Synthesis and molecular structure of a dirhodium complex of bis(cyclopentadienyl)methane containing a .mu.-methylidene bridge: CH2[C5H4Rh(CO)]2-.mu.-CH2

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Organometallics, **1987**, 6 (10), 2138-2140• DOI: 10.1021/om00153a018 • Publication Date (Web): 01 May 2002

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Synthesis and Molecular Structure of a Dirhodium Complex of Bis(cyclopentadienyl)methane Containing a μ-Methylidene Bridge: $CH_2[C_5H_4Rh(CO)]_2$-μ-CH_2

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Received February 18, 1987

A novel dirhodium μ-methylidene complex, $CH_2[CpRh(CO)]_2$-μ-CH_2, has been prepared by reaction of $CH_2[CpRh(CO)]_2$-μ-CO and *N*-methyl-*N*-nitrosourea in refluxing benzene. The compound has been fully characterized by elemental analysis, by infrared and ^1H and ^{13}C NMR spectroscopies, and by an X-ray crystallographic analysis. $C_{14}H_{12}O_2Rh_2$: orthorhombic, *Pnma*, $a = 15.234$ (3) Å, $b = 13.940$ (2) Å, $c = 6.013$ (1) Å, $V = 1276.9$ (4) Å^3, $Z = 4$; $R_F = 2.84$. The molecular structure of the μ-methylidene complex is isomorphous with that of $CH_2[CpRh(CO)]_2$-μ-CO which has recently been reported.

μ-Alkylidene dinuclear complexes are presently the focus of active research interest because of their similarity to surface intermediates which are thought to form during Fischer–Tropsch syntheses.[1] Additionally, these compounds may mimic the chemistry of these surface catalysts permitting the development of homogeneous dinuclear catalysts for these reactions. Maitlis and his co-workers have reported the synthesis of a dinuclear rhodium complex, *cis*-$[CpRh(CH_3)]_2(\mu$-$CH_2)_2$, which undergoes thermolysis to produce products identical with those observed in Fischer–Tropsch chemistry.[2] Numerous μ-alkylidene compounds have now been reported, and their chemistry has been the subject of two recent reviews.[3,4]

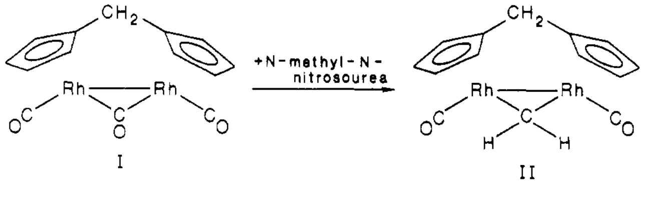
We have been for some time concerned with the chemistry of dinuclear organometallic complexes and have recently reported the synthesis of a family of dinuclear metal carbonyl complexes that use bis(cyclopentadienyl)methane as a foundation.[5] These compounds, like the related fulvalene compounds that have been reported by several groups,[6] are unusual in that the integrity of the dinuclear species is retained despite reactions that may occur at the metal. In contrast to the fulvalene compounds, the metal atoms in dinuclear compounds of bis(cyclopentadienyl)methane are well-positioned to form metal–metal bonds without introducing significant strain into the ring portion of the molecule.

We have found that $CH_2[CpRh(CO)_2]_2$ readily undergoes decarbonylation to give $CH_2[CpRh(CO)]_2$-μ-CO (I). Werner and his co-workers[7] have also reported the synthesis of I by an alternate route and have determined the molecular structure. Reaction of I with SO_2 readily forms a μ-SO_2 compound[8] which is closely related to the μ-SO_2 derivative of $[CpRh(CO)]_2$-μ-CO reported by Herrmann et al.[9] This latter reaction suggested to us the possibility of preparing a μ-CH_2 derivative using a procedure similar to that reported by Herrmann for the synthesis of the analogous $[CpRh(CO)]_2$-μ-CH_2.[10] In this paper we describe the synthesis and molecular structure of the new compound $CH_2[CpRh(CO)]_2$-μ-CH_2 (II) and in a subsequent paper will describe its reactions with protic acids.

Discussion

Herrmann and his co-workers reported that $[CpRh(CO)]_2$-μ-CO reacts in refluxing benzene with *N*-alkyl-*N*-nitrosoureas to give μ-alkylidene derivatives in good yield.[10] A crystal structure of the μ-methylidene compound showed that the cyclopentadienyl rings (and carbonyl groups) were oriented trans relative to the plane formed by the two rhodium atoms and the methylidene. Further details of this structure are described below.

N-Methyl-*N*-nitrosourea reacted with I in refluxing benzene overnight to give dark red solutions which were concentrated and chromatographed on alumina. Elution with 1:1 petroleum ether/methylene chloride cleanly separated an orange band from the slower moving red band of I. After solvent removal and recrystallization from methylene chloride/petroleum ether, II was obtained as orange-red crystals in good yield. Since unreacted I is efficiently recovered during the chromatographic workup, the overall conversion of I to II can be quite high.



Infrared spectra of II show two bands at 2003 and 1960 cm^{-1} whose relative intensities (strong, medium) are characteristic of cis dicarbonyl compounds. Similar features are found in the spectra of I and its μ-SO_2 derivative.

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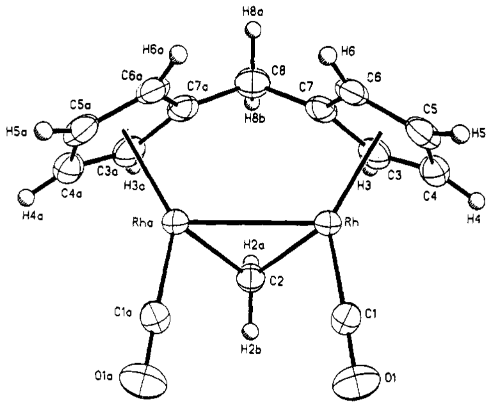

Figure 1. The molecular structure and labeling scheme for $CH_2[CpRh(CO)]_2$-μ-CH_2 (II). Hydrogen atoms are depicted with arbitrary radii.

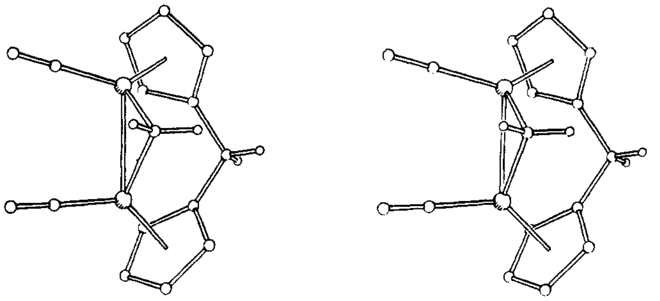

Figure 2. A stereoview of the structure of II.

The electronic spectrum of II contains one well-defined band at 449.0 nm and a pair of shoulders as the absorbance rises in the ultraviolet. I has a band at 447.0 nm that, like that of II, probably can be attributed to excitation of the Rh–Rh bond. In addition, the spectrum of I has a moderately strong absorption band at 372.0 nm that may be a charge transfer from the metals to the bridging carbonyl ligand.

In the ^1H spectrum of II, the cyclopentadienyl ring protons give rise to four well-defined resonances, while the CH_2 linkage between the rings produces an AB quartet. The low-field μ-methylidene protons resonances gave separate resonances, both of which were shown to be doublets of triplets. The two methylidene hydrogen atoms have different coupling constants with the two equivalent rhodium atoms. A similar observation has been reported by Maitlis for bridging methylidene groups in *cis*-$[CpRh(CH_3)]_2(\mu\text{-}CH_2)_2$.[2] In these compounds, one of the methylidene hydrogen atoms is oriented to couple with the two rhodium atoms giving rise to a triplet, while the other methylidene hydrogen atom is not found to couple at the resolution of the experiment. The two dissimilar geminal methylidene hydrogen atoms couple weakly as in II. Additional studies of the NMR spectra of II are continuing.

A variable-temperature study of the ^1H spectra of II found that the spectral features are almost constant down to −50 °C with only minor changes in the various chemical shifts.

A ^{13}C NMR spectrum of II was recorded. Resonances assigned to the cyclopentadienyl ring carbons and the ring coupling methylene were found as well as a well-resolved triplet for the μ-CH_2 group and a doublet for the carbonyl resonance.

Description of Structure

The structure of II has been determined by X-ray diffraction; it is crystallographically isomorphous with the recently reported structure of I.[7] In II, a μ-CH_2 group replaces the μ-CO group in I. The Rh–Rh distance, 2.638 (1) Å, in II is slightly shorter than that in I, 2.650 (1) Å. The CH_2Cp_2 ligand is experimentally identical in the two structures. The Rh-μ-CH_2 distance, 2.038 (4) Å, is longer than the Rh-μ-CO distance in I, 2.010 (5) Å; correspondingly the Rh–C–Rh_a angle is more acute in II: for I, 82.5 (2)°; for II, 80.7 (2)°. The Rh-μ-CH_2-Rh_a plane makes a smaller angle to the CNT–Rh–Rh_a–CNT_a plane in II (115.7°) than the comparable angle in I (122.1°) and makes a larger angle to the C(1)–Rh–Rh_a–C(1a) plane (82.1°) as compared to that in I (75.6°). Other minor differences in the two structures are only marginally beyond significance levels and have no chemical importance. The bond parameters associated with the Rh-μ-CH_2-Rh_a bridge are not significantly different from those found in $[CpRh(CO)]_2$-μ-CH_2 or $[C_5Me_5Rh(CO)]_2$-μ-CH_2 structures.

Table I. Crystal, Data Collection, and Refinement Parameters for $CH_2[CpRh(CO)]_2$-μ-CH_2 (II)

(a) Crystal Parameters[a]	
formula	$C_{14}H_{12}O_2Rh_2$
crystal system	orthorhombic
space group	*Pnma*
a, Å	15.234 (3)
b, Å	13.940 (2)
c, Å	6.013 (1)
V, Å^3	1276.9 (4)
z	4
μ (Mo Kα), cm^{-1}	25.0
D(calcd), g cm^{-3}	2.17
color	red
size, mm	0.10 × 0.28 × 0.36
temp, K	294
(b) Data Collection	
diffractometer	Nicolet R3m μ
radiation	Mo K_α
wavelength, Å	λ = 0.710 73 Å
scan limits, deg	$4 \le 2\theta \le 55$
scan type	ω
scan speed, deg min^{-1}	variable 6–20
rflns collected	1728
non sys absent	1522
obsd rflns ($3\sigma(F_o)$)	1353
std rflns	3 std/97 rflns
decay	<1%
T_{max}/T_{min}	1.40
(c) Refinement	
R_F, R_{wF}, %	2.84, 3.63
GOF	1.130
N_v/N_o	15.7
Δ/σ(max)	0.008
$\Delta(\rho)$(max), e Å^{-3}	0.53
g, $[w^{-1} = \sigma^2(F_o + gF_o^2)]$	0.001

[a] Unit cell parameters derived from the least-squares fit of the angular settings of 25 reflections ($23° \le 2\theta \le 32°$).

Experimental Section

$CH_2[CpRh(CO)]_2$-μ-CO (I)[5] and *N*-methyl-*N*-nitrosourea[12] were prepared by published procedures. Benzene was dried with sodium and distilled under dinitrogen.

Infrared spectra were recorded by using a Perkin-Elmer 1750 FTIR spectrometer. Electronic spectra were recorded by using a Beckman DU-7 spectrophotometer. NMR spectra were recorded on a Varian XL-300 NMR spectrometer at the University of Massachusetts. Elemental analyses were conducted by Galbraith Laboratory, Inc. of Knoxville, TN.

Synthesis of $CH_2[CpRh(CO)]_2$-μ-CH_2 (II). Into a 100-mL round-bottom flask are placed 0.5 g (1.15 mmol) of I and 1.0 g (9.70 mmol) of *N*-methyl-*N*-nitrosourea, a magnetic spin bar, and 50 mL of dry, degassed benzene. A reflux condenser is fitted to the flask, and the mixture is refluxed overnight under N_2. After the mixture is cooled, it is filtered through a bed of Celite in a medium porosity fritted glass filter and stripped of benzene by

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)

	x	*y*	*z*	U^a
Rh	735 (1)	6554 (1)	1840 (1)	29 (1)
O(1)	−694 (2)	6276 (3)	5170 (7)	65 (1)
C(1)	−141 (3)	6371 (3)	3936 (7)	39 (1)
C(2)	−60 (3)	7500	223 (9)	36 (2)
C(3)	1367 (3)	5861 (3)	−1164 (8)	46 (1)
C(4)	1259 (3)	5157 (3)	479 (8)	45 (1)
C(5)	1794 (2)	5436 (4)	2383 (7)	46 (1)
C(6)	2219 (3)	6288 (3)	1874 (7)	40 (1)
C(7)	1934 (3)	6601 (3)	−308 (7)	38 (1)
C(8)	2196 (4)	7500	−1537 (11)	48 (2)

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

Table III. Selected Bond Distances (Å) and Angles (deg) for $CH_2[CpRh(CO)]_2$-μ-CH_2 (II)

(a) Bond Distances			
Rh–Rha$_a$	2.638 (1)	Rh–C(7)	2.238 (4)
Rh–CNT[a]	1.910 (4)	C(1)–O(1)	1.131 (6)
Rh–C(1)	1.853 (4)	C(7)–C(8)	1.509 (5)
Rh–C(2)	2.038 (4)	C(3)–C(4)	1.402 (6)
Rh–C(3)	2.263 (4)	C(4)–C(5)	1.458 (6)
Rh–C(4)	2.258 (4)	C(5)–C(6)	1.387 (6)
Rh–C(5)	2.266 (4)	C(6)–C(7)	1.449 (6)
Rh–C(6)	2.291 (4)	C(7)–C(3)	1.441 (6)
(b) Bond Angles			
CNT–Rh–Rh$_a$	120.0 (1)	C(2)–Rh–Rh$_a$	49.7 (1)
CNT–Rh–C(1)	138.4 (2)	Rh–C(1)–O(1)	177.7 (4)
CNT–Rh–C(2)	127.6 (2)	Rh–C(2)–Rha	80.7 (2)
C(1)–Rh–Rh$_a$	97.9 (1)	C(7)–C(8)–C(7a)	112.4 (5)
C(1)–Rh–C(2)	89.2 (2)		
(c) Interplanar Angles			
[CNT–Rh–Rh$_a$–CNT$_a$]–[Rh–C(2)–Rh$_a$]	115.7		
[CNT–Rh–Rh$_a$–CNT$_a$]–[C(7)–C(8)–C(7a)]	36.1		
[Rh–C(2)–Rh$_a$]–[Rh$_a$–Rh–C(1)–O(1)]	82.1		
[C(3) to C(7)]–[C(3a) to C(7a)]	120.4		

[a] CNT = centroid of the atoms C(3) to C(7).

using a rotary evaporator to give a red solid. The red solid is taken up in 1:1 petroleum ether/methylene chloride and chromatographed on a 30 cm × 2 cm column of neutral alumina (Brockmann III). In some preparations a pale yellow band of $CH_2[CpRh(CO)_2]_2$ is eluted rapidly. An orange band followed by a red band are eluted slowly and with good separation. Removal of the solvent from the orange band gives II as an air-stable, orange crystalline powder: 0.1 g (yield 19%); mp 170 °C dec; IR (CH_2Cl_2) 2003 (s), 1960 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.13 (1 H, t of d, J_{Rh-H1} = 3.07 Hz, J_{H1-H2} = 0.77 Hz), 6.66 (1 H, t of d, J_{Rh-H2} = 1.18 Hz, J_{H1-H2} = 0.77 Hz), 5.90 (2 H, s), 5.79 (2 H, s), 5.55 (2 H, s), 4.70 (2 H, s), 3.98 (1 H, AB quartet, J_{A-B} = 14.72 Hz), 3.50 (1 H, AB quartet, J_{A-B} = 14.72 Hz); ^{13}C NMR ($CDCl_3$): δ 191.08 (d, J_{Rh-C} = 89.15 Hz), 102.39 (t, J_{Rh-C} = 28.83 Hz), 90.37 (s), 90.07 (s), 88.79 (s), 88.59 (s), 86.13 (s), 26.87 (s). Anal. Calcd: C, 40.19; H, 2.87. Found: C, 40.22; H, 3.04.

X-ray Structure Determination. Diffraction-quality crystals of II were obtained by recrystallization from methylene chloride/ligroin; selected specimens, formed as hexagonal plates, were epoxied to glass fibers and found to possess *mmm* Laue symmetry. Systematic absences in the diffraction data provided either of the orthorhombic space groups *Pnma* or *Pn*2$_1$*a*. Both the statistical distribution of $|E^2 - 1|$ values and the expected molecular structure with *Z* = 4 led to an initial assumption of centrosymmetry that was confirmed by the chemically reasonable and crystallographically well-behaved solution and refinement of the structure. A learned profile routine was used to process the intensity data to improve the precision in the measurement of weak reflections. The data were empirically corrected for absorption (216 data). Pertinent data relating to the crystal, data collection, and refinement are presented in Table I.

The structure was solved by direct methods, before recognition of the isomorphous relationship to I, and subsequent difference Fourier syntheses. The asymmetric unit is one-half of a molecule of II divided along a mirror plane containing C(2) and C(8) and perpendicular to the Rh–Rh$_a$ vector. All non-hydrogen atoms were anisotropically refined; hydrogen atoms were placed in idealized locations (*d*(C–H) = 0.96 A) and not refined. All computer programs and sources of scattering factors are from the SHELXTL program library (version 4.1), Nicolet Corp., Madison, WI.

Atomic coordinates are given in Table II, and selected bond distances and angles are in Table III. Additional crystallographic data are available (see note).

Acknowledgment. We wish to thank Miss Poonam Singh and Mr. Craig Spink of the University of Massachusetts and Prof. Alessandro Gambaro of The University of Padova for their work on the high-field NMR spectra of these compounds. We thank Professor Marvin Rausch for his numerous helpful suggestions on this research. T.E.B. wishes to thank the Research Corp. for their support of this research and the Johnson-Matthey Co. for a generous loan of rhodium trichloride. A.L.R. thanks the National Science Foundation for assistance in the purchase of the diffractometer.

Registry No. I, 99936-62-6; II, 109975-50-0; Rh, 7440-16-6.

Supplementary Material Available: Tables of bond angles and distances, anisotropic temperature factors, and hydrogen atom coordinates (5 pages); a listing of F_o and F_c (13 pages). Ordering information is given on any current masthead page.