P$_2$O$_5$ under argon. n-Butyllithium was obtained from Fluka. Isobutylene was obtained from Matheson. (η^5-2,4-Cyclopentadien-1-yl)diiodo(triphenylphosphine)cobalt was prepared by literature methods[3] from dicarbonyl(η^5-2,4-cyclopentadien-1-yl)cobalt purchased from Alfa or from bis(μ-carbonyl)hexacarbonyldicobalt purchased from Aldrich.

Preparation of (C$_4$H$_6$)Li$_2$(TMEDA)$_2$. To a septum-capped test tube was added 6.6 mL (10.58 mmol) of n-butyllithium and 1.6 mL (10.58 mmol) of TMEDA, followed by the addition of 0.5 mL (5.29 mmol) of condensed isobutylene. The reaction mixture was allowed to stand for 3 days and was prepared for reaction with the transition-metal halide by removal of the supernatant under pressure. The precipitate was washed with pentane, dried under a flow of argon, weighed while still in the test tube, and dissolved in 5 mL of THF. The yield was determined by difference from the weight of the empty test tube, and either the THF solution of dilithiated isobutylene or an appropriate aliquot of it was used in the reaction with the transition-metal halide.

Preparation of TMMCoCp. To 1.27 g of CpCo(PPh$_3$)I$_2$ (1.99 mmol) in 45 mL of THF at −78 °C were added 0.598 g of (C$_4$H$_6$)-Li$_2$(TMEDA)$_2$ (1.99 mmol). The dark red-brown solution was allowed to stir for 15 min. The solvent was removed under vacuum and replaced with 15 mL of pentane. After the solution was stirred overnight, the pentane-soluble material was chromatographed on silica with additional pentane as eluent. The first band, which was orange-yellow, was collected and the solvent removed under vacuum. The dark orange concentrated solution was place in a sublimator, the remaining solvent removed under vacuum, and the product sublimed at 25 °C (10^{-4} Torr). Yield: 0.064 g (18%).

Metalation of TMMCoCp. n-Butyllithium and TMEDA (0.016 mL of a 1.29 M stock solution, 21.2 mmol) were placed in an NMR tube with 0.80 mL of C$_6$D$_6$, and the spectrum of the

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for TMMCoCp

	x	y	z	U^a
Co	5000	5000	5000	69 (1)
C(1)	4188 (11)	3234 (10)	3630 (10)	97 (1)
C(2)	4885 (11)	4438 (9)	2723 (9)	145 (1)
C(3)	6060(11)	3158 (11)	3712 (11)	163 (1)
C(4)	4639 (11)	2513 (10)	4820 (9)	91 (1)
C(5)	2548 (12)	3319 (11)	4569 (11)	206 (1)
C(6)	2703 (12)	4510 (11)	3313 (10)	124 (1)
C(7)	5624 (12)	2271 (11)	4411 (12)	232 (1)
C(8)	2330 (11)	3543 (11)	4321 (11)	229 (1)

^{a}Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Selected Bond Distances and Angles for TMMCoCp

(a) Bond Distances (Å)

Co–Cp(cent)	1.584 (8)	C(2)–C(3)	1.489 (11)
Co–C(1)	1.891 (8)	C(3)–C(4)	1.429 (12)
Co–C(2)	2.052 (8)	C(4)–C(5)	1.424 (10)
Co–C(3)	1.972 (9)	C(5)–C(6)	1.459 (13)
Co–C(4)	1.980 (8)	C(2)–C(6)	1.447 (10)
Co–C(5)	2.012 (8)	C(1)–C(2)	1.325 (11)
Co–C(6)	2.019 (8)	C(1)–C(7)	1.321 (11)
Co–C(7)	2.251 (9)	C(1)–C(8)	1.330 (11)
Co–C(8)	2.048 (7)		

(b) Bond Angles (deg)

Cp(cent)–Co–C(1)	176.1 (3)	C(4)–C(5)–C(6)	108.2 (7)
Cp(cent)–Co–C(2)	141.5 (3)	C(5)–C(6)–C(2)	110.1 (6)
Cp(cent)–Co–C(7)	140.5 (4)	C(6)–C(2)–C(3)	103.5 (7)
Cp(cent)–Co–C(8)	143.6 (3)	C(2)–C(1)–C(7)	120.3 (7)
C(2)–C(3)–C(4)	110.8 (6)	C(2)–C(1)–C(8)	116.7 (7)
C(3)–C(4)–C(5)	107.3 (7)	C(7)–C(1)–C(8)	114.6 (8)

metalating system was taken. TMMCoCp (0.40 mL of 0.1059 M solution in benzene-d_6, 42.4 mmol) was added and the spectrum taken. In rapid succession three more additions of 0.016 mL of the metalating system were made, with the ^{1}H NMR spectrum taken after each addition.

Crystal Structure Determination. Crystal data for TMMCoCp are given in Table II. The data were empirically corrected for absorption. Systematic absences in the diffraction data uniquely determined the space group at $P2_1/n$. The unit cell is isomorphous with cobaltocene and the structure was solved by analogy to that structure (i.e., Co was placed at the origin). Due to the overlapping atom positions caused by end-for-end inversional disorder, pentagonal constraints were applied to the CH ring in the early stages of refinement. The final refinement without constraint and with all atoms anisotropic (hydrogen atoms were ignored) was dampened to prevent large excursions in atom positions. All atoms, except C(2) which is shared by both ligands, were refined at half occupancy. The superimposition of ligands is shown in Figure 2.

All computations used SHELXTL (5.1) software (G. Sheldrick, Nicolet XRD, Madison, WI). Atomic coordinates are provided in Table III and selected bond distances and angles in Table IV.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (5 pages); a listing of structure factors (4 pages). Ordering information is given on any current masthead page.