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Synthesis and Characterization of (μ-Cyclopropylidene)diiron Complexes *cis*- and *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}\overline{CCH_2C}H_2)$. Models for Intermediates in Hydrocarbation and Fischer–Tropsch Mechanisms

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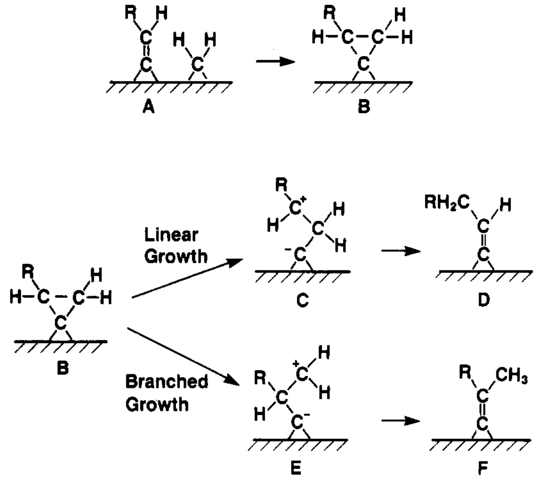
Diiron complexes, containing the novel μ-cyclopropylidene ligand, *cis*- and *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}\overline{CCH_2C}H_2)$ have been prepared by reaction of the corresponding μ-vinylidene complexes with diazomethane in the presence of CuCl. The structures were characterized by ^1H and ^{13}C NMR, IR, and mass spectra and by an X-ray crystal structure of the cis complex. This complex crystallizes from ether in the orthorhombic space group *Pnma* with a = 13.008 (77) Å, b = 14.126 (71) Å, c = 7.835 (127) Å, and Z = 4. The structure was refined to R = 0.032 and R_w = 0.037 for 446 observed reflections. The bridging cyclopropylidene ring has 1.51 (2) Å (average) C–C bonds typical of 1,1-disubstituted cyclopropanes and occupies the crystallographic mirror plane bisecting the Fe–Fe bond (2.503 (7) Å). The remainder of the molecule has bonding similar to that in other *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CX)$ species. These complexes are models for intermediates in hydrocarbation and Fischer–Tropsch reactions.

Introduction

The relevance of transition-metal complexes with carbene and carbyne ligands to mechanisms of important catalytic processes such as the Fischer–Tropsch synthesis and olefin metathesis has led to extensive recent research into the chemistry of these species.[1] Of pertinence to this report, a large number of μ-alkylidene complexes have been synthesized and characterized where the pendant groups R and R′ on the bridging alkylidene ligand μ-CRR′ may be hydrogen, alkyls, aryls, or more complex structures such as cycloalkylidenes.[1,2] Herrmann and co-workers, in particular, have recently reported synthesis of the bridging cycloalkylidene species with ring sizes of four carbons and larger.[2] The work reported herein was begun for the purpose of finding models for intermediates postulated by McCandlish in a novel mechanism for carbon–carbon bond formation in the Fischer–Tropsch synthesis.[3] While it was in progress, Casey and Fagan reported the hydrocarbation reaction wherein the C–H bond of the bridging methylidyne ligand in $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)]^+$ (Cp = η^5-C_5H_5) adds across alkenes[4] and suggested as a possible intermediate the protonated form of a cyclopropylidene complex. We wish to report here the first synthesis of stable complexes with the bridging cyclopropylidene ligand and the crystallographic characterization of one of them. The chemistry of this complex as a model for hydrocarbation and Fischer–Tropsch synthesis mechanisms has been explored and will be reported elsewhere.



The McCandlish mechanism for chain growth in CO hydrogenation was proposed to account for certain regularities observed, in branching distributions of Fischer–Tropsch products.[3] The key steps, leading to branched or linear chain growth, are shown in Scheme I. In the first step in chain growth, the vinylidene species A was postulated to react with methylene to yield a cyclopropylidene species, B, a reaction with many analogues in the organic chemistry of alkenes.[5] The cyclopropylidene was then proposed to rearrange to a homologous vinylidene species, D or F. One possible route for such a rearrangement, shown in Scheme I, is a heterolytic bond scission followed by hydride transfer to the carbenium ion center. If one postulates such a heterolytic bond breaking (perhaps with stabilization of the negative charge by additional bonding to the metal surface of a carbyne nature), then the relative stabilities of the carbenium ions in C and E predict, in accordance with observed branching distributions, that linear chain growth should predominate.

There are many organometallic models for surface-bound methylene,[1] and the recent work of Pettit and co-

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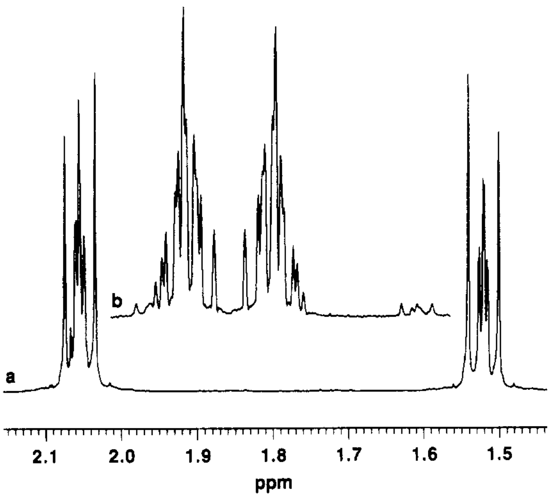
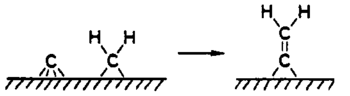


Figure 1. 400-MHz ^1H NMR spectra of the cyclopropylidene hydrogens of **2c** (a, in acetone-d_6) and **2t** (b, in $CDCl_3$). In spectrum b, peaks due to **2c** in $CDCl_3$ (which arose from equilibration of **2t** during the time of spectral accumulation) are visible, centered at δ 1.61 and 1.96. Spectrum b was plotted with 2-Hz resolution enhancement.

workers[6] strongly implicates the intermediacy of methylene in the Fischer–Tropsch reaction. There are also many examples of briding vinylidene and derivatives in organometallic chemistry,[7] and surface-bound vinylidenes have been reported to form from acetylene adsorbed on Pt(111) and Pd(111) surfaces.[8]

Although, during Fischer–Tropsch synthesis, the vinylidene species could very conceivably be formed from reaction of methylene with a surface carbide atom (eq 1),



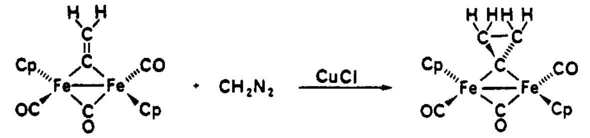
(1)

there had been no suggestion, prior to that of McCandlish, that vinylidene might play a role in the mechanism. Very recently, however, Ibach and co-workers have reported finding what they identify by EELS spectroscopy as vinylidene, along with CH_2 and CH species, on an Fe(110) surface following a period of Fischer–Tropsch synthesis.[9]

For the key intermediate in Scheme I, the cyclopropylidene species B, there was neither an organometallic model nor mechanistic precedent. For this reason, we set out to synthesize an analogue and to study its chemistry.

Results and Discussion

The bridging vinylidene complexes $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$, **1t** and **1c**, with the cyclopentadienyl groups trans and cis, respectively, to the $Fe_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ plane were chosen as convenient model complexes and were synthesized according to literature methods.[7a,b] Treatment of **1t** or **1c** directly with excess diazomethane in ether produced no apparent reaction. However, taking a cue from the literature on cyclopropanation of alkenes,[10] cuprous chloride was found to be an effective catalyst for the smooth conversion of the bridging vinylidene to bridging cyclopropylidene with diazomethane (eq 2). For example, dropwise addition of



(2)

1t **2t**

0.2 M diazomethane in ether to **1t** and CuCl slurried in ether led to decomposition of the diazomethane and reaction with the vinylidene ligand. The progress of the reaction was followed by IR spectroscopy (hexane) which showed smooth replacement of **1t** bands (1962 (vs), 1808 (s), 1603 (vw), 1562 (w) cm^{-1}) by those of **2t** (1954 (vs), 1802 (s) cm^{-1}). After about 5–10 equiv of CH_2N_2 were added, only **2t** was visible in solution. Filtration to remove CuCl, evaporation of the filtrate, and recrystallization from pentane gave purple **2t**. The red cis complex **2c** was prepared similarly but could be recrystallized from ether because of its lower solubility.

These cyclopropylidene complexes are air stable in the solid state, and even the solutions are stable in the air for several hours, provided they are kept in the dark. However, upon exposure to fluorescent light, solutions begin to decompose within minutes. Solutions of pure **2t** or **2c** like those of **1t** and **1c**[7c] and other alkylidene complexes[7b] slowly interconvert. The final equilibrium cis to trans ratio of **2c**:**2t** by NMR (after 2 weeks in solution) is 4.8:1.

Formulation of the products **2t** and **2c** as containing a bridging cyclopropylidene ligand was supported by IR, NMR, and mass spectral data. Their IR spectra (hexane) showed loss of the two weak bands associated with the vinylidene ligand (at 1603 (vw) and 1562 (w) cm^{-1} in both **1t** and **1c**) but implied retention of the gross carbonyl structure with two terminal and one bridging carbonyl. The 400-MHz ^1H NMR spectrum of both **2t** and **2c** showed 10 equivalent cyclopentadienyl protons and four additional protons in the methylene region with structure consistent with the expected AA′BB′ coupling patterns (Figure 1). For **2t**, the two hydrogens on each of the carbon atoms of the cyclopropylidene that are not bonded to iron are chemically nonequivalent, one being closer to a terminal carbonyl and the other closer to the cyclopentadienyl, but the chemical shift difference is small. There is a C_2 axis in the idealized structure that relates each hydrogen atom to a chemically equivalent but magnetically nonequivalent hydrogen atom on the other car-

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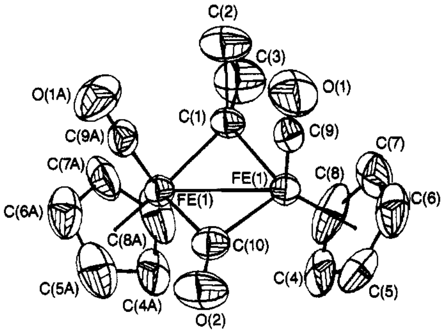

Figure 2. ORTEP drawing of the molecular structure of *cis*-$Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}\overline{CCH_2CH_2})$ (**2c**) (minus hydrogens) with thermal ellipsoids at the 50% probability level.

bon. In the idealized structure of **2c**, the plane of the cyclopropylidene ring is a mirror plane. Thus the two hydrogen atoms attached to a carbon are chemically equivalent but are magnetically nonequivalent due to different cis and trans coupling to the other proton pair. The chemical shift difference between the CH_2 on the cyclopentadienyl side of the molecule and the CH_2 on the carbonyl side is greater than was the A – B difference in **2t**. In fact, the methylene protons of **2c** in acetone-d_6 give symmetrical 10-line patterns sufficiently separated in chemical shift (δ 2.054 and 1.521) for analysis as an AA′XX′ spectrum.[11] This analysis gives $J_{AA'} = -8.1$ Hz, $J_{XX'} = -7.6$ Hz, J_{AX}(cis) = 10.4 Hz, and $J_{AX'}$(trans) = 5.7 Hz. Which CH_2 is the A pair and which is the X is not known. These coupling constants are consistent with reported constants for cyclopropyl protons.[12] The $^{13}C\{^1H\}$ NMR chemical shifts of **2t** and **2c** are consistent with those reported for alkylidene complexes of the $Cp_2M_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CRR')$ type.[1,7b,e,16] The gated coupled ^{13}C NMR spectra show triplets of triplets for the resonances at δ 22.3 for **2t** and at δ 22.3 and 21.6 for **2c**, doublets of quintets for the cyclopentadienyls, and a quintet for the bridging carbon of the cyclopropylidene ligand, consistent with their assignments.

Mass spectra (70 eV, EI) for **2t** and **2c** are essentially identical and show molecular ions at *m/e* 366 and major peaks for sequential loss of three CO's and a C_3H_4 fragment to reach $Cp_2Fe_2^+$; Cp_2Fe^+ is the base peak of the spectra.

X-ray Crystal Structure. Due to the novelty of the cyclopropylidene ligand, a single-crystal X-ray structural analysis of **2c** was undertaken.

A labeled ORTEP drawing of the complex is shown in Figure 2. A summary of crystallographic data and the experimental conditions are given in Table I and the Experimental Section. The atomic parameters and important bond lengths and angles are given in Tables II and III, respectively.

Table I

A. Crystal Data

formula	$Fe_2C_{16}H_{14}O_3$
fw	366.0
space group	*Pnma*
lattice constants	
a, Å	13.008 (77)
b, Å	14.126 (71)
c, Å	7.835 (127)
V, Å^3	1439.7
Z	4
ρ_{calcd}, g/cm^3	1.688

B. Data Collection

diffractometer	Enraf-Nonius CAD-4
radiatn	Mo Kα, 0.7107 Å
monochromator	graphite
scan range, deg	$0 < 2\theta < 25$
scan speed, deg/min	4-20
reflctns examined	1299
reflctns obsd	446
criterion	$I > 3\sigma(I)$
abs corr	
μ, cm^{-1}	20.20
scan type	ψ scans
max/min, deg	0.91-1.00
stability	no intensity decay in 3 check reflctns

Table II. Positional Parameters for 2c and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, Å^2
Fe(1)	0.14778 (8)	0.33858 (7)	0.0409 (1)	3.09 (2)
C(1)	0.2432 (7)	0.250	−0.064 (1)	3.4 (2)
C(2)	0.296 (1)	0.250	−0.237 (2)	6.4 (4)
C(3)	0.359 (1)	0.250	−0.077 (2)	7.1 (4)
C(4)	0.1555 (9)	0.3722 (7)	0.3037 (9)	7.6 (3)
C(5)	0.0936 (8)	0.4349 (6)	0.224 (1)	7.0 (3)
C(6)	0.1460 (9)	0.4820 (6)	0.104 (1)	6.3 (2)
C(7)	0.2479 (7)	0.4489 (6)	0.105 (1)	6.2 (2)
C(8)	0.2529 (7)	0.3801 (7)	0.229 (1)	6.9 (2)
C(9)	0.1013 (5)	0.3612 (5)	−0.1617 (9)	3.5 (2)
C(10)	0.0387 (8)	0.250	0.078 (1)	3.6 (3)
O(1)	0.0734 (5)	0.3773 (5)	−0.2966 (6)	6.0 (2)
O(2)	−0.0493 (6)	0.250	0.110 (1)	6.0 (2)
H1	0.306	0.337	0.259	5.0
H2	0.140	0.336	0.402	5.0
H3	0.029	0.451	0.253	5.0
H4	0.127	0.525	0.019	5.0
H5	0.301	0.474	0.030	5.0
H6	0.296	0.195	−0.310	5.0
H7	0.389	0.195	−0.033	5.0

[a] Hydrogen atoms were not refined. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Each of the four $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}\overline{CCH_2CH_2})$ molecules per unit cell has a crystallographically imposed mirror plane that includes the plane of the cyclopropylidene ligand and the atoms of the bridging carbonyl ligand. The two Fe atoms are related by this plane at an Fe–Fe bond distance of 2.503 (7) Å. Distances and angles for related molecules are given in Table IV. The Fe–Fe bond length for **2c** is significantly shorter than that of the parent carbonyl (**6**) and the ethylidene complex **3** and slightly shorter than complexes with vinylidene bridges (**4**, **5**). Shortening of the Fe–Fe distance, relative to the dicarbonyl complex **6**, has been attributed to enhanced π acceptance by the bridging ligand,[14] but this behavior was also associated with shorter Fe–C (bridge) bonds as well (note complexes **4**, **7**, **8**). Complex **5**, however, has similar geometry to **2c**: a shorter Fe–Fe bond and yet a longer

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Table III. Selected Bond Lengths (Å) and Angles (deg) for **2c**

Bond Lengths

bond	length
Metal-Metal	
Fe(1)-Fe(1)′	2.503 (7)
Fe to Carbonyl	
Fe(1)-C(10)	1.914 (10)[a]
Fe(1)-C(9)	1.728 (10)[b]
Fe to Ring Carbons	
Fe(1)-C(1)	1.943 (8)[c]
Fe(1)-C(4)	2.116 (9)[d]
Fe(1)-C(5)	2.099 (11)[d]
Fe(1)-C(5)	2.086 (9)[d]
Fe(1)-C(7)	2.092 (9)[d]
Fe(1)-C(8)	2.091 (9)[d]
Carbon to Oxygen	
C(10)-O(2)	1.173 (13)[a]
C(9)-O(1)	1.141 (10)[b]
Carbon to Carbon	
C(1)-C(2)	1.519 (18)[c]
C(1)-C(3)	1.513 (17)[c]
C(2)-C(3)	1.501 (19)[c]
C(4)-C(5)	1.351 (16)[d]
C(4)-C(8)	1.401 (15)[d]
C(5)-C(6)	1.336 (16)[d]
C(6)-C(7)	1.406 (16)[d]
C(7)-C(8)	1.373 (15)[d]

Bond Angles

C(1)-Fe(1)-C(10)	96.7 (3)	C(4)-C(5)-C(6)	110.3 (13)	C(5)-Fe(1)-C(10)	94.1 (5)
C(1)-Fe(1)-C(9)	87.5 (4)	C(5)-C(6)-C(7)	108.2 (10)	C(6)-Fe(1)-C(1)	137.1 (5)
C(10)-Fe(1)-C(9)	90.0 (4)	C(6)-C(7)-C(8)	106.5 (11)	C(6)-Fe(1)-C(9)	92.0 (4)
Fe(1)-C(1)-C(2)	131.6 (5)	C(7)-C(8)-C(4)	108.0 (10)	C(6)-Fe(1)-C(10)	126.2 (6)
Fe(1)-C(1)-C(3)	131.7 (5)	Fe(1)-C(1)-Fe(1)′	80.2 (3)	C(7)-Fe(1)-C(1)	100.6 (5)
Fe(1)-C(10)-O(2)	139.2 (3)	Fe(1)-C(10)-Fe(1)′	81.7 (3)	C(7)-Fe(1)-C(9)	107.5 (4)
Fe(1)-C(9)-O(1)	178.0 (5)	C(4)-Fe(1)-C(1)	121.6 (6)	C(7)-Fe(1)-C(10)	155.8 (4)
C(2)-C(1)-C(3)	59.4 (9)	C(4)-Fe(1)-C(9)	150.3 (6)	C(8)-Fe(1)-C(1)	93.4 (4)
C(1)-C(2)-C(3)	60.1 (9)	C(4)-Fe(1)-C(10)	96.7 (3)	C(8)-Fe(1)-C(9)	145.3 (6)
C(2)-C(3)-C(1)	60.5 (9)	C(5)-Fe(1)-C(1)	156.9 (5)	C(8)-Fe(1)-C(10)	124.2 (6)
C(5)-C(4)-C(8)	107.1 (11)	C(5)-Fe(1)-C(9)	113.0 (5)		

[a] Bridged. [b] Terminal. [c] Cyclopropylidene. [d] Cyclopentadienyl.

Table IV. Comparison of Geometric Parameters for Related Diiron Complexes[a]

complex	ref	Fe-Fe	Fe-CO (bridge)	Fe-CO (terminal)	Fe-C (bridge)	fold angle
2c, *cis*-$Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_2)$	*b*	2.503 (7)	1.914 (10)	1.728 (10)	1.943 (8)	158
3, *cis*-$Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$	13	2.525 (1)	1.905 (3)	1.742 (1)	1.987 (1)	166
4, *cis*-$Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}C(CN)_2)$[c]	14	2.511 (4)	1.94 (3)	1.79 (2)	1.87 (2)	162
5, *cis*-$Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}C(Ph)CH_2Ph)$	15	2.5104 (5)	1.928 (3)	1.741 (3)	1.940 (2)	155
6, *cis*-$Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$	16	2.531 (2)	1.92 (1)	1.75 (2)	1.92 (1)	164
7, *cis*-$Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CS)$[c]	17	2.505 (3)	1.916 (8)	1.746 (8)	1.886 (8)	166
8, *cis*-$Cp_2Fe_2(CO)_2(\mu\text{-}CO\cdot AlEt_3)_2$	18	2.491 (8)		1.70 (2)	1.88 (2)	167

[a] Bond lengths in Å and angles in deg. Fold angle is dihedral angle between Fe–C–Fe′ planes. [b] This work. [c] Average values for two independent molecules.

Fe–C(bridge) than **6**. In general, the overall geometry of **2c** more closely resembles that of the vinylidene complex **5** than that of the ethylidene complex **3**. It has been noted before that cyclopropyl groups are similar to double bonds in many respects, including the ability to conjugate with neighboring π orbitals[19] and for methylenecyclopropane to mimic 1,2-dienes in complexes with transition metals.[20]

The C–C bond lengths within the cyclopropylidene ligand are all equal, within the accuracy of the determination, and average 1.51 (2) Å. This average is in good agreement with the value normally found in cyclopropane rings.[19,21] However, the commonly observed shortening of the C–C bond across the ring from substituents with π-bonding capabilities[19] cannot be confirmed for **2c** due to experimental uncertainty.

Other crystallographic data is given in the supplementary material.

Experimental Section

All reactions were carried out under a nitrogen atmosphere—either in a drybox or by use of standard Schlenk techniques. Methylene chloride was distilled from P_4O_{10}; other solvents were distilled from sodium benzophenone ketyl, and all were stored under N_2 prior to use. Diazomethane in ether (~0.2–0.3 M) was prepared according to the published procedure.[22] The cis and trans isomers of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$, **1c** and **1t**, were prepared by literature procedures,[7a-c] separated by CH_2Cl_2/hexane chromatography on neutral alumina (3% water added), and recrystallized prior to use from ether (**1c**) or pentane (**1t**). Cuprous chloride (99.99%) was purchased from Aldrich and used as received.

Infrared spectra were recorded on a Perkin-Elmer Model 684 infrared spectrophotometer. Proton and ^{13}C NMR spectra were obtained with a JEOL JNM GX-400 FT NMR spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C. Mass spectra were provided by our Analytical Division. Galbraith Laboratories, Knoxville, TN, performed the microanalyses.

***trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_2)$ (2t).** A solution of CH_2N_2 in ether (20 mL of 0.19 M, 5 equiv) was added slowly with vigorous stirring to a slurry of **1t** (275 mg, 0.76 mmol) and CuCl (0.20 g, 2.0 mmol) in 10 mL of ether. The mixture was filtered, and the filtrate was evaporated to dryness and then extracted with 100 mL of pentane. Yield after evaporation of pentene, collection of the crystals, and washing with pentane was 112 mg (40%) of purple **2t**: mp 164–165 °C dec; IR (hexane) 1954 (vs), 1802 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.52 (10 H, s, Cp), 1.86

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(center, 4 H, AA′BB′, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 274.5 (μ-CO), 212.2 (CO), 158.5 (μ-C, quintet, $J_{C\text{-}C\text{-}H}$ = 4.5 Hz), 90.3 (C_5H_5, doublet of quintets, $J_{C\text{-}H}$ = 178.5 Hz, $J_{C\text{-}C\text{-}H}$ = $J_{C\text{-}C\text{-}C\text{-}H}$ = 6.7 Hz), 22.2 (CH_2CH_2, triplet of triplets, $J_{C\text{-}H}$ = 159.1 Hz, $J_{C\text{-}C\text{-}H}$ = 4.1 Hz), MS (70 eV), *m/e* 366 (M^+), 338 (M^+ − CO), 310 (M^+ − 2CO), 282 (M^+ − 3CO), 242 (M^+ − 3CO − C_3H_4). Anal. Calcd for $C_{16}H_{14}O_3Fe_2$: C, 52.51; H, 3.86; Fe, 30.52. Found: C, 52.30; H, 3.97; Fe, 29.89.

***cis*-(η^5-C_5H_5)$_2$$Fe_2(CO)_2$($\mu$-CO)($\mu$-$\overline{\text{CCH}_2\text{C}}\text{H}_2$) (2c).** A total of 165 mL of CH_2N_2 in ether (0.19 M, 11.2 equiv) was added dropwise with vigorious stirring to a slurry of **1c** (1.00 g, 2.8 mmol) and CuCl (0.5 g, 5 mmol) in ether (15 mL). The mixture was filtered and the ether solution concentrated to yield 836 mg (80%) of red crystalline **2c**: mp 161–162 °C dec; IR (hexane) 1996 (vs), 1961 (m), 1802 (s) cm^{-1}; ^1H NMR (acetone-d_6) δ 4.76 (10 H, s, Cp), 2.05, 1.52 (4 H, AA′XX′, $J_{AA'}$ = −8.1 Hz, $J_{XX'}$ = −7.6 Hz, J_{AX}(cis) = 10.4 Hz, $J_{AX'}$(trans) = 5.7 Hz, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 273.5 (μ-CO), 212.4 (CO), 155.8 (μ-C, quintet, $J_{C\text{-}C\text{-}H}$ = 4.5 Hz), 88.3 (C_5H_5 doublet of quintets, $J_{C\text{-}H}$ = 177.9 Hz, $J_{C\text{-}C\text{-}H}$ = $J_{C\text{-}C\text{-}C\text{-}H}$ = 6.6 Hz), 22.3 (CH_2, triplet of triplets, $J_{C\text{-}H}$ = 157 Hz, $J_{C\text{-}C\text{-}H}$ = 2.5 Hz), 21.6 (CH_2, triplet of triplets, $J_{C\text{-}H}$ = 158 Hz, $J_{C\text{-}C\text{-}H}$ = 2.5 Hz); MS (70 eV), *m/e* 366 (M^+), 338 (M^+ − CO), 310 (M^+ − 2CO), 282 (M^+ − 3CO), 242 (M^+ − 3CO − C_3H_4). Anal. Calcd for $C_{16}H_{14}O_3Fe_2$: C, 52.51; H, 3.86; Fe, 30.52. Found: C, 52.69; H, 3.93; Fe, 30.75.

X-ray Analysis. The complex crystallizes from ether as red prisms. Diffraction data were collected on a crystal of dimensions 0.40 mm × 0.30 mm × 0.20 mm. A summary of crystallographic data and the experimental conditions are given in Table I. Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer and were corrected for absorption (μ = 20.2 cm^{-1}, empirical ψ scan technique). All calculations were performed by using the SDP package provided by Enraf-Nonius. The iron atoms were located by inspection of a three-dimensional Patterson function and the remaining non-hydrogen atoms by least-squares structure factor calculations and difference Fourier techniques. Positions of the hydrogen atoms were then found by a combination of difference Fourier techniques and the use of HYDRO from the SDP package. The hydrogen positions were not refined. All non-hydrogen positions were then refined with anisotropic thermal parameters. Least-squares refinement converged with residuals of $R = 0.032$, $R_w = 0.037$, using 446 data with $I > 3\sigma(I)$ from 2θ(Mo Kα) = 0–25°, the esd of an observation of unit weight was 1.091.

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Registry No. **1c**, 86420-26-0; **1t**, 86420-25-9; **2c**, 91547-48-7; **2t**, 91443-97-9; CH_2N_2, 334-88-3.

Supplementary Material Available: Tables listing least-squares planes and deviations (Table V), dihedral angles between the planes (Table VI), anisotropic thermal parameters (Table VII), and observed and calculated structure factor amplitudes (Table VIII) (6 pages). Ordering information is given on any current masthead page.

Syntheses, Molecular Structures, and Stabilities of Binuclear Complexes [$Pt_2Me_4(\mu\text{-}R_2PCH_2PR_2)_2$]

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Synthetic routes to binuclear complexes [$Pt_2Me_4(\mu\text{-}R_2PCH_2PR_2)_2$] (**1**, R = Me; **2**, R = Ph; **3**, R = Et) and to the mononuclear complexes [$PtMe_2(R_2PCH_2PR_2)$] (**4**, R = Ph; **5**, R = *i*-Pr) have been developed. The structures and conformations of the binuclear complexes have been studied in solution by variable-temperature ^1H and ^{31}P NMR spectroscopy. The molecular structures of **1** and **2**, determined by X-ray diffraction techniques, each contain two *cis*-$PtMe_2$ fragments held together by two bridging $R_2PCH_2PR_2$ ligands. The approximate molecular symmetry is C_{2h} in **1** and C_2 in **2**, and the eight-membered $Pt_2P_4C_2$ dimetallacycles adopt twist-chair and twist-boat conformations, respectively. In **1** the local environments of the platinum atoms are sterically more open than in **2**, where the phenyl substituents may hinder access of reagents to the metal centers. Crystals of **1** are monoclinic of space group $P2_1/a$ with a = 16.634 (4) Å, b = 11.112 (3) Å, c = 12.469 (3) Å, β = 103.40 (2)°, and Z = 4. Crystals of **2** are monoclinic of space group $P2_1/c$ with a = 13.957 (7) Å, b = 17.218 (5) Å, c = 21.649 (5) Å, β = 106.45 (3)°, and Z = 4. Least-squares refinement of the structural model of **1** defined by 181 parameters converged at a conventional R index on F of 0.043 for 3646 reflections with $I \geq 3\sigma(I)$. For **2**, the structural model involved 175 parameters and the final value of the R factor based on F was 0.068 for 3818 reflections. It is concluded that increasing steric bulk of substituents R (i) stabilizes the mononuclear with respect to the binuclear complex, (ii) is primarily responsible for determining the ground-state conformations of the binuclear complexes and the activation energies for fluxionality, and (iii) greatly decreases the reactivity of the complexes, and particularly the binuclear ones, toward oxidative addition reactions.

Introduction

In the development of the chemistry of binuclear complexes, it is often desirable to lock together two metal centers using bridging ligands.[2,3] Di(tertiary phosphines) are particularly useful for this purpose, but there is much to be learned about the factors that influence whether such ligands will bridge or chelate.[4-7] For example, ligands

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