but also new insight into the silicon migration from oxygen to carbon, which has previously thought to proceed intramolecularly.[8]

Registry No. 1, 51425-66-2; 2, 57025-69-1; 3, 91390-63-5; 4, 91390-59-9; 5, 74477-44-4; *cis*-6, 91390-60-2; *trans*-6, 91390-65-7; 7, 91390-64-6; *cis*-8, 91390-61-3; *trans*-8, 91390-66-8; (*E*)-[(1-ethoxy-1-propenyl)oxy]trimethylsilane, 73967-97-2; [(1-methoxy-2-methyl-1-propenyl)oxy]trimethylsilane, 31469-15-5; ethyl 2-(trimethylsilyl)propanoate, 13950-55-5; methyl 2-methyl-2-(trimethylsilyl)propanoate, 55499-73-5; dimethyl[(1-methoxyethenyl)oxy]*tert*-butylsilane, 77086-38-5; methyl (dimethyl(*tert*-butyl)silyl)acetate, 91390-62-4.

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(8) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77. Lutsenko, I. F.; Baukov, Y. I.; Kostyuk, A. S.; Savelyeva, N. I.; Krysina, V. K. *J. Organomet. Chem.* **1969**, *17*, 241. Woodbury, R. P.; Rathke, M. W. *J. Org. Chem.* **1978**, *43*, 881. Casey, C. P.; Jones, C. R.; Tukada, H. *Ibid.* **1981**, *46*, 2089.

Carbonylation of $(\eta^5\text{-}C_5H_5)_2Zr(Cl)CH_2P(C_6H_5)_2$: Formation of a Dinuclear Zirconocene(IV) Phosphine Complex via Intermolecular Proton Transfer

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Summary: Carbonylation of $Cp_2Zr(Cl)CH_2PPh_2$ results in the formation of Ph_2PCH_3 and $(Cp_2ZrCl)_2(\mu\text{-}Ph_2PCH{=}CO)$. The latter has been characterized by IR and NMR, and the structure has been determined by X-ray diffraction. A mechanism is proposed involving cleavage of an alkyl-Zr bond by a methylene proton of a simple acyl. Bridging by oxygen and phosphorus then leads to the observed product.

In a recent report Choukroun and Gervais describe the carbonylation of $Cp_2Zr(Cl)CH_2PPh_2$ (1) as leading to the normal acyl product $Cp_2Zr(Cl)COCH_2PPh_2$ (2).[1] In the course of our work in this area[2,3] we had attempted to carry out the same reaction but were puzzled by both the unexpected insolubility of the carbonylation product as well as by its anomalously low infrared CO stretching frequency (ν_{CO} = 1520 cm^{-1}). Typical values for $Cp_2Zr(Cl)COR$ are $\nu_{CO} > 1550$ cm^{-1}.[4] Via a modified carbonylation technique we have recently succeeded in crystallizing a carbonylation product of 1. Herein we describe the structure of this material, an unusually bridged dinuclear complex the formation of which has significant implications on other recent studies of the carbonylation of group 4 metallocene derivatives.

We have carried out carbonylation reactions on 1 in several different ways. Bubbling dry CO through a THF or benzene solution 0.01–0.1 M in 1, or stirring, or shaking such a solution under 1 atm of CO gives rise first to a deep reddish solution showing numerous new NMR resonances in the Cp region. Over a period of hours, the color of the solution fades as the insoluble, white powdery carbonylation product appears. The material is sufficiently soluble in $CDCl_3$ to allow the collection of the following 360-MHz NMR data: δ 5.19 (d, J = 1.5 Hz, 1 H), 6.06 (s, 10 H), 6.12 (d, J = 0.8 Hz, 10 H), 7.45 (m, 6 H), 7.86 (m, 4 H), clearly inconsistent with structure 2. The elemental analysis, even given the usual problems associated with analyses of zirconocene alkyls, is also at odds with a simple acyl.[5] In an attempt to generate crystals of sufficient quality for X-ray analysis, the space above a concentrated THF solution of 1 in an NMR tube was gently flushed and filled with CO, and the system left undisturbed to permit slow diffusion of the gas into the solution. This experiment resulted in the formation of small but suitable crystals for X-ray examination.

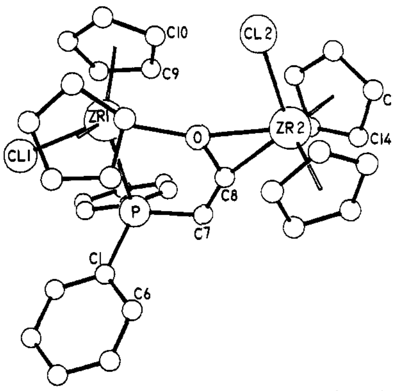

Figure 1. Computer drawn representation of 3. A mirror plane containing atoms Zr(1), Zr(2), Cl(1), Cl(2), P, O, C(7), and C(8) bisects the molecule; thus the two Cp rings on Zr(1) are identical, as are the two Cp rings on Zr(2) and the two phenyl groups on P. In this figure the top of the mirror plane is tilted toward the viewer.

Table I. Selected Bond Lengths (Å) and Angles (deg) for 3

Bond Distances			
Zr(1)-Cl(1)	2.564 (3)	Zr(2)-C(8)	2.231 (9)
Zr(1)-P	2.752 (3)	P-C(7)	1.776 (12)
Zr(1)-O	2.303 (8)	C(7)-C(8)	1.313 (14)
Zr(2)-Cl(2)	2.563 (3)	C(8)-O	1.330 (16)
Zr(2)-O	2.278 (7)		

Bond Angles			
Cl(1)-Zr(1)-P	74.1 (1)	Zr(1)-P-C(7)	101.6 (4)
P-Zr(1)-O	69.7 (2)	Zr(1)-O-C(8)	127.1 (5)
Cl(2)-Zr(2)-O	83.2 (2)	Zr(2)-C(8)-C(7)	159.9 (11)
O-Zr(2)-C(8)	34.3 (4)	Zr(2)-C(8)-O	74.8 (5)
Zr(1)-O-Zr(2)	161.9 (4)	P-C(7)-C(8)	116.3 (10)

Crystals of this material are monoclinic of space group $C2/m$ with a = 16.762 (4) Å, b = 16.366 (4) Å, c = 11.488 (3) Å, β = 112.65 (2)°, V = 2908 (1) Å^3 (T = 140 K), and Z = 4. The structure, determined from 1347 graphite-monochromatized Mo Kα reflections (λ = 0.71069 Å) measured at 140 K for which $I > 3\sigma(I)$, was solved by direct methods (program SHELXTL, version 3). Blocked cascade least-squares refinement of 193 parameters (non-hydrogen atoms anisotropic, hydrogen atoms in calculated positions with fixed geometry) gave final $R = R_w = 0.039$.

The compound is thus identified as an oxygen-bridged dinuclear species with two distinct Cp_2ZrCl fragments also linked by a PCC bridge (Figures 1 and 2 and structure 3). In the bridge, the PCC bond angle is 116°, the OCC bond

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(1) Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1982**, 1300.

(2) Schore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251.

(3) Schore, N. E.; Young, S. J.; Olmstead, M. M.; Hofmann, P. *Organometallics* **1983**, *2*, 1769.

(4) (a) Bertelo, C. A.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 228. (b) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* **1980**, *201*, 389.

(5) Anal. Calcd for $C_{24}H_{22}ClOPZr$ (simple acyl): C, 59.54; H, 4.58; Cl, 7.32; P, 6.40. Calcd for $C_{34}H_{31}Cl_2OPZr_2$ (actual product): C, 55.19; H, 4.22; Cl, 9.58; P, 4.19. Found: C, 53.07; H, 4.20; Cl, 8.83; P, 3.46. The actual purity of **3** as isolated has been determined by NMR of a fully dissolved sample (CD_2Cl_2, 500 MHz): **3**, 97.6%; $(CpZrCl)_2O$, 2.4%; Cp_2ZrCl_2, undetectable (<0.3%). No other non-solvent-derived signals are present.

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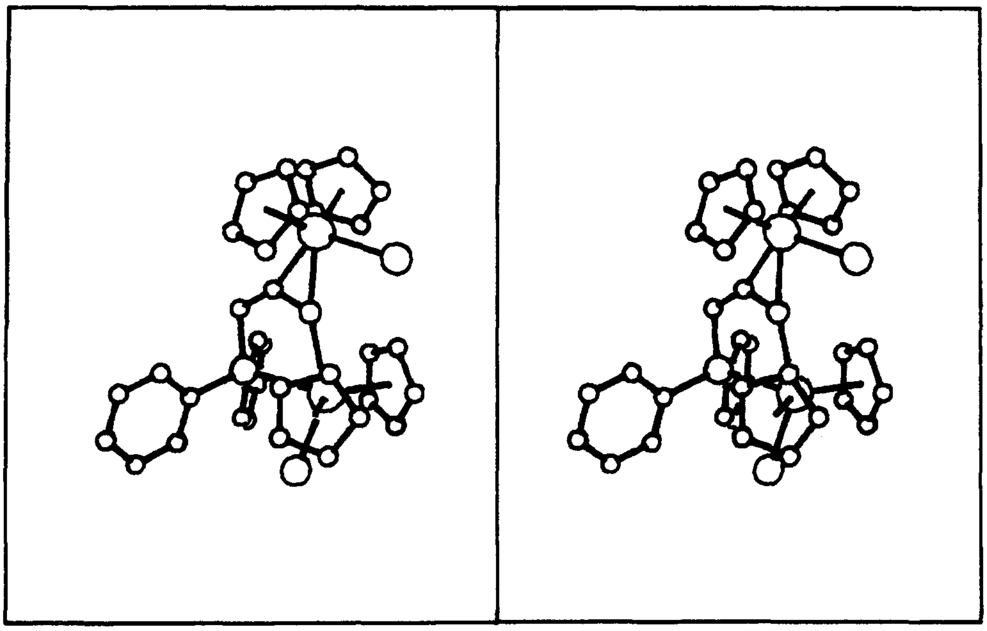


Figure 2. Stereorepresentation of Figure 1.

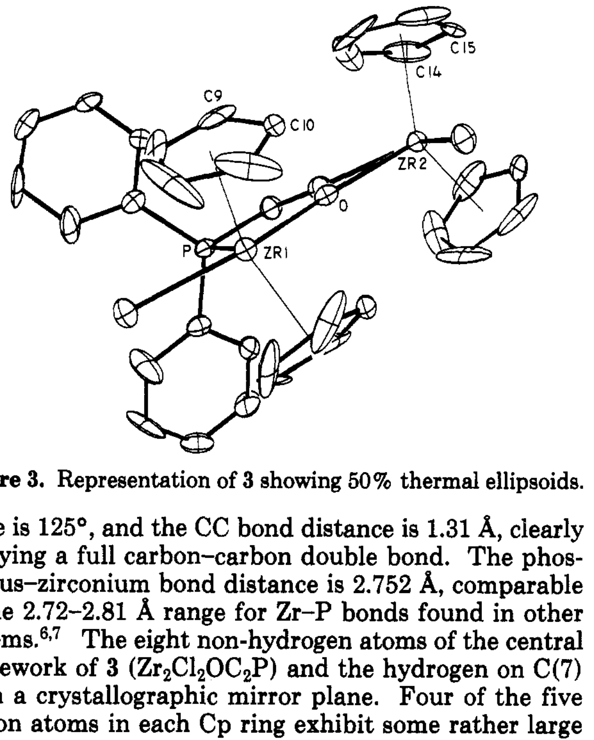
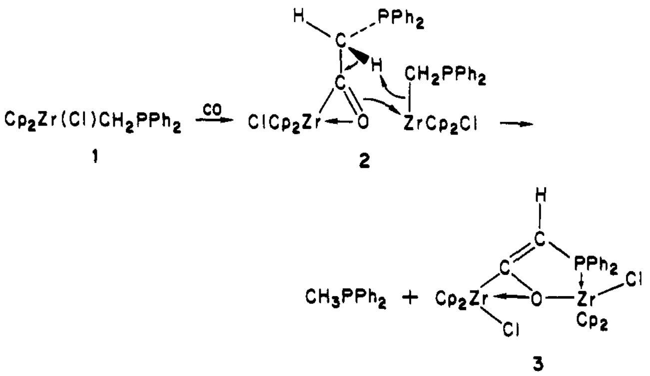


Figure 3. Representation of 3 showing 50% thermal ellipsoids.

Scheme I



angle is 125°, and the CC bond distance is 1.31 Å, clearly implying a full carbon–carbon double bond. The phosphorus–zirconium bond distance is 2.752 Å, comparable to the 2.72–2.81 Å range for Zr–P bonds found in other systems.[6,7] The eight non-hydrogen atoms of the central framework of 3 ($Zr_2Cl_2OC_2P$) and the hydrogen on C(7) lie in a crystallographic mirror plane. Four of the five carbon atoms in each Cp ring exhibit some rather large anisotropic temperature factors, apparently associated with rocking and tilting motions of the rings in the solid state (Figure 3). Bond distances and angles associated with this molecular framework are listed in Table I. The ^{31}P NMR signal for 3 appears at +26.2 ppm, which may be compared with the −1.8 ppm chemical shift for the uncomplexed phosphine of 1.

The structure of 3 is noteworthy for several reasons. It is one of only a very small number of phosphine complexes of any Zr(IV) zirconocene derivative.[7,8] It is also, formally, an "adduct" of the $Ph_2PCH{=}C$: ligand and $(Cp_2ZrCl)_2O$ and is therefore related to the μ-oxymethylene complex recently isolated by Floriani and co-workers,[9] formally an adduct of $:CH_2$ with the same μ-oxide. The presence of this bridging phosphine effectively locks 3 into a planar arrangement. As required by the reaction stoichiometry, methyldiphenylphosphine is observed as the other major product of the carbonylation process. The oxide $(Cp_2ZrCl)_2O$ appears in small amounts (ca. 5%) and is probably due to adventitious hydrolysis of the starting material.

Mechanistically we suggest that the normal acyl 2 is indeed the primary product of the reaction. We believe, however, that the acidity of its methylene protons has been sufficiently enhanced by the surrounding carbonyl and phosphine groups that 2 can directly induce the nucleophile-assisted electrophilic cleavage of the Zr–C bond of an unreacted molecule of 1, utilizing a lone pair on acyl oxygen or, perhaps, phosphorus (e.g., Scheme I).[10] Our observations are therefore in agreement with those of Straus and Grubbs regarding the likely mechanism of the unusual results of carbonylation of $Cp_2Zr(CHPh_2)R$ re-

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(6) See, e.g.: Fischer, M. B.; James, E. J.; McNeese, T. J.; Nybing, S. C.; Posin, B.; Wong-Ng, W.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4941. Fryzuk, M. D.; Williams, H. D.; Rettig, S. J. *Inor. Chem.* **1983**, *22*, 863.

(7) The unstable $(C_5Me_5)_2ZrH_2(PF_3)$ has been characterized spectroscopically at low temperature: Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6733; **1978**, *100*, 2716. Zirconocene "half-sandwich" phosphine complexes are also known: Wengrovius, J. H.; Schrock, R. R. *J. Organomet. Chem.* **1981**, *205*, 319.

(8) Subsequent to the initial submission of this paper the structure determination of a compound analogous to 3 but containing a dimethylphosphine unit appeared: Engelhardt, L. M.; Jacobsen, G. E.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1984**, 220.

(9) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690.

(10) Cf. Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499.

cently reported by the Lappert group.[11]

In preliminary attempts to isolate a true simple acyl of this system, we have found that reaction of 3 with HCl results in quantitative conversion to Cp_2ZrCl_2. Neither Ph_2PCH_3 nor any simple aldehyde is detected, and the fate of the bridging organic ligand is as yet undetermined. Further efforts along these lines are underway, as is a complete mechanistic study of the carbonylation process, which will be published separately.

Acknowledgment. We thank Mr. M. J. Knudsen for providing the 360-MHz NMR spectral data. Purchase of the NT-360 instrument was made possible by an instrumental grant from the National Science Foundation. Grateful acknowledgment is made to the Committee on Research of the University of California and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. N.E.S. thanks the Camille and Henry Dreyfus Foundation for a Teacher–Scholar grant.

Registry No. 1, 74380-49-7; 2, 85369-34-2; 3, 91741-68-3; Ph_2PCH_3, 1486-28-8.

Supplementary Material Available: Experimental details of preparation and X-ray crystal structure determination of 3 and tables of atomic coordinates, bond lengths, bond angles, temperature factors, and derived hydrogen coordinates for 3 (6 pages). Ordering information is given on any current masthead page.

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[11] Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, 462.

Directed Synthesis of Phosphorus-Substituted Cyclopentadienones and Cyclobutadienes via Metal Carbonyl Promoted Coupling of Acetylenes Held Proximate to a Metal

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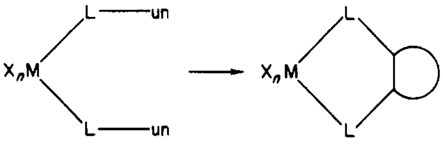
Summary: A strategy for the synthesis of heteroatom-substituted cyclobutadienes and cyclopentadienones via metal carbonyl promoted coupling of acetylenes held proximate via cis coordination to square-planar Pt(II) is outlined. Reaction of *cis*-$Cl_2Pt(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)_2$ with $Fe_2(CO)_9$ gives good yields of the η^4-cyclobutadiene complex $Cl_2Pt[(Ph_2P)_2C_4\text{-}t\text{-}Bu_2]Fe(CO)_3$ (II) which has been characterized by X-ray diffraction. Treatment of *cis*-$X_2Pt(Ph_2PC{\equiv}CR)_2$ (I, X = Cl, Br, I, Ph, 2-Me-C_6H_4, CF_3, C_6F_5; 2X = 1,2-$C_6H_4O_2$; R = Ph, Cy, $SiMe_3$) with $Fe_2(CO)_9$ generates cyclopentadienone derivatives IV (e.g., $Cl_2Pt[(Ph_2P)_2C_4Ph_2CO]Fe(CO)_3$) and/or V (e.g., $(C_6F_5)_2Pt[(Ph_2P)_2C_4Ph_2CO]$), examples of which have been characterized by X-ray analysis.

An attractive strategy for the synthesis of heteroatom-substituted carbocyclic systems is the directed coupling of two unsaturated groups held proximate *outside* the coordination sphere of a transition metal by cis coordination of the heteroatom substituents:



un = -C≡CR; C(H) = CRR'

In principle the method should be applicable to the generation of a wide variety of heteroatom-substituted ring systems including cyclobutadienes (un = C≡CR) or other products of acetylene cyclization and cyclobutanes (un = CH═CRR′) via thermal, photochemical, or organometallic induced coupling.[1] Precoordination of the heteroatoms cis on a metal template has two advantages: (i) competitive involvement of the heteroatom in coupling mechanisms is avoided;[2] (ii) for steric reasons the unsaturated groups can be forced to approach one another quite closely thus facilitating coupling.[3,4] In this communication we describe the application of this strategy to the directed synthesis of novel ligated phosphorus-substituted cyclobutadienes and cyclopentadienones via reactions of the cis platinum(II) compounds $X_2Pt(Ph_2PC{\equiv}CR)_2$ (I, X = Cl, Br, I, Ph, 2-Me-C_6H_4, CF_3, C_6F_5; 2X = 1,2-$C_6H_4O_2$; R = Ph, *t*-Bu, Cy, $SiMe_3$) with $Fe_2(CO)_9$ and $(\eta^5\text{-}C_5H_5)Co(CO)_2$.

Reaction of I (X = Cl, R = *t*-Bu) (0.9 g, 1.13 mmol) with $Fe_2(CO)_9$ (0.41 g, 1.13 mmol) in dichloromethane at room temperature for 1 day followed by column chromatography (Florisil, eluant dichloromethane) and recrystallization from dichloromethane–petroleum ether (30–60 °C) afforded pale yellow crystals of II [76%; IR ($CHCl_3$) ν(CO) 2052, 1997, 1981 cm^{-1}, (Nujol) ν(Pt–Cl) 312, 290 cm^{-1}; ^{31}P NMR ($CDCl_3$) δ 40.3 (1:4:1 t, $^1J_{^{195}Pt\text{-}P}$ = 3760 Hz)]. X-ray crystallography[5] confirmed that II is an η^4-1,2-di-*tert*-butyl-3,4-bis(diphenylphosphino)cyclobutadiene complex (Figure 1). The corresponding photolytic reaction with $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (C_6H_6, 6 h at room temperature) yielded the η^5-cyclopentadienyl η^4-cyclobutadiene complex III in 70% yield. The remarkable feature of these two reactions is the specificity for a single product, the cyclobutadiene complex in relatively high yield. The contrast with other (acetylene)iron carbonyl reactions[6] where cyclobutadiene complexes are produced in low yield, among a plethora of

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[1] For reviews of thermal, photochemical and metal catalyzed alkyne oligomerizations see: (a) Fuks, R.; Viehe, H. G. In "Chemistry of Acetylenes" Viehe, H. G., Ed.; Marcel Dekker: New York, 1969; Chapter 8. (b) Coyle, R. D. In "The Chemistry of the Carbon-Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1978; Chapter 12. (c) Collman, J. P.; Hegedus, L. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; Chapter 13.

[2] Transition metal catalyzed or stoichiometric alkyne cyclizations are not generally applicable to N-, P-, or S-substituted acetylenes because the heteroatom, a Lewis base, competes effectively for metal coordination sites blocking the normal oligomerization mechanisms.

[3] Carty, A. J.; Taylor, N. J.; Johnson, D. K. *J. Am. Chem. Soc.* **1979**, *101*, 5422.

[4] Carty, A. J.; Johnson, D. K.; Jacobson, S. E. *J. Am. Chem. Soc.* **1979**, *101*, 5612.

[5] Crystal data for $PtFeCl_2P_2O_3C_{39}H_{38}\cdot 2CHCl_3\cdot 0.5CH_2Cl_2$: space group $P2_1/n$, a = 14.649 (1) Å, b = 18.517 (2) Å, c = 18.135 (2) Å, β = 91.52 (1)°, Z = 4, ρ_{calcd} = 1.647 g cm^{-3}, and $F(000)$ = 2404. The structure was solved and refined by using 4736 observed intensities measured on a Syntex $P2_1$ diffractometer to R and R_w values of 0.049 and 0.060, respectively. Full details of data collection, reduction, and refinement are listed in Table SI. The molecule consists of a planar cyclobutadiene ring with *cis*-di-*tert*-butyl and *cis*-diphenylphosphino groups, coordinated in η^4-fashion to an $Fe(CO)_3$ moiety and formed via coupling of the two phosphinoacetylene groups coordinated cis to the square-planar platinum atom. The C_4 ring is slightly rectangular with the C(4)–C(5) and C(6)–C(7) bond lengths (average 1.492 Å) being slightly longer than the C(5)–C(6) and C(4)–C(7) bonds (average 1.447 Å). The iron atom is symmetrically bound to the C_4 ring (Fe–C(4) = 1.989 (10) Å, Fe–C(5) = 2.109 (10) Å, Fe–C(6) = 2.136 (10) Å, and Fe–C(7) = 2.020 (10) Å).

[6] (a) Hubel, W. In "Organic Synthesis via Metal Carbonyls"; Wender, I., and Pino, P., Eds.; Wiley: New York, 1968; p 273. (b) Efraty, A. *Chem. Rev.* **1977**, *77*, 691.

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