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Synthesis of Heterotrinuclear Complexes Containing Pt–Hg–M (M = Mo, W) Chains via Platinum(0) Insertion Reactions. Crystal Structure of $(PPh_3)_2(C_6Cl_5)Pt–Hg–W(CO)_3(\eta\text{-}C_5H_5)$

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The organobimetallic complexes $(C_6Cl_5)Hg–M(CO)_3Cp$ (M = Mo, W; Cp = η-C_5H_5) react in toluene with 1 equiv of $Pt(CH_2{=}CH_2)(PPh_3)_2$, affording the insertion products $[(PPh_3)_2(C_6Cl_5)Pt–Hg–M(CO)_3Cp]$ (M = Mo, 1; M = W, 2). That Pt(0) insertion had occurred into the Hg–C bond and not into the Hg–M bond was established by an X-ray diffraction study of 2. It crystallizes in the space group $P\bar{1}$ with a = 12.122 (3) Å, b = 13.287 (6) Å, c = 18.961 (17) Å, α = 63.27 (6)°, β = 65.25 (6)°, γ = 70.24 (4)°, V = 2434 (4) Å^3, and Z = 2. The structure was refined by using the 2330 reflections with $I \geq 2.5\sigma(I)$ to R = 0.022 and R_w = 0.025. The mercury atom shows a linear coordination with the W–Hg–Pt angle equal to 171.9 (1)° and the Hg–Pt and W–Hg bond distances are 2.572 (1) and 2.755 (1) Å, respectively.

Introduction

Insertion of the 14-electron, carbene-like "PtL_2" fragment into Hg–X (X = halide) or Hg–E (E = group 4 atom) bonds is a general method for obtaining heterobimetallic platinum–mercury bonded complexes. Typical sources of "$Pt(PPh_3)_2$" are the complexes $Pt(PPh_3)_n$ (n = 3 or 4) and $Pt(CH_2{=}CH_2)(PPh_3)_2$. Reactions of zerovalent platinum complexes with *symmetrical* HgX_2 or HgE_2 complexes, e.g., $HgCl_2$,[1] $Hg[GeR_3]_2$,[2] or HgR_2 (R = organic group),[3] have been reported. In general, only *monoinsertion* reactions are observed because this step usually deactivates the second Hg–X or Hg–E bond toward further insertion. However, two exceptions have been reported recently:the *diinsertion* of PtL_2 into HgR_2 (R = polychloroaryl groups) and into $Hg[Ge(CF_3)_3]_2$ can occur to afford R–Pt–Hg–Pt–R[4] and Ge–Pt–Hg–Pt–Ge arrays,[5] respectively. These studies lead to the following general observations: (i) Stable platinum–mercury compounds are best obtained by this route when R is a strongly electronegative group (e.g., R = CF_3,[6a] C_6F_5[6b]) or when steric crowding occurs near the intermetallic bond (e.g., R = C_6Cl_5[3b]). (ii) In general, "$Pt(PPh_3)_2$" insertion into Hg–X bonds affords a trans product whereas insertion into Hg–E bonds affords a cis product. However, isomerization subsequent to the insertion reaction is possible and may be reversible, as shown, e.g., by the temperature-dependent cis $\rightleftharpoons$ trans dynamic behavior of $(PPh_3)_2Pt(HgGePh_3)(GePh_3)$.[7] (iii) The migration of Cl from Hg to Pt is easier than that of R, and within the organic groups the following sequence is observed: alkyl > phenyl.[8] This trend contrasts with the results reported for tin in place of mercury.[9]

Using *unsymmetrical* mercury complexes as precursors, e.g., X–Hg–E or E–Hg–E′ types, raises the question of the selectivity of the insertion reaction.[10] Where will Pt(0) insertion occur and will a mono- or diinsertion be observed? Thus, reacting RHgCl with $Pt(C_2H_4)(PPh_3)_2$ selectively affords the product of insertion into the Hg–Cl bond, *trans*-$(PPh_3)_2ClPtHgR$.[11] This is consistent with the general trends indicated above under (ii) and (iii). Within the E–Hg–E′ series, $Pt(PPh_3)_2$ insertion only occurs into the Hg–Ge bond of Et–Hg–$Ge(C_6F_5)_3$,[12] whereas the major insertion product obtained from $(C_6F_5)_3Ge$–Hg–$Sn(C_6F_5)_3$ contains the linkage Ge-Hg-Pt-Sn, the minor isomer having a Ge–Pt–Hg–Sn skeleton.[13] Thus, the re-

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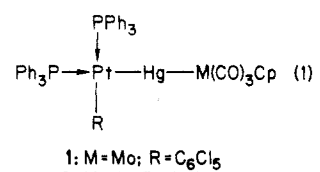
activity of the Hg–E bond toward "PtL_2" insertion increases along the series Hg–C < Hg–Ge < Hg–Sn.

We have studied Pt(0) insertion reactions into heterobimetallic complexes of the type m–Hg–X or m–Hg–R (m = transition-metal carbonyl fragment), and in this paper, we describe the reaction of the heterobimetallic complexes R–Hg–M(CO)$_3$Cp (M = Mo, W; R = C_6Cl_5; Cp = η-C_5H_5)[14] with $Pt(C_2H_4)(PPh_3)_2$, which could, in principle, form Pt–Hg–M or Hg–Pt–M arrays.

Results and Discussion

The reaction of R–Hg–M(CO)$_3$Cp (Cp = η-C_5H_5) with 1 equiv of $[Pt(C_2H_4)(PPh_3)_2]$ in toluene affords the new insertion products *cis*-[$(PPh_3)_2$(R)Pt–Hg–M(CO)$_3$Cp] (M = Mo, 1; M = W, 2) according to eq 1.



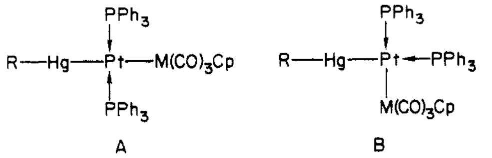
1: M = Mo; R = C_6Cl_5
2: M = W; R = C_6Cl_5

The nature of these heterotrimetallic complexes was deduced from analytical and spectroscpic data and the Pt(0) insertion into the Hg–R bond was established by an X-ray diffraction study of 2 (see below).

The infrared spectra of 1 and 2 are very similar and present in the ν(CO) region two main absorptions at ca. 1950 and 1860 cm^{-1}, similar to those of their bimetallic precursors.[14] Their low-energy shift by ca. 20 cm^{-1} is easily accounted for by the increased electron donation from the $PtR(PPh_3)_2$ fragment compared to that of the R group in [R–Hg–M(CO)$_3$Cp].

The ^1H NMR data confirm the presence of the η-C_5H_5 ligand (δ ~4.4) and of two triphenylphosphine ligands. More informative are the ^{31}P NMR spectra (Table I). Thus, two sets of resonances are observed, each flanked with ^{195}Pt and ^{199}Hg satellites. This indicates a cis arrangement for the PPh_3 ligands (^2J(PP) = 11 and 12 Hz for 1 and 2, respectively). No ^{31}P–^{183}W coupling was detected, consistent with the phosphine ligands having remained coordinated to platinum. From the values of the coupling constants to the metals, the P(1) and P(2) resonances were assigned as indicated in Table I. The values fall in the expected range,[15] as found for example in the related *cis*-[RHg–Pt(R)$(PPh_3)_2$] complex.[3b]

The NMR data did not unambigously establish where the $Pt(PPh_3)_2$ insertion had occurred in R–Hg–M(CO)$_3$Cp. Thus, although many examples of Pt(0) insertions into mercury–carbon bonds are known to afford stable compounds, an insertion into the Hg–M instead of the Hg–R bond would have produced the possibilities A or B.



A B

The trans arrangement shown in A could be easily ruled out on the basis of the ^{31}P NMR data (see above) and of previous studies showing that for steric reasons, heterotrinuclear chain complexes such as *trans*-[Pt{M(CO)$_3$Cp}$_2$$(PPh_3)_2$] cannot be isolated[16] and that the het-

Table I. Spectroscopic $^{31}P\{^1H\}$ NMR Data[a]

	1		2	
	P(1)	P(2)	P(1)	P(2)
δ	17.4	41.8	17.1	44.3
^2J[P(1)P(2)], Hz	11		12	
^1J(PPt), Hz	2720	2636	2734	2610
^2J(PHg), Hz	280	2912	270	2810

[a] P(2) is trans to Hg.

Table II. Summary of Crystallographic Parameters for $(PPh_3)_2(C_6Cl_5)$Pt–Hg–W(CO)$_3$Cp (2)

(A) Crystal Parameters

formula	$C_{50}H_{35}Cl_5HgO_3P_2PtW$	a, Å	12.122 (3)
fw	1520.57	b, Å	13.287 (6)
F(000)	1412	c, Å	18.961 (17)
space group	$P\bar{1}$	α, deg	63.27 (6)
cryst system	triclinic	β, deg	65.25 (6)
V, Å^3	2434 (4)	γ, deg	70.24 (4)
Z	2		
D(calcd), g/cm^3	2.05		

(B) Measurements of Intensity Data and Treatment

data collectn instrument	Philips PW-1100
radiation	Mo Kα (λ = 0.7093 Å)
scan technique	$\theta/2\theta$
data collectn range	$1 \le \theta \le 23.5°$
collected intensities	5466
unique data ($I \ge 2.5\sigma(I)$)	2330
μ(Mo Kα), cm^{-1}	90.99
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.022
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.025

Table III. Selected Interatomic Distances (Å) and Angles (deg) in [$(PPh_3)_2(C_6Cl_5)$Pt–Hg–W(CO)$_3$Cp] (2)

Bond Lengths

Pt–Hg	2.572 (1)	W–C(21)	2.14 (2)
Pt–P(1)	2.286 (3)	W–C(22)	1.80 (2)
Pt–P(2)	2.293 (4)	W–C(23)	1.93 (2)
Pt–C(1)	2.117 (6)	W–C(Cp)$_{(av)}$	2.40 (8)
W–Hg	2.755 (1)		

Bond Angles

W–Hg–Pt	171.9 (1)	Hg–W–C(21)	132.9 (3)
Hg–Pt–P(1)	87.5 (1)	Hg–W–C(22)	73.3 (3)
Hg–Pt–P(2)	166.4 (1)	Hg–W–C(23)	67.3 (3)
Hg–Pt–C(1)	77.4 (2)	C(21)–W–C(22)	76.8 (7)
P(1)–Pt–P(2)	103.2 (1)	C(21)–W–C(23)	85.5 (10)
C(1)–Pt–P(1)	164.8 (2)	C(22)–W–C(23)	103.1 (7)
C(1)–Pt–P(2)	91.9 (2)		

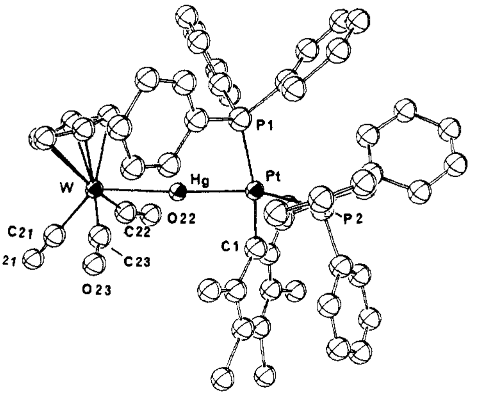


Figure 1. Perspective view of the $(PPh_3)_2(C_6Cl_5)$Pt–Hg–W(CO)$_3$Cp molecule.

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erobimetallic [$(PPh_3)_2(H)Pt-Mo(CO)_3Cp$] complex adopts a cis structure.[17] Structure B could, therefore, not be ruled out although a Pt(0) insertion reaction into a mercury–transition-metal bond does not seem to have been reported as yet. Thus, it was important to establish the structure of these trimetallic complexes by X-ray diffraction.

The molecular structure of 2 is shown in Figure 1. Insertion of the $Pt(PPh_3)_2$ fragment has occurred into the mercury–carbon bond, affording a linear heterotrimetallic Pt–Hg–W array (eq 1). Crystallographic data and data collection parameters for the structure are given in Table II. Selected bond lengths and angles are listed in Table III. With a Pt–Hg–W angle for 171.9 (1)°, the slight deviation from linearity of the mercury coordination may be the result of steric factors or packing forces, but it is smaller than that noted in [$ClHg-Mo(CO)_3Cp$] (160.02 (9) Å).[18] The Hg–Pt bond distance of 2.572 (1) Å is shorter than those in the related $Hg[Pt(C_6H_2Cl_3)(PPh_3)_2]_2$ (average 2.637 (1) Å)[4] or $Hg[(CF_3)_3GePt(PPh_3)_2]_2$ complexes (2.630 (2) and 2.665 (2) Å). The value of 2.755 (1) Å appears to be the first reported for a Hg–W bond distance. The $CpM(CO)_3Hg$ portion of the molecule has the usual irregular "four-legged piano-stool" structure, typical of bimetallic [$CpM(CO)_3X$] (M = Cr, Mo, W) derivatives.[18,19] The trans Hg–W–C(21) and C(22)–W–C(23) angles are 132.9 (3) and 103.1 (7)°, comparing well with the corresponding values in [$ClHg-Mo(CO)_3Cp$] of 128.8 (5) and 112.0 (7)°.[18] The Pt atom displays a distorted square-planar coordination, with the Hg atom out of the mean plane by −0.348 (1) Å. The C_6Cl_5 ligand makes an angle of 94.4 (3)° with this plane, which minimizes the steric repulsions within the molecule. The value of 103.2 (1)° for the P(1)–Pt–P(2) angle results from the steric repulsion between the bulky cis ligands.

Further studies are in progress to evaluate how general is the present observation that in R–Hg–M complexes, the Hg–C bond is more reactive than the Hg–M bond toward Pt(0) insertion.

Experimental Section

Solvents were dried by standard methods, and all manipulations and reactions were performed in Schlenk-type flasks under dry nitrogen.[16] Elemental analyses of C and H were carried out at the Institut de Bio Organica de Barcelona. The $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian XL-200 Fourier transform spectrometer for benzene solutions using 85% H_3PO_4 as external reference. ^1H shifts are relative to Me_4Si. Infrared spectra were recorded on a Beckman IR-20A spectrophotometer. $(C_6Cl_5)Hg-Mo(CO)_3Cp$, $(C_6Cl_5)Hg-W(CO)_3Cp$, and $Pt(C_2H_4)(PPh_3)_2$ were prepared according to the methods described previously.[14,20]

Preparation of $(PPh_3)_2(C_6Cl_5)Pt-Hg-Mo(CO)_3Cp$ (1). [$Pt(C_2H_4)(PPh_3)_2$] (0.74 g, 1.0 mmol) was added under nitrogen to a suspension of [$(C_6Cl_5)Hg-Mo(CO)_3Cp$] (0.69 g, 1.0 mmol) in toluene (50 mL) cooled to −50 °C. When the reaction mixture was stirred at room temperature, it turned into a yellow solution and the solid dissolved. After a few minutes, the solution was evaporated to dryness and the residue was recrystallized from toluene–hexane to yield an air-stable yellow powder of 1 (90% yield): mp 217–222 °C; IR (KBr) ν(CO) 1940 (vs), 1855 (vs) cm^{-1}; ^1H NMR (C_6D_6) δ 4.45 (Cp). Anal. Calcd for $C_{50}H_{35}Cl_5HgMoO_3P_2Pt$: C, 42.45; H, 2.49. Found: C, 42.43; H, 2.47.

Preparation of $(PPh_3)_2(C_6Cl_5)Pt-Hg-W(CO)_3Cp$ (2). The synthesis of 2 was carried out following the same procedure as used in the preparation of 1 (95% yield): mp 212–215 °C; IR (KBr) ν(CO) 1950 (vs), 1860 (vs) cm^{-1}; ^1H NMR (C_6D_6) δ 4.40 (Cp). Anal. Calcd for $C_{50}H_{35}Cl_5HgO_3P_2PtW$: C, 39.96; H, 2.34. Found: C, 40.38; H, 2.37.

Table IV. Positional Parameters (×10⁴) and Their Estimated Standard Deviations for 2

	x/a	y/b	z/c
Hg	29303 (6)	17695 (4)	23069 (5)
Pt	19174 (4)	1036 (4)	26785 (3)
W	38928 (7)	37067 (6)	17195 (6)
C(1)	6439 (6)	757 (7)	7005 (6)
C(2)	6494 (6)	1133 (7)	6177 (6)
C(3)	5458 (6)	1807 (7)	5934 (6)
C(4)	4367 (6)	2106 (7)	6517 (6)
C(5)	4313 (6)	1731 (7)	7345 (6)
C(6)	5349 (6)	1056 (7)	7588 (6)
Cl(2)	7861 (4)	767 (4)	5451 (2)
Cl(3)	5599 (5)	2305 (5)	4877 (3)
Cl(4)	3164 (4)	3034 (4)	6177 (4)
Cl(5)	3035 (3)	2152 (4)	8029 (3)
Cl(6)	5253 (3)	516 (4)	8609 (2)
P(1)	321 (3)	1421 (3)	2267 (2)
C(101)	−317 (8)	2512 (7)	2766 (5)
C(102)	−1042 (8)	3562 (7)	2444 (5)
C(103)	−1529 (8)	4344 (7)	2850 (5)
C(104)	−1289 (8)	4076 (7)	3579 (5)
C(105)	−564 (8)	3027 (7)	3902 (5)
C(106)	−77 (8)	2245 (7)	3496 (5)
C(111)	−1113 (7)	1054 (8)	2470 (7)
C(112)	−1192 (7)	660 (8)	1927 (7)
C(113)	−2279 (7)	337 (8)	2085 (7)
C(114)	−3287 (7)	407 (8)	2787 (7)
C(115)	−3208 (7)	800 (8)	3331 (7)
C(116)	−2121 (7)	1124 (8)	3172 (7)
C(121)	741 (11)	2272 (7)	1134 (4)
C(122)	−110 (11)	3031 (7)	725 (4)
C(123)	300 (11)	3663 (7)	−126 (4)
C(124)	1560 (11)	3534 (7)	−568 (4)
C(125)	2411 (11)	2775 (7)	−158 (4)
C(126)	2001 (11)	2144 (7)	692 (4)
P(2)	1488 (3)	−1579 (3)	2883 (2)
C(201)	149 (8)	−2142 (8)	3755 (5)
C(202)	−686 (8)	−1440 (8)	4195 (5)
C(203)	−1669 (8)	−1859 (8)	4893 (5)
C(204)	−1817 (8)	−2981 (8)	5150 (5)
C(205)	−982 (8)	−3684 (8)	4710 (5)
C(206)	1 (8)	−3264 (8)	4013 (5)
C(211)	1226 (10)	−1531 (8)	1972 (6)
C(212)	414 (10)	−2119 (8)	2029 (6)
C(213)	297 (10)	−2053 (8)	1308 (6)
C(214)	994 (10)	−1400 (8)	529 (6)
C(215)	1806 (10)	−812 (8)	471 (6)
C(216)	1923 (10)	−878 (8)	1193 (6)
C(221)	2768 (8)	−2827 (7)	3064 (7)
C(222)	3673 (8)	−3134 (7)	2403 (7)
C(223)	4656 (8)	−4037 (7)	2547 (7)
C(224)	4734 (8)	−4634 (7)	3351 (7)
C(225)	3829 (8)	−4327 (7)	4012 (7)
C(226)	2846 (8)	−3424 (7)	3869 (7)
C(21)	5667 (16)	3962 (19)	1527 (11)
O(21)	6520 (10)	4002 (17)	1473 (15)
C(22)	4151 (13)	2819 (9)	2705 (11)
O(22)	4118 (9)	2197 (14)	3428 (9)
C(23)	4803 (17)	2756 (15)	1055 (12)
O(23)	5328 (38)	2558 (35)	253 (34)
O(23)	5689 (25)	2124 (22)	692 (22)
C(11)	2117 (78)	5030 (42)	1271 (37)
C(12)	1813 (17)	4577 (16)	2076 (16)
C(13)	2609 (39)	5364 (30)	1960 (26)
C(14)	3514 (28)	5780 (24)	1200 (26)
C(15)	3163 (36)	5376 (38)	740 (31)
C(11)′	2050 (48)	4581 (25)	1277 (36)
C(14)′	3025 (23)	5609 (22)	1162 (34)
C(15)′	3119 (75)	5097 (89)	476 (58)

Crystallographic Studies

A single crystal of 2 was mounted on a Philips PW-1100 four-circle diffractometer. The unit-cell parameters were measured from 20 reflections (4.5 ≤ θ ≤ 10.5°). Intensities were

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collected with graphite-monochromatized Mo Kα radiation, using the $\theta/2\theta$ scan technique. No intensity decay was observed during the data collection period. Lorentz-polarization and absorption corrections were made (maximum and minimum transmission factors are 0.86 and 0.80, respectively). Details are given in Table II.

The structure was solved by direct methods, using the MULTAN system of computer programs,[21] which gave the position of the 20 heaviest atoms. The remaining non-hydrogen atoms were obtained from a subsequent weighted Fourier synthesis. The structure was refined by a full-matrix least-squares method using the Shelx 76 computer program.[22] The function minimized was $w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}|F_o|$. As the number of observed reflections was limited by the poor quality of the crystal, each phenyl ring was refined with constrained geometry (planar, C–C = 1.395 Å, and C–C–C = 120°) and with overall anisotropic thermal coefficients, in order to reduce the number of parameters to be refined. A difference synthesis showed a disorder in the localization of the C(11), C(14), and C(15) atoms of the cyclopentadienyl and the C(23)O(23) ligand, which were refined with an occupancy factor of 0.5, according to peaks observed in a Fourier synthesis. The refinements results are given in Table II.

The final positional parameters of the refined atoms are given in Table IV. A table of thermal parameters, a full list of bond distances and angles, and a table of observed and calculated structure factor amplitudes are available as supplementary material.[23]

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Registry No. **1**, 101224-88-8; **2**, 101224-89-9; $Pt(C_2H_4)(PPh_3)_2$, 12120-15-9; $(C_6Cl_5)Hg–M_0(CO)_3Cp$, 93939-29-8; $(C_6Cl_5)Hg–W(CO)_3Cp$, 93939-32-3.

Supplementary Material Available: Complete lists of bond lengths and angles (Table SI), thermal parameters (Table SII), and observed and calculated structure factors (Table SIII) for **2** and a view of the molecular structure of **2** with the complete numbering scheme (Figure 2) (16 pages). Ordering information is given on any current masthead page.

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Synthesis, Molecular Structure, and 2-D NMR Analysis of Bis(tetraphenylcyclopentadienyl)iron(II)

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Tetraphenylcyclopentadiene (I) may be prepared in 82% yield in a one-step synthesis from tetraphenylcyclopentadienone. The reaction between $Li(C_5HPh_4)$ (II) and $FeCl_2$ in THF solvent produces $(C_5HPh_4)_2Fe$ (III). Treatment of the latter complex with $AgPF_6$ affords $[(C_5HPh_4)_2Fe]PF_6$. The oxidation potential of III is similar to that of ferrocene. Crystals of III belong to the space group $P\bar{1}$ with a = 8.339 (4) Å, b = 10.867 (5) Å, c = 12.830 (7) Å, α = 66.40 (4)°, β = 73.471 (4)°, γ = 83.721 (4)°, and V = 1021.3 (9) Å^3. Solution of the structure led to final values of R = 4.52 and R_w = 5.09. Complex III possesses rigorous inversion symmetry in the solid state and the two cyclopentadienyl rings adopt a staggered 180° configuration. Phenyl-substituted carbon–iron distances (average Fe–C = 2.094 (3) Å) are significantly longer than for the methine carbon (Fe–C = 2.054 (3) Å) of the cyclopentadienyl ring and longer than similar Fe–C distances in $(C_5H_5)_2Fe$, $(C_5Me_5)_2Fe$, and $(C_5HMe_4)_2Fe$. Through a combination of ^1H COSY NMR spectroscopy, selective deuteration of III, and ^{13}C NMR spectroscopy, with selective proton decoupling, a complete assignment of proton and carbon NMR spectra is provided. Analysis of the temperature dependence of the 500-MHz ^1H NMR spectra suggests that rotation of the two tetraphenylcyclopentadienyl rings is rapid to −95 °C; however, ordering of the phenyl ring conformations occurs below −20 °C. Spectral data suggest that at low temperature the phenyl rings adjacent to the lone cyclopentadienyl hydrogen become coplanar with the C_5 ring and the remaining phenyl groups lie perpendicular to this plane.

Introduction

The cyclopentadienyl ligand has occupied a central role in the development of organometallic chemistry.[2] Methyl-substituted derivatives, especially pentamethylcyclopentadienyl,[3] have been used in place of cyclopentadienyl because of their increased steric bulk, solubility, stability, and electron donor properties. Coordination chemistry of other cyclopentadienyl ligands that can be prepared conveniently has not been developed extensively. A few complexes that contain the pentaphenylcyclopentadienyl ligand are known;[4-8] however, this ligand limits access to

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