

Synthesis of $\text{Cp}(\text{CO})\text{CoPt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$ and $\text{Cp}_2\text{Co}_2\text{Pt}(\text{PPh}_3)_2(\mu\text{-CO})_2$ from the reaction of $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ with $[\text{CpCo}(\text{CO})]_2(\mu\text{-CH}_2)$

Phillip D. Macklin, Chad A. Mirkin, Nathan Viswanathan, Gregory D. Williams,
 Gregory L. Geoffroy*

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802 (U.S.A.)

and Arnold L. Rheingold

Department of Chemistry, The University of Delaware, Newark, DE 19716 (U.S.A.)

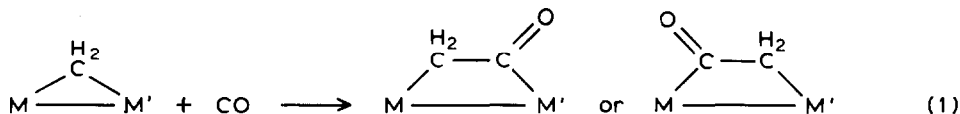
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Abstract

Addition of $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ to $[\text{CpCo}(\text{CO})]_2(\mu\text{-CH}_2)$ yields the bimetallic μ -methylene complex $\text{Cp}(\text{CO})\text{CoPt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$ (**3**) along with the trimetallic cluster $\text{Cp}_2\text{Co}_2\text{Pt}(\text{PPh}_3)_2(\mu\text{-CO})_2$ (**4**). Both complexes have been structurally characterized: **3**, $P2_1/n$, a 12.240(6) Å, b 17.395(8) Å, c 17.887(9) Å, β 97.36(3)°, V 3777(2) Å³, $Z = 4$, R_f 4.8%, R_{wf} 4.9% for 3352 reflections with $F_0 \geq 3\sigma(F_0)$; **4**, $P1$, a 11.511(3) Å, b 12.775(3) Å, c 16.526(4) Å, α 70.46(3)°, β 89.59(3)°, γ 64.18(2)°, V 2034.1(8) Å³, $Z = 2$, R_f 5.88%, R_{wf} 6.67% for 5865 reflections with $F_0 \geq 3\sigma(F_0)$. The Co–Pt bond in **3** is bridged by the $\mu\text{-CH}_2$ ligand with the Co further ligated by Cp and CO ligands and the Pt has two PPh₃ ligands. Cluster **4** has a closed PtCo₂ triangular structure with two semi-triply bridging CO ligands above and below the metal plane which interact with Pt less than with the two Co atoms. The Co atoms are each ligated by a Cp ligand and the Pt by two PPh₃ ligands. Since complexes **3**, and **4** are all isolobal with $\text{Pt}(\text{PPh}_3)_2(\text{CH}_2=\text{CH}_2)$, the reactions reported herein simply represent the interchange of one isolobal fragment with another.

There are now several examples of μ -ketene complexes formed by insertion of CO into metal–($\mu\text{-CH}_2$) bonds [1,2], a reaction which models a possible chain growth step during CO hydrogenation on metal catalysts [3]. All known examples of $\mu\text{-CH}_2$ to $\mu\text{-CH}_2\text{CO}$ conversions presently involve homometallic complexes. This reaction with heterometallic $\mu\text{-CH}_2$ complexes is particularly interesting since CO insertion can potentially occur from either end to give isomeric ketene complexes,

eq. 1, which could differ markedly in their reactivity characteristics: However, no



heterobimetallic μ -ketene complexes are known which have been derived from CO addition to bimetallic μ -CH₂ complexes [1]. In an effort to prepare possible candidates for such reactions we earlier reported the synthesis of Os₃Pt(CO)₁₁⁻(PPh₃)₂(μ -CH₂) (**1**) with a PtOs(μ -CH₂) unit by the addition of "Pt(PPh₃)₂" across the Os-CH₂ bond of Os₃(CO)₁₁(μ -CH₂) [4]. However, complex **1** did not yield a μ -ketene complex upon reaction with CO and instead gave only substitution of CO for PPh₃.

The structure of complex **1** suggested its formation by addition of "Pt(PPh₃)₂" across a terminal Os=CH₂ bond in a transient intermediate derived from Os₃(CO)₁₁(μ -CH₂) [4]. Although this was subsequently shown to be unlikely [4], we considered the possibility of adding "Pt(PPh₃)₂" to other μ -CH₂ complexes which are believed to be in equilibrium with terminal M=CH₂ complexes. One such compound is [CpCo(CO)]₂(μ -CH₂) (**2**) for which an intermediate with a terminal methylene ligand was suggested to account for its observed *cis-trans* isomerization [5]. We accordingly examined the reaction of Pt(PPh₃)₂(C₂H₄) with **2**, expecting the formation of a trimetallic Co₂Pt(μ -methylene) cluster. As described herein, Pt(PPh₃)₂(C₂H₄) does react with **2**, but the products are not those expected. Instead the binuclear μ -methylene complex Cp(CO)CoPt(PPh₃)₂(μ -CH₂) (**3**) is formed along with the trinuclear cluster Cp₂Co₂Pt(PPh₃)₂(μ -CO)₂ (**4**). Since complexes **1**, **3**, and **4** are all isolobal with Pt(PPh₃)₂(CH₂=CH₂), the reactions reported herein simply represent the interchange of one isolobal fragment with another. Complex **3** is the first example of a compound with a methylene ligand bridging Co and Pt atoms, but unfortunately, this complex does not react with CO and the issue raised in eq. 1 cannot be addressed in this study.

Results and discussion

*Synthesis of Cp(CO)CoPt(PPh₃)₂(μ -CH₂) (**3**) and Cp₂Co₂Pt(PPh₃)₂(μ -CO)₂ (**4**).* The complex Pt(PPh₃)₂(C₂H₄) reacts with [CpCo(CO)]₂(μ -CH₂) upon heating to yield the heterobinuclear complex **3** and a trace of the Co₂Pt trimer **4**, eq. 2. These products were readily separated by Al₂O₃ chromatography and have been obtained as microcrystalline solids. Both are slightly air-sensitive in solution giving complete decomposition after ~ 5 h air exposure. They have been spectroscopically characterized and further defined by X-ray diffraction studies, Fig. 1 and 2.

The ¹H NMR spectrum of **3** shows two broad singlets due to the inequivalent methylene protons at δ 6.21 and 5.69 ppm along with a cyclopentadienyl resonance at δ 4.61 ppm. The broadening is presumably due to unresolved ¹H-¹H or ¹H-³¹P coupling or may be a consequence of the quadrupolar Co nucleus. The inequivalent PPh₃ ligands of **3** give rise to two ³¹P NMR doublets at δ 36.1 ppm (*J*(P-P) 17 Hz) and δ 26.9 ppm with *J*(P-Pt) couplings of 2689 and 3619 Hz, respectively.

Complex **4** shows a parent ion at *m/z* = 1023 in its mass spectrum (FD) and a single ³¹P NMR resonance at δ 20.3 ppm (*J*(P-Pt) 3924 Hz) due to the equivalent

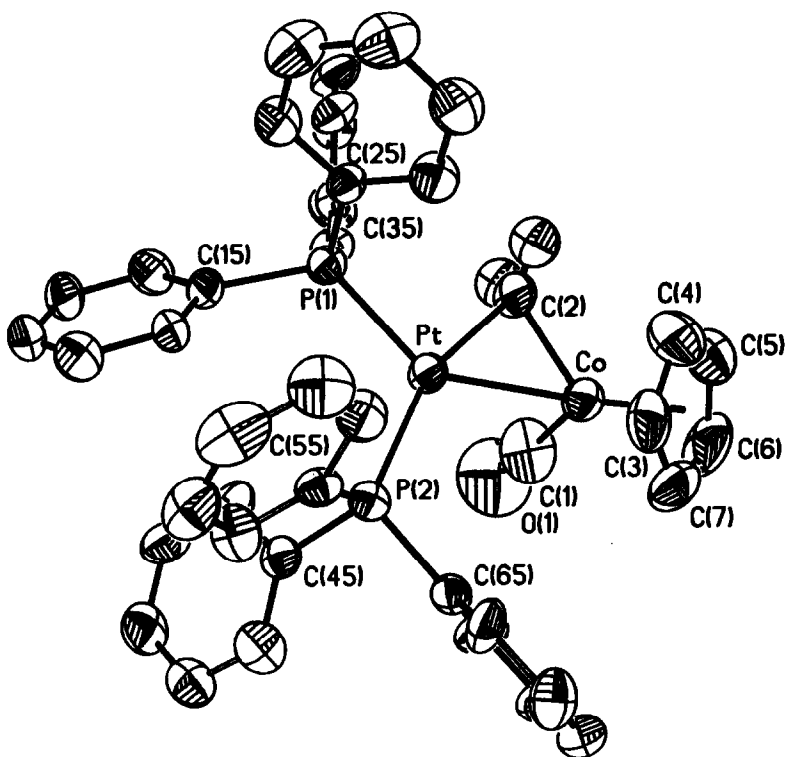


Fig. 1. An ORTEP drawing of $\text{Cp}(\text{CO})\text{CoPt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$ (**3**). Thermal ellipsoids are drawn at the 40% probability level.

PPh_3 ligands. A Cp resonance at δ 4.15 ppm is apparent in the ^1H NMR spectrum of **4**, and the μ_3 -CO ligands give rise to a low energy $\nu(\text{CO})$ band at 1685 cm^{-1} .

The previously reported formation of $[\text{Cp}(\text{CO})\text{Co}][(\text{MeCp})(\text{CO})\text{Co}](\mu\text{-CH}_2)$ upon heating $[\text{Cp}(\text{CO})\text{Co}]_2(\mu\text{-CH}_2)$ (**1**) with $[(\text{MeCp})(\text{CO})\text{Co}]_2(\mu\text{-CH}_2)$ along with the established synthesis of $[\text{Cp}(\text{CO})\text{Co}][\text{Cp}(\text{CO})\text{Rh}](\mu\text{-CH}_2)$ from the reaction of **1** with $\text{CpRh}(\text{CO})_2$ have led Bergman and co-workers to conclude that **1** undergoes reversible dissociation into $\text{Cp}(\text{CO})\text{Co}=\text{CH}_2$ and $\text{Cp}(\text{CO})\text{Co}$ fragments under conditions similar to those used for the synthesis of **3** and **4** [5]. On this basis we suggest that the products **3** and **4** of our reaction form by the sequence of reactions outlined in Scheme 1.

Addition of $\text{Pt}(\text{PPh}_3)_2$ to $\text{Cp}(\text{CO})\text{Co}=\text{CH}_2$ has precedent in Bergman's study cited above [5], and the proposed $5 \rightarrow 4$ conversion is similar to the established addition of metal fragments to the C_5Me_5 analogue of **5** to form trinuclear clusters [6]. Interestingly, complexes **1**, **3**, and **4** are all isolobal with $\text{Pt}(\text{PPh}_3)_2(\text{CH}_2=\text{CH}_2)$, since $\text{Cp}(\text{CO})\text{Co}$ is isolobal with CH_2 [7], and the reactions reported herein simply represent the interchange of one isolobal fragment with another.

The impetus for the present study was to prepare a heteronuclear CoPt μ -methylene cluster for study of its ability to insert CO to form a ketene derivative. However, complex **3** does not react when placed under 1 atm CO pressure at 25°C nor does $[\text{CpCo}(\text{CO})]_2(\mu\text{-CH}_2)$ from which **3** was prepared. While several $\mu\text{-CH}_2$ complexes

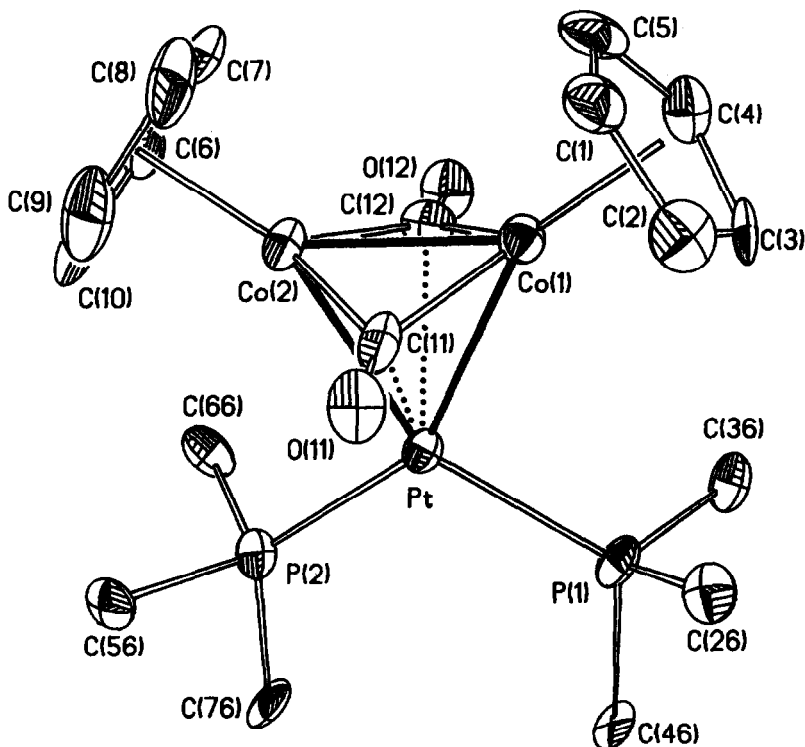
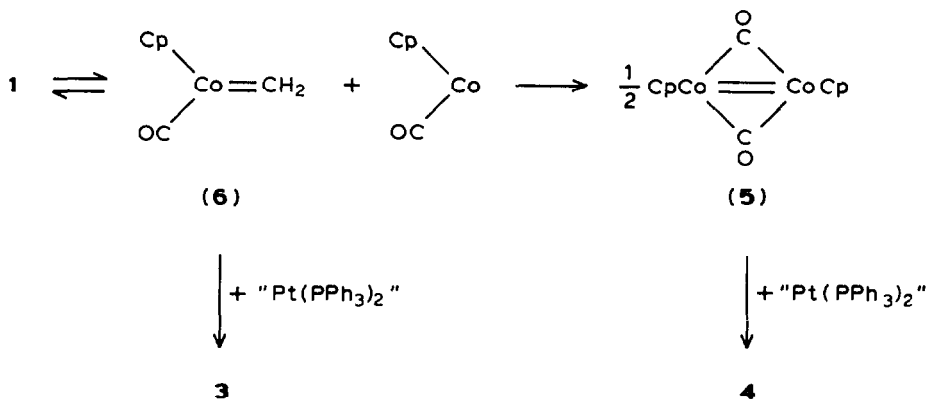
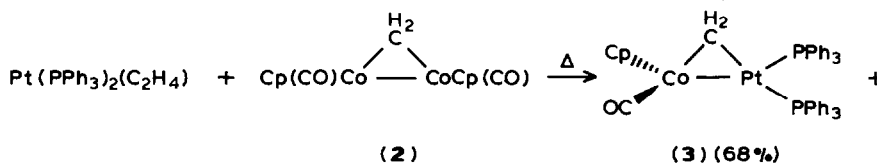


Fig. 2. An ORTEP drawing of $\text{Cp}_2\text{Co}_2\text{Pt}(\text{PPh}_3)_2(\mu\text{-CO})_2$ (**4**). Thermal ellipsoids are drawn at the 40% probability level. Only the phenyl *ipso* carbons are shown for clarity.

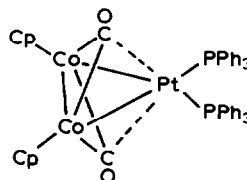
are known to form μ -ketene complexes via carbonylation of the methylene ligand, there are many more methylene complexes which do not undergo such chemistry [1]. The factors which influence the methylene to ketene conversion are not well understood, and this reaction requires further study before structure-reactivity correlations can be made.



Scheme 1.

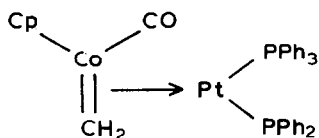


(2)



(4) (4%)

Structural characterization of $\text{Cp}(\text{CO})\text{CoPt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$ (3). An ORTEP drawing of **3** is shown in Fig. 1 and pertinent crystallographic details are given in Tables 1–3. The methylene ligand of **3** bridges the Co–Pt bond with the Co atom further coordinated by CO and cyclopentadienyl ligands and the Pt center by two PPh_3 ligands. The coordination geometry about Pt may be described as a distorted square plane defined by the two phosphines, the cobalt, and the methylene ligand. Alternatively, the Pt can be viewed as having a trigonal planar geometry with a π -bonded $\text{Co}=\text{CH}_2$ unit as sketched in I.



(I)

The latter structure is similar to that found for $(\text{CH}_2=\text{CH}_2)\text{Pt}(\text{PPh}_3)_2$ [8] and is reflected in the isolobal relationship between $\text{CH}_2=\text{CH}_2$ and $\text{Cp}(\text{CO})\text{Co}=\text{CH}_2$. The $107.9(1)^\circ$ P(1)–Pt–P(2) bond angle is closer to the 120° trigonal-planar angle than it is to the 90° square-planar angle and is only slightly less than the corresponding P–Pt–P angle of 111.5° in $(\text{CH}_2=\text{CH}_2)\text{Pt}(\text{PPh}_3)_2$ [8].

Although no other complexes which possess methylene ligands bridging Co–Pt bonds have been reported, a comparison to other compounds which contain Co– CH_2 and Pt– CH_2 linkages indicates normal M–C single bonds for **3**. The Co– CH_2 bond length of $1.959(12)$ Å in **3** is only slightly longer than the Co– CH_2 bond lengths in **1** ($1.920(2)$, $1.925(2)$ Å) [5], and the Pt– CH_2 distance of $2.096(12)$ Å for **3** compares well to the Pt– CH_2 distances in $\text{Os}_3\text{Pt}(\mu\text{-CH}_2)(\text{CO})_{11}(\text{PPh}_3)_2$ ($1.95(6)$ Å) [4], $\text{Pt}_2\text{Cl}_2(\mu\text{-CH}_2)(\text{dppm})_2$ ($2.01(2)$ Å) [9] and $[\text{Pt}_2\text{Cl}(\text{CH}_2\text{PPh}_3)(\mu\text{-CH}_2)(\mu\text{-dppm})_2][\text{PF}_6]$ ($2.13(3)$ Å) [9]. The Co–Pt bond length of $2.547(2)$ Å falls within the $2.50(1)$ – $2.85(1)$ Å range reported for other Co–Pt clusters [10] and compares particularly well to those found in $\text{PtCo}_2(\text{CO})_8(\text{PPh}_3)$ ($2.519(1)$, $2.532(1)$ Å [10c]) and $\text{Pt}_2\text{Co}_2(\text{CO})_8(\text{PPh}_3)_2$ (2.550 ave [10b]). The Pt–C(2)–Co angle of $77.7(4)^\circ$ is within the usual 74.0 – 87.4° range found for methylene ligands bridging metal–metal bonds [11].

Table 1

Crystal, data collection and refinement parameters for Cp(CO)CoPt(PPh₃)₂(μ-CH₂) (3) and Cp₂Co₂Pt(PPh₃)₂(μ-CO)₂ (4)

	3	4
<i>(a) crystal parameters</i>		
Formula	C ₄₃ H ₃₇ CoOP ₂ Pt	C ₄₈ H ₄₀ Co ₂ O ₂ P ₂ Pt·H ₂ O
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1
<i>a</i> , Å	12.240(6)	11.511(3)
<i>b</i> , Å	17.395(8)	12.775(3)
<i>c</i> , Å	17.887(9)	16.526(4)
α , deg.	–	70.46(3)
β , deg.	97.36(3)	89.59(3)
γ , deg.	–	64.18(2)
<i>V</i> , Å ³	3777(2)	2034.1(8)
<i>Z</i>	4	2
μ , cm ⁻¹	44.4	45.7
ρ , g cm ⁻³ (calcd)	1.565	1.67
Size, mm	0.25 × 0.30 × 0.39	0.26 × 0.28 × 0.30
Color	orange red	black
<i>T</i> _{max} / <i>T</i> _{min}	1.45	1.43
<i>(b) data collection</i>		
Diffractometer	Nicolet R3m/μ	
Radiation	Mo- <i>K</i> _α (λ 0.71073 Å)	
Monochromator	graphite	
Scan range, deg.	4 ≤ 2θ ≤ 50	
Scan type	omega	
Scan speed, deg min ⁻¹	var. 4–20	
Temperature, K	293(1)	
Standard reflections	3 std./197 reflns.	
Decay	≈ 6%	< 3%
Reflections collected	5832	7437
Unique reflections	5408	7167
Unique reflections with <i>F</i> ₀ ≥ 3σ(<i>F</i> ₀)	3352	5865
<i>R</i> (int), %	3.1	2.3
<i>(c) data reduction and refinement</i>		
<i>R</i> _t , % ^a	4.8	5.9
<i>R</i> _{wf} , %(<i>g</i> = 0.001) ^a	4.9	6.7
GOF	1.18	1.45
Data/parameter	9.3	13.7
Δ/σ (last cycle)	0.10	0.09
Highest peak final diff. Fourier, e Å ⁻³	0.77	1.8 (1.0 Å from Pt)

$$^a w^{-1} = \sigma^2 (F_0) + g(F_0^2); R_t = \Sigma |\Delta| / \Sigma |F_0|; R_{wf} = \Sigma (|\Delta| w^{1/2}) / \Sigma (|F_0| w^{1/2}); \Delta = |F_0| - |F_c|.$$

Structural characterization of 4. An ORTEP drawing of 4 is shown in Fig. 2 and pertinent crystallographic details are given in Tables 1, 4, and 5. The cluster has a triangular Co₂Pt core with a Cp ligand bound to each Co and with two PPh₃ ligands attached to Pt. Two semi-triply bridging [9c,12] CO ligands lie above and below the Co₂Pt plane. These symmetrically bridge the Co atoms (ave. Co–C 1.868 Å) but are less strongly bonded to Pt with Pt–C(11) and Pt–C(12) distances of 2.337

Table 2

Atomic coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$) for $\text{Cp}(\text{CO})\text{CoPt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$ (3)

Atom	x	y	z	U_{iso}^a
Pt	1270.2(4)	7044.6(3)	9066.2(3)	46.4(2)
Co	2608(1)	5991(1)	9573(1)	58.5(6)
P(1)	606(2)	8186(2)	9388(2)	46(1)
P(2)	230(3)	6645(2)	7933(2)	47(1)
C(1)	3304(11)	6363(10)	8905(10)	96(7)
O(1)	3824(11)	6645(10)	8510(9)	165(8)
C(2)	2448(10)	7004(7)	10025(7)	68(5)
C(3)	1470(13)	5126(8)	9739(9)	83(7)
C(4)	2029(19)	5401(10)	10441(9)	122(10)
C(5)	3170(14)	5290(9)	10477(9)	105(8)
C(6)	3308(14)	4932(10)	9819(12)	114(9)
C(7)	2277(14)	4804(8)	9376(9)	94(7)
C(10)	-1131(7)	8604(4)	8263(4)	62(5)
C(11)	-1670	9060	7689	71(6)
C(12)	-1226	9768	7520	73(6)
C(13)	-242	10021	7926	67(5)
C(14)	298	9565	8501	62(5)
C(15)	-147	8857	8669	53(5)
C(20)	-1052(7)	8680(4)	10201(5)	58(5)
C(21)	-1748	8599	10755	80(6)
C(22)	-1729	7923	11176	83(6)
C(23)	-1013	7329	11044	82(6)
C(24)	-317	7410	10489	67(5)
C(25)	-336	8086	10068	45(4)
C(30)	2677(7)	8893(4)	9502(4)	59(5)
C(31)	3537	9368	9808	68(6)
C(32)	3466	9759	10482	69(6)
C(33)	2534	9673	10849	75(6)
C(34)	1674	9197	10542	58(5)
C(35)	1745	8807	9869	45(4)
C(40)	187(6)	6851(4)	6360(5)	73(6)
C(41)	305	7294	5724	69(6)
C(42)	676	8051	5808	80(6)
C(43)	929	8366	6526	76(6)
C(44)	810	7924	7162	64(5)
C(45)	439	7167	7078	51(4)
C(50)	-2027(6)	6899(5)	7286(4)	64(5)
C(51)	-3142	6990	7356	78(6)
C(52)	-3517	6859	8050	91(7)
C(53)	-2779	6638	8672	83(6)
C(54)	-1664	6548	8601	65(5)
C(55)	-1289	6678	7908	47(4)
C(60)	-326(5)	5071(4)	7675(5)	65(5)
C(61)	-84	4320	7478	71(6)
C(62)	946	4146	7266	77(6)
C(63)	1733	4724	7250	82(7)
C(64)	1491	5475	7447	65(5)
C(65)	461	5649	7650	48(4)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

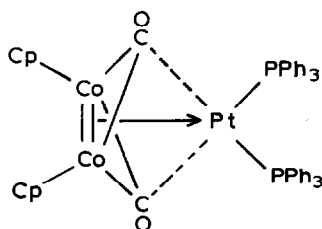
Selected bond distances and angles for $\text{Cp}(\text{CO})\text{CoPt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$ (**3**)

(a) bond distances (Å)			
Pt–Co	2.547(2)	Co–C(2)	1.959(12)
Pt–P(1)	2.248(3)	Co–C(1)	1.68(2)
Pt–P(2)	2.356(3)	C(1)–O(1)	1.12(2)
Pt–C(2)	2.096(12)	Co–CNT ^a	1.71(1)
(b) bond angles (deg)			
P(1)–Pt–P(2)	107.9(1)	Pt–Co–CNT	133.7(5)
P(1)–Pt–Co	141.4(1)	Pt–Co–C(2)	53.5(3)
P(1)–Pt–C(2)	93.1(3)	Pt–C(2)–Co	77.7(4)
P(2)–Pt–Co	110.3(2)	C(2)–Co–C(1)	91.9(7)
P(2)–Pt–C(2)	159.0(3)	C(2)–Co–CNT	127.7(6)
Co–Pt–C(2)	48.7(3)	C(1)–Co–CNT	137.2(7)
Pt–Co–C(1)	80.2(5)	Co–C(1)–O(1)	174(2)

^a CNT is the center of the C_5H_5 ring bonded to Co.

and 2.386 Å. These latter distances are slightly shorter than the Pt–C distance of 2.570(10) Å between Pt and the semi-triply bridging CO ligand in $\text{Co}_2\text{Pt}(\text{CO})_7(\mu_3\text{-CO})(\text{PPh}_3)$ [9c] but substantially longer than a typical Pt–CO distance of 1.897(6) Å as found in $\text{PtMn}_2(\text{CO})_{12}$ [13]. The structure of **4** with two semi-triply bridging CO's closely resembles the established structure of $[\text{Cp}_2\text{Rh}_3(\text{CO})_4]^-$ [12a]. The dihedral angle between the $[\text{Co}(1)\text{--Co}(2)\text{--C}(11)]$ and $[\text{Co}(1)\text{--Co}(2)\text{--C}(12)]$ planes is 148.3° , further reflecting the bending of the $\mu\text{-CO}$'s toward Pt.

The PtCo_2P_2 core of the molecule is planar with a maximum deviation shown by Co(1) which is displaced 0.021 Å from the least-squares plane. If the semi-triply bridging CO's are neglected, the coordination geometry about Pt may be described as a distorted square-plane or alternatively as a trigonal plane with a π -coordinated Co=Co unit as in II.



(II)

The latter is similar to the suggestion made above for the structure of **3** and is related to the established geometry of $(\text{CH}_2=\text{CH}_2)\text{Pt}(\text{PPh}_3)_2$ [8]. This view is supported by the isolobal relationship between $\text{CH}_2=\text{CH}_2$ and $[\text{CpCo}=\text{CoCp}](\mu\text{-CO})_2$ and by the very short Co–Co bond length of 2.372(2) Å in **4**. This is in fact a typical Co=Co double bond distance and compares well to those found in other molecules with Co=Co double bonds: $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Co}_2(\mu\text{-CO})_2$, 2.338(2) Å [14]; $\text{Co}_2(\mu\text{-PPh}_2)_2(\text{CO})_2(\text{PET}_2\text{Ph})_2$, 2.343(2) Å [15]; $\text{Co}_2(\mu\text{-P}^t\text{Bu}_2)(\text{PMe}_3)_2(\text{CO})_2$, 2.399(4) Å [16]; $\text{Co}_2(\mu\text{-P}^t\text{Bu}_2)(\text{PMe}_3)_2(\text{N}_2)_2$, 2.414(1) Å [16]. Also supporting the proposed structural rationalization II is the P(1)–Pt–P(2) bond angle of $114.1(1)^\circ$

Table 4. Atomic coordinates ($\times 10^4$) and temp. factors ($\text{\AA}^2 \times 10^3$) for $\text{Cp}_2\text{Co}_2\text{Pt}(\text{PPh}_3)_2(\mu\text{-CO})_2$ (4)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
Pt	2519(1)	4901(1)	2209(1)	24(1)
Co(1)	2984(2)	3899(2)	1059(1)	28(1)
Co(2)	1987(2)	6114(1)	558(1)	29(1)
P(1)	3345(3)	3058(3)	3387(2)	29(1)
P(2)	1660(3)	6644(3)	2560(2)	29(1)
O(11)	4795(8)	4881(8)	1152(6)	39(4)
O(12)	188(9)	5100(9)	1070(7)	42(5)
O(13)	7521(12)	4967(10)	2825(9)	78(8)
C(1)	4128(14)	3091(13)	244(9)	42(7)
C(2)	4681(13)	2319(14)	1138(10)	45(7)
C(3)	3734(15)	1908(11)	1529(10)	45(6)
C(4)	2582(14)	2543(12)	851(10)	44(7)
C(5)	2862(15)	3287(14)	69(11)	59(8)
C(6)	279(13)	7746(11)	-172(8)	35(6)
C(7)	879(16)	6991(13)	-664(9)	48(7)
C(8)	2112(16)	6895(13)	-747(11)	58(8)
C(9)	2308(16)	7581(15)	-265(12)	61(8)
C(10)	1190(15)	8071(13)	81(10)	51(7)
C(11)	3756(13)	4930(11)	1086(8)	33(5)
C(12)	1242(12)	5054(12)	1023(8)	35(6)
C(21)	5858(8)	2617(7)	3098(7)	48(7)
C(22)	7142	1925	2999	60(9)
C(23)	7617	662	3135	71(10)
C(24)	6809	90	3369	64(8)
C(25)	5526	782	3468	53(7)
C(26)	5050	2046	3332	36(6)
C(31)	1336(8)	2565(7)	2922(5)	39(6)
C(32)	609	1906	3050	57(9)
C(33)	970	826	3788	51(8)
C(34)	2059	405	4398	49(7)
C(35)	2787	1063	4271	44(7)
C(36)	2425	2143	3533	35(6)
C(41)	2310(7)	3622(9)	4804(6)	50(8)
C(42)	2350	3618	5649	73(11)
C(43)	3552	3086	6181	84(16)
C(44)	4713	2558	5868	80(12)
C(45)	4672	2563	5023	54(9)
C(46)	3471	3095	4491	33(6)
C(51)	3510(9)	7331(7)	1768(7)	48(8)
C(52)	4106	8105	1474	56(9)
C(53)	3624	9234	1605	66(10)
C(54)	2546	9591	2028	66(9)
C(55)	1950	8818	2321	50(8)
C(56)	2432	7688	2191	34(6)
C(61)	-734(9)	8811(7)	1650(7)	53(8)
C(62)	-2048	9386	1281	79(10)
C(63)	-2713	8674	1376	64(8)
C(64)	-2062	7386	1840	56(9)
C(65)	-748	6811	2209	47(8)
C(66)	-84	7523	2114	37(7)
C(71)	2878(7)	6123(10)	4177(6)	55(8)
C(72)	2958	6110	5023	71(11)
C(73)	1819	6608	5364	71(5)
C(74)	599	7119	4860	83(14)
C(75)	519	7133	4014	50(8)
C(76)	1658	6635	3673	35(6)

^a Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor. ^b Isotropic *U*.

Table 5

Selected bond distances and angles for $\text{Cp}_2\text{Co}_2\text{Pt}(\text{PPh}_3)_2(\mu\text{-CO})_2$ (**4**)

(a) bond distances (Å)			
Co(1)–Co(2)	2.372(2)	Co(1)–C(11)	1.89(2)
Pt–Co(1)	2.560(2)	Co(1)–C(12)	1.89(1)
Pt–Co(2)	2.566(2)	Co(2)–C(11)	1.91(1)
Pt–P(1)	2.291(3)	Co(2)–C(12)	1.86(2)
Pt–P(2)	2.283(4)	Co(1)–CNT(1)	1.697(8)
Pt–C(11)	2.33(1)	Co(2)–CNT(2)	1.711(8)
Pt–C(12)	2.36(1)		
(b) bond angles (deg)			
P(1)–Pt–P(2)	114.1(1)	CNT(1)–Co(1)–Co(2)	145.7(4)
P(1)–Pt–Co(1)	95.9(1)	CNT(2)–Co(2)–Co(1)	144.0(4)
P(1)–Pt–Co(2)	151.0(1)	CNT(2)–Co(2)–Pt	153.7(3)
P(2)–Pt–Co(1)	150.0(1)	CNT(2)–Co(2)–C(11)	130.8(4)
P(2)–Pt–Co(2)	94.9(1)	CNT(2)–Co(2)–C(12)	127.3(4)
CNT(1)–Co(1)–Pt	151.6(4)	Co(1)–C(11)–Co(2)	77.1(6)
CNT(1)–Co(1)–C(11)	128.3(4)	Co(1)–C(12)–Co(2)	78.4(6)
CNT(1)–Co(1)–C(12)	131.2(5)		

^a CNT(*x*) is the center of the C_5H_5 ring bonded to Co(*x*).

which is much closer to the 120° trigonal-planar angle than it is to the 90° square-planar angle and is actually greater than the corresponding 111.5° angle in $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$ [8]. The Co(1)–Pt and Co(2)–Pt bond lengths of 2.560(2) and 2.566(2) Å are in the typical range of Co–Pt single bonds as found in compound **3** and the other compounds mentioned above.

Experimental

$[\text{Cp}(\text{CO})\text{Co}]_2(\mu\text{-CH}_2)$ [5] and $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$ [17] were prepared by literature procedures. Solvents used were dried and degassed by standard methods. All manipulations, unless otherwise specified, were conducted under prepurified N_2 using standard Schlenk and high vacuum line techniques. Instruments used in this research were as previously described [4].

*Synthesis of $\text{Cp}(\text{CO})\text{CoPt}(\text{PPh}_3)_2(\mu\text{-CH}_2)$ (**3**) and $\text{Cp}_2\text{Co}_2(\text{PPh}_3)_2(\mu\text{-CO})_2$ (**4**).* Complex **2** (0.195 g, 0.613 mmol) and $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$ (0.748 g, 1.00 mmol) were combined in a 25 ml two neck flask equipped with an N_2 inlet and a reflux condenser. THF (12 ml) was added and the dark red mixture was refluxed for 16 h followed by cooling to 22°C to give a dark brown solution. Removal of solvent by evaporation left a dark oil which was dissolved in a minimum amount of hexane/benzene (1/1) and chromatographed on Al_2O_3 (Alcoa grade CG20, activity II, 1.9% H_2O). Elution with hexane/benzene (1/1) gave a small amount of an unidentified yellow material. Further elution with 1 : 2 hexane/benzene yielded a red fraction which gave **3** (0.603 g, 0.681 mmol, 68% yield) as a red crystalline solid upon solvent evaporation. **3**: Anal. Found: C, 56.45; H, 4.21. $\text{C}_{43}\text{H}_{37}\text{CoOP}_2\text{Pt}$ calcd.: C, 56.94; H, 3.62%. IR (THF): $\nu(\text{CO})$ 1929 cm^{-1} . ^1H NMR (C_6D_6): δ 7.66–6.90 (m, Ph's), 6.21 (br s, $\mu\text{-CH}_2$), 5.69 (br s, $\mu\text{-CH}_2$), 4.61 (s, C_5H_5). ^{31}P NMR (C_6D_6): δ 36.1 (d, $J(\text{P-P})$ 17 Hz, $J(\text{P-Pt})$ 2689 Hz), δ 26.9 (d, $J(\text{P-Pt})$ 3619 Hz).

Further elution with benzene gave a green band of **4** which was isolated as a green solid upon solvent evaporation (0.044 g, 0.043 mmol, 4.3%). **4**: Anal. Found: C, 55.35; H, 4.09. $C_{48}H_{40}Co_2O_2P_2Pt \cdot H_2O$ calcd.: C, 55.33; H, 4.03%. IR (CH_2Cl_2): $\nu(CO)$ 1685 cm^{-1} . 1H NMR (C_6D_6): δ 7.44–7.15 (m, Ph's), δ 4.14 (s, C_5H_5). ^{31}P NMR (C_6D_6): δ 20.3 (s, $J(P-Pt)$ 3924 Hz). m/z (FD) = 1023 (M^+).

The state of Al_2O_3 hydration is critical in the chromatographic separation of **3** and **4** as only decomposition occurred when chromatography was conducted on activated Al_2O_3 (Thomas Scientific Cat. No. C019-G20).

Crystal and molecular structure of 3. Crystals were grown from a CH_2Cl_2/THF solution by slow evaporation. A specimen mounted on a glass fiber was uniquely identified as belonging to the monoclinic space group, $P2_1/n$. Table 1 provides the crystal parameters as well as details of data collection and refinement. The intensity data were corrected for decay (6%, linear), Lp effects and for absorption (ψ -scan, seven reflections, 10° increments). The metal atoms were located by heavy-atom methods, and the structure was completed by difference Fourier syntheses. Phenyl rings were constrained to rigid, planar hexagons ($d(C-C)$ 1.395 Å) and hydrogen atoms were treated as idealized ($d(C-H)$ 0.96 Å, updated isotropic contributions, but not refined. All non-hydrogen atoms were refined anisotropically. All computer programs used are contained in the SHELXTL (5.1) and P3 program libraries (Nicolet Corporation, Madison, WI). Lists of structure factors and other crystallographic information may be obtained from the authors upon request.

Crystal and molecular structure of 4. A suitable crystal was obtained by recrystallization from CH_2Cl_2 /hexane and was glued to a glass fiber. Table 1 contains the crystal, data collection and refinement parameters. Photographic characterization and Delauney reduction failed to reveal symmetry higher than triclinic. An empirical ellipsoidal absorption correction based on 216 data (six reflections, 10° increments) was applied to the diffraction data. The metal atom coordinates were obtained by heavy-atom methods and the structure completed by subsequent difference Fourier syntheses. A difference density peak remote from the main structure refined well as an oxygen atom, O(13), and is tentatively assigned as a molecule of water. All non-hydrogen atoms were anisotropically refined with the exception of C(73) which persistently remained non-positive definite. All phenyl rings were constrained to rigid, planar, hexagonal geometry ($d(C-C)$ 1.395 Å). Hydrogen atoms were idealized ($d(C-H)$ 0.96 Å). Atomic coordinates are given in Table 4 and selected bond distances and angles in Table 5. All computations were accomplished as above.

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