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Contribution from the Departments of Inorganic and Organic Chemistry,
University of Sydney, Sydney, NSW 2006, Australia

Crystal and Molecular Structures of Pentaphenylcyclopentadiene and of an Isomer, 4,8-Diphenyltribenzo[*b*,*f*,*i*]tricyclo[6.2.1.$0^{1,5}$]undecane, the Product of a Novel Metal-Assisted Photoreaction

Leslie D. Field,* Trevor W. Hambley, Charles M. Lindall, and Anthony F. Masters*

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The crystal and molecular structures of two isomers of $C_{35}H_{26}$, pentaphenylcyclopentadiene, $C_5(C_6H_5)_5H$ (I), and 4,8-diphenyltribenzo[*b*,*f*,*i*]tricyclo[6.2.1.$0^{1,5}$]undecane (II) are described. Pentaphenylcyclopentadiene crystallizes from tetrahydrofuran in the monoclinic space group $P2_1/c$ with $a = 15.954$ (4) Å, $b = 6.267$ (1) Å, $c = 24.517$ (8) Å, $\beta = 93.94$ (2)°, $V = 2445$ (1) Å^3, $Z = 4$, $D_{calcd} = 1.213$ g cm^{-3}, $R = 0.038$, and $R_w = 0.045$. 4,8-Diphenyltribenzo[*b*,*f*,*i*]tricyclo[6.2.1.$0^{1,5}$]undecane crystallizes from methanol/ether/hexane (1:1:2) in the monoclinic space group $P2_1/n$ with $a = 10.710$ (2) Å, $b = 10.754$ (3) Å, $c = 20.683$ (4) Å, $\beta = 97.30$ (2)°, $V = 2363$ (9) Å^3, $Z = 4$, $D_{calcd} = 1.256$ g cm^{-3}, $R = 0.034$, and $R_w = 0.043$. Compound II was obtained by the photochemical isomerization of the pentaphenylcyclopentadienyl ligand attached to the iron center in $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+BPh_4^-$ in the presence of triethyl phosphite.

Introduction

Although pentaphenylcyclopentadiene was first synthesized in 1926,[1] the first complexes of the pentaphenylcyclopentadienyl anion were not reported until 1964.[2] Since then, well-characterized pentaphenylcyclopentadienyl complexes of chromium,[3] molybdenum,[2,5-8] iron,[4,9-13] ruthenium,[14-16] cobalt,[17-20] rhodium,[17-19,21] nickel,[20,22-24] palladium,[25-29] germanium,[30,31] tin,[30-32] lead,[30,31] and lutetium[33] have been reported. The pentaphenylcyclopentadienyl anion has proven to be a versatile ligand, conferring unique steric and electronic properties upon some complexes. Thus, for example, nickelocene has two unpaired electrons,[34,35] while decaphenylnickelocene is diamagnetic.[22] Decaphenylstannocene[32] has two parallel C_5 rings, while the two C_5 rings of stannocene[36] and decamethylstannocene[37] are inclined at 143.7 and 148.0° and 143.6 and 144.6°, respectively (two independent molecules in each). The dimer $[\{Ni(\mu\text{-}Br)(\eta^5\text{-}C_5R_5)\}_2]$ is unknown for R = H, must be stored below −10 °C for R = Me, and melts with decomposition above 200 °C when R = Ph.[20]

Several bonding modes have been identified for the pentaphenylcyclopentadienyl ligand. Complexes with η^n (n = 1,[38] 5,[2-33] 6[11]) coordination have been well-characterized. Pentaphenylcyclopentadiene can also act as a ligand, and complexes with η^n (n = 4,[38] 6[3,11]) coordination have been reported, although no structural data exist for such complexes. In this regard, the structure of pentaphenylcyclopentadiene is important in the comparative structural chemistry of complexes of the pentaphenylcyclopentadiene and pentaphenylcyclopentadienyl ligands.

During the course of our investigations into pentaphenylcyclopentadienyl complexes, we have discovered a unique, apparently metal-assisted photoisomerization of the ligand. Although the photoproduct has been isolated in low yield, its formation is of significance, given the important photoreactions of cyclopentadienyl and pentamethylcyclopentadienyl complexes and the intense interest in the photochemistry of $[Fe(C_5R_5)(arene)]^+$ cations.[39-55] In particular, $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-arene})]^+$ cations are

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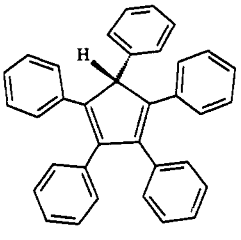
Table I. Crystal Data for Pentaphenylcyclopentadiene (I) and 4,8-Diphenyltribenzo[*b,f,i*]tricyclo[6.2.1.0^{1,5}]undecane (II)

	I	II
chem formula	$C_{35}H_{26}$	$C_{35}H_{26}$
fw	446.6	446.6
space group	$P2_1/c$	$P2_1/n$
a, Å	15.954 (4)	10.710 (2)
b, Å	6.267 (1)	10.754 (3)
c, Å	24.517 (8)	20.683 (4)
β, deg	93.94 (2)	97.30 (2)
V, Å^3	2445 (1)	2363 (9)
D_{calcd}, g cm^{-3}	1.213	1.256
Z	4	4
μ, cm^{-1}	0.35	0.36
transm coeff	n/a	n/a
temp, °C	21	21
λ, Å	0.71069	0.71069
$R(F_o)^a$	0.038	0.034
$R_w{}^b$	0.045	0.043

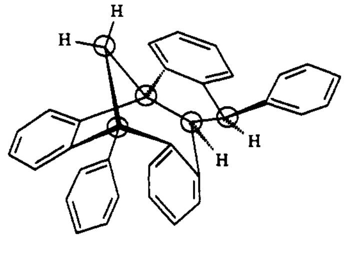
$^a R(F_o) = \sum(||F_o| - |F_c||)/\sum|F_o|$. $^b R_w(F_o) = \sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}|F_o|$.

reported to undergo photolytic ligand-exchange reactions and to photocatalyze the valence isomerization of hexamethyl Dewar benzene to hexamethylbenzene.[48] Additionally, cyclopentadienyl and substituted cyclopentadienyl complexes are finding increasing applications in photoablative MOCVD procedures[56,57] and as photoinitiators for photoimaging systems.[58,59]

We report here the crystal and molecular structures of pentaphenylcyclopentadiene (I) and of an isomer 4,8-diphenyltribenzo[*b,f,i*]tricyclo[6.2.1.0^{1,5}]undecane (II).



I



II

Experimental Section

All synthetic manipulations were carried out under an inert atmosphere (nitrogen or argon) using standard Schlenk techniques. Pentaphenylcyclopentadiene was prepared following the method of Chambers et al.[17] Pentaphenylcyclopentadienyl bromide was prepared as described previously.[9] Pentaphenylcyclopentadienyllithium was prepared following the method of Zhang et al.[60] Acetonitrile and dichloromethane were distilled from calcium hydride. Benzene and diethyl ether were distilled from sodium benzophenone ketyl. Methanol was distilled from magnesium. Acetone was distilled from potassium carbonate and used immediately. $[Cr(CO)_6]$ and $P(OEt)_3$ (Aldrich) were used as received. $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+BPh_4^-$ was prepared as previously reported.[12]

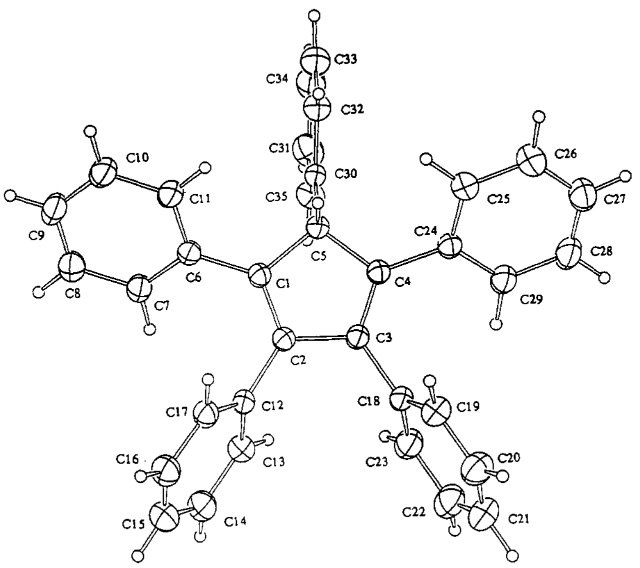


Figure 1. ORTEP (30% probability) plot of pentaphenylcyclopentadiene (I) viewed along the normal to the C_5 plane.

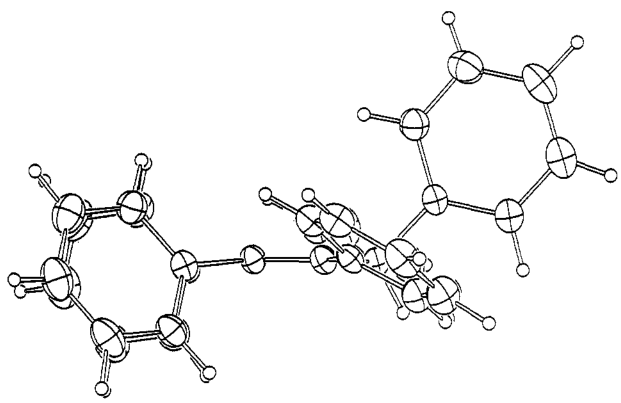


Figure 2. ORTEP (30% probability) plot of pentaphenylcyclopentadiene (I) viewed perpendicular to the normal to the C_5 plane.

Melting points were recorded in air and are uncorrected. Infrared data were recorded as KBr disks using a Digilab 20/80 FTS spectrometer. ^{1}H NMR spectra (200 MHz) were recorded on a Bruker AC-200F spectrometer, and shifts were referenced to residual solvent resonances. Photolysis experiments used 150- and 250-W incandescent floodlamps.

Crystals of pentaphenylcyclopentadiene were isolated during the purification of $[Cr(CO)_3\{\eta^6\text{-}C_6H_5)C_5(C_6H_5)_4H\}]$.[3] Crystals of 4,8-diphenyltribenzo[*b,f,i*]tricyclo[6.2.1.0^{1,5}]undecane were isolated in low yield from the attempted photolysis of $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+BPh_4^-$ in the presence of $P(OEt)_3$ in dichloromethane. $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+BPh_4^-$ (0.22 g, 0.25 mmol) and triethyl phosphite, (1.1 g, 6 mmol) were combined in CH_2Cl_2 (20 mL) at 0 °C under visible light (150 W) for 15 h. The solvent was removed in vacuo to yield an orange solid. The orange solid was first extracted with benzene and then with ether to yield a pale yellow solid (ca. 10 mg, 9% based on the originally coordinated pentaphenylcyclopentadienyl ligand), which was recrystallized from methanol/ether/hexane (1:1:2) in air to yield colorless crystals, mp 253–255 °C. IR (KBr, cm^{-1}): 3064, w; 3045, w; 3032, w; 3023, w; 2994, w; 2964, w; 1493, m; 1478, w; 1463, w; 1450, m; 1443, w; 1599, m; 1252, s; 1099, s; 1021, s; 800, s; 774, w; 766, w; 754, s; 743, s; 701, s; 686, w; 629, w; 600, w; 594, w; 583, w; 543, m. ^{1}H NMR (CD_2Cl_2): δ 2.30 (d of d, 1 H), 2.60 (d, 1 H), 3.70 (d, 1 H), 5.16 (d, 1 H), 6.88–7.47 (m, 22 H).

Structure Determination. Details of the structure determination are summarized in Table I. Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections. Data were measured on an Enraf-Nonius CAD4-F diffractometer within the limit $2\theta_{max} = 50°$, with Mo Kα radiation, λ = 0.71069 Å, graphite monochromator, and operating in the ω-1.33θ mode. Data were reduced and Lorentz, polarization, and decomposition corrections were applied using a local data reduction program. The structures were solved by direct methods using SHELXS-86[61a] and were refined by full-matrix

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Table II. Positional Parameters ($\times 10^4$) for Pentaphenylcyclopentadiene (I)

	x	*y*	*z*
C(1)	2437 (1)	1523 (3)	3208 (1)
C(2)	1959 (1)	671 (3)	3589 (1)
C(3)	2221 (1)	1565 (3)	4131 (1)
C(4)	2862 (1)	2954 (3)	4081 (1)
C(5)	3048 (1)	3105 (3)	3483 (1)
C(6)	2410 (1)	1087 (3)	2616 (1)
C(7)	2202 (1)	−910 (4)	2401 (1)
C(8)	2176 (1)	−1292 (4)	1846 (1)
C(9)	2364 (1)	316 (5)	1494 (1)
C(10)	2586 (2)	2294 (5)	1696 (1)
C(11)	2610 (1)	2677 (4)	2249 (1)
C(12)	1230 (1)	−768 (3)	3481 (1)
C(13)	1226 (2)	−2844 (4)	3675 (1)
C(14)	549 (2)	−4169 (4)	3553 (1)
C(15)	−133 (2)	−3423 (5)	3239 (1)
C(16)	−142 (1)	−1373 (5)	3044 (1)
C(17)	532 (1)	−50 (4)	3164 (1)
C(18)	1765 (1)	1140 (3)	4632 (1)
C(19)	1275 (1)	2731 (4)	4837 (1)
C(20)	833 (2)	2382 (4)	5292 (1)
C(21)	875 (2)	459 (5)	5552 (1)
C(22)	1366 (2)	−1123 (5)	5358 (1)
C(23)	1811 (2)	−795 (4)	4899 (1)
C(24)	3322 (1)	4227 (3)	4508 (1)
C(25)	3645 (1)	6206 (4)	4380 (1)
C(26)	4079 (2)	7446 (5)	4775 (1)
C(27)	4200 (2)	6712 (5)	5299 (1)
C(28)	3895 (2)	4747 (5)	5431 (1)
C(29)	3454 (1)	3506 (4)	5042 (1)
C(30)	3960 (1)	2718 (3)	3370 (1)
C(31)	5138 (2)	351 (5)	3384 (1)
C(32)	4444 (1)	4279 (4)	3152 (1)
C(33)	5277 (2)	3879 (5)	3058 (1)
C(34)	5622 (2)	1915 (5)	3174 (1)
C(35)	4318 (1)	751 (4)	3480 (1)

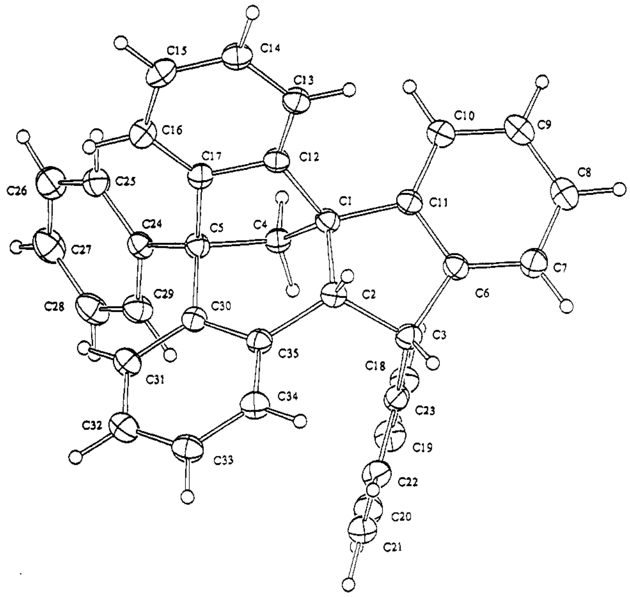

Figure 3. ORTEP (30% probability) plot of 4,8-diphenyltribenzo[*b*,*f*,*i*]tricyclo[6.2.1.0^{1,5}]undecane (II).

least-squares analysis with SHELX-76.[61b] All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were refined with isotropic thermal parameters. Final atomic coordinates are listed in Tables II and III. Scattering factors and anomalous dispersion corrections were taken from the values supplied in SHELX-76.[61b] Figures were drawn using the program ORTEP.[62]

Table III. Positional Parameters ($\times 10^4$) for 4,8-Diphenyltribenzo[*b*,*f*,*i*]tricyclo[6.2.1.0^{1,5}]undecane (II)

	x	*y*	*z*
C(1)	1337 (2)	3410 (2)	2574 (1)
C(2)	604 (2)	4600 (2)	2333 (1)
C(3)	−786 (2)	4368 (2)	2492 (1)
C(4)	1284 (2)	2488 (2)	2006 (1)
C(5)	2184 (2)	3092 (2)	1569 (1)
C(6)	−529 (2)	3547 (2)	3090 (1)
C(7)	−1323 (2)	3273 (2)	3552 (1)
C(8)	−910 (2)	2468 (2)	4055 (1)
C(9)	261 (2)	1914 (2)	4089 (1)
C(10)	1053 (2)	2169 (2)	3625 (1)
C(11)	657 (2)	2995 (2)	3133 (1)
C(12)	2737 (2)	3682 (2)	2683 (1)
C(13)	3475 (2)	4121 (2)	3233 (1)
C(14)	4725 (2)	4409 (2)	3193 (1)
C(15)	5211 (2)	4298 (2)	2609 (1)
C(16)	4472 (2)	3876 (2)	2056 (1)
C(17)	3235 (2)	3532 (2)	2096 (1)
C(18)	−1692 (2)	3793 (2)	1947 (1)
C(19)	−2321 (2)	4546 (2)	1466 (1)
C(20)	−3109 (2)	4044 (2)	946 (1)
C(21)	−3285 (2)	2778 (3)	903 (1)
C(22)	−2703 (2)	2018 (2)	1385 (1)
C(23)	−1920 (2)	2522 (2)	1903 (1)
C(24)	2492 (2)	2145 (2)	1068 (1)
C(25)	3636 (2)	1532 (2)	1099 (1)
C(26)	3822 (3)	587 (2)	662 (1)
C(27)	2872 (3)	245 (3)	190 (1)
C(28)	1723 (3)	849 (2)	148 (1)
C(29)	1539 (2)	1786 (2)	584 (1)
C(30)	1539 (2)	4279 (2)	1277 (1)
C(31)	1742 (2)	4720 (2)	663 (1)
C(32)	1203 (2)	5819 (2)	419 (1)
C(33)	495 (2)	6520 (2)	793 (1)
C(34)	306 (2)	6114 (2)	1408 (1)
C(35)	796 (2)	4984 (2)	1652 (1)

Table IV. Bond Lengths (Å) for Pentaphenylcyclopentadiene (I)

C(2)–C(1)	1.355 (3)	C(5)–C(1)	1.515 (3)
C(6)–C(1)	1.475 (3)	C(3)–C(2)	1.475 (2)
C(12)–C(2)	1.481 (3)	C(4)–C(3)	1.355 (3)
C(18)–C(3)	1.494 (3)	C(5)–C(4)	1.517 (3)
C(24)–C(4)	1.472 (3)	C(30)–C(5)	1.520 (3)
C(7)–C(6)	1.390 (3)	C(11)–C(6)	1.393 (3)
C(8)–C(7)	1.381 (3)	C(9)–C(8)	1.374 (4)
C(10)–C(9)	1.372 (4)	C(11)–C(10)	1.376 (3)
C(13)–C(12)	1.385 (3)	C(17)–C(12)	1.389 (3)
C(14)–C(13)	1.379 (4)	C(15)–C(14)	1.372 (4)
C(16)–C(15)	1.370 (4)	C(17)–C(16)	1.375 (3)
C(19)–C(18)	1.384 (3)	C(23)–C(18)	1.379 (3)
C(20)–C(19)	1.378 (3)	C(21)–C(20)	1.362 (4)
C(22)–C(21)	1.369 (4)	C(23)–C(22)	1.387 (4)
C(25)–C(24)	1.387 (3)	C(29)–C(24)	1.387 (3)
C(26)–C(25)	1.389 (4)	C(27)–C(26)	1.366 (4)
C(28)–C(27)	1.372 (4)	C(29)–C(28)	1.385 (3)
C(32)–C(30)	1.378 (3)	C(35)–C(30)	1.378 (3)
C(34)–C(31)	1.370 (4)	C(35)–C(31)	1.368 (3)
C(33)–C(32)	1.386 (3)	C(34)–C(33)	1.370 (4)

Results and Discussion

The structures of I and II consist of discrete molecules. Final atomic positional coordinates, with estimated standard deviations, bond lengths and angles, and anisotropic thermal parameters have been deposited as supplementary material. Bond distances and angles are given in Tables IV–VII. The atomic nomenclature for I is defined in Figures 1 and 2 and for II in Figure 3. Figures 1 and 2 illustrate the molecular geometry of pentaphenylcyclopentadiene viewed along, and perpendicular to, the normal to the C_5 plane.

(i) Pentaphenylcyclopentadiene, C_5Ph_5H (I). The C_5Ph_5H molecule comprises a planar C_5 ring which is bisected by an

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Table V. Bond Lengths (Å) for 4,8-Diphenyltribenzo[*b*,*f*,*i*]tricyclo[6.2.1.0^{1,5}]undecane (II)

C(2)–C(1)	1.550 (3)	C(4)–C(1)	1.533 (3)
C(11)–C(1)	1.510 (3)	C(12)–C(1)	1.517 (3)
C(3)–C(2)	1.585 (3)	C(35)–C(2)	1.506 (3)
C(6)–C(3)	1.516 (3)	C(18)–C(3)	1.523 (3)
C(5)–C(4)	1.545 (3)	C(17)–C(5)	1.538 (3)
C(24)–C(5)	1.519 (3)	C(30)–C(5)	1.538 (3)
C(7)–C(6)	1.388 (3)	C(11)–C(6)	1.396 (3)
C(8)–C(7)	1.382 (3)	C(9)–C(8)	1.383 (3)
C(10)–C(9)	1.386 (3)	C(11)–C(10)	1.377 (3)
C(13)–C(12)	1.384 (3)	C(17)–C(12)	1.396 (3)
C(14)–C(13)	1.387 (3)	C(15)–C(14)	1.380 (3)
C(16)–C(15)	1.382 (3)	C(17)–C(16)	1.388 (3)
C(19)–C(18)	1.389 (3)	C(23)–C(18)	1.389 (3)
C(20)–C(19)	1.389 (3)	C(21)–C(20)	1.376 (4)
C(22)–C(21)	1.376 (3)	C(23)–C(22)	1.384 (3)
C(25)–C(24)	1.386 (3)	C(29)–C(24)	1.390 (3)
C(26)–C(25)	1.391 (3)	C(27)–C(26)	1.368 (4)
C(28)–C(27)	1.384 (4)	C(29)–C(28)	1.383 (3)
C(31)–C(30)	1.397 (3)	C(35)–C(30)	1.403 (3)
C(32)–C(31)	1.382 (3)	C(33)–C(32)	1.376 (3)
C(34)–C(33)	1.383 (3)	C(35)–C(34)	1.393 (3)

Table VI. Bond Angles (deg) for Pentaphenylcyclopentadiene (I)

C(5)–C(1)–C(2)	109.0 (2)	C(6)–C(1)–C(2)	128.7 (2)
C(6)–C(1)–C(5)	122.3 (2)	C(3)–C(2)–C(1)	109.5 (2)
C(12)–C(2)–C(1)	126.1 (2)	C(12)–C(2)–C(3)	124.2 (2)
C(4)–C(3)–C(2)	109.3 (2)	C(18)–C(3)–C(2)	123.3 (2)
C(18)–C(3)–C(4)	127.0 (2)	C(5)–C(4)–C(3)	109.0 (2)
C(24)–C(4)–C(3)	128.8 (2)	C(24)–C(4)–C(5)	122.2 (2)
C(4)–C(5)–C(1)	103.1 (1)	C(30)–C(5)–C(1)	114.1 (2)
C(30)–C(5)–C(4)	114.8 (1)	C(7)–C(6)–C(1)	122.0 (2)
C(11)–C(6)–C(1)	120.7 (2)	C(11)–C(6)–C(7)	117.3 (2)
C(8)–C(7)–C(6)	121.4 (2)	C(9)–C(8)–C(7)	119.9 (2)
C(10)–C(9)–C(8)	119.9 (2)	C(11)–C(10)–C(9)	120.2 (2)
C(10)–C(11)–C(6)	121.3 (2)	C(13)–C(12)–C(2)	122.2 (2)
C(17)–C(12)–C(2)	119.5 (2)	C(17)–C(12)–C(13)	118.3 (2)
C(14)–C(13)–C(12)	120.9 (2)	C(15)–C(14)–C(13)	119.8 (3)
C(16)–C(15)–C(14)	120.3 (3)	C(17)–C(16)–C(15)	120.1 (2)
C(16)–C(17)–C(12)	120.7 (2)	C(19)–C(18)–C(3)	119.4 (2)
C(23)–C(18)–C(3)	122.3 (2)	C(23)–C(18)–C(19)	118.3 (2)
C(20)–C(19)–C(18)	120.9 (2)	C(21)–C(20)–C(19)	120.5 (2)
C(22)–C(21)–C(20)	119.3 (3)	C(23)–C(22)–C(21)	120.8 (3)
C(22)–C(23)–C(18)	120.2 (2)	C(25)–C(24)–C(4)	119.9 (3)
C(29)–C(24)–C(4)	122.0 (2)	C(29)–C(24)–C(25)	118.1 (2)
C(26)–C(25)–C(24)	121.2 (2)	C(27)–C(26)–C(25)	119.8 (3)
C(28)–C(27)–C(26)	119.8 (3)	C(29)–C(28)–C(27)	120.8 (2)
C(28)–C(29)–C(24)	120.3 (2)	C(32)–C(30)–C(5)	121.9 (2)
C(35)–C(30)–C(5)	119.8 (2)	C(35)–C(30)–C(32)	118.3 (2)
C(35)–C(31)–C(34)	120.2 (3)	C(33)–C(32)–C(30)	120.4 (2)
C(34)–C(33)–C(32)	120.3 (3)	C(33)–C(34)–C(31)	119.5 (2)
C(31)–C(35)–C(30)	121.3 (2)		

Table VII. Bond Angles (deg) for 4,8-Diphenyltribenzo[*b*,*f*,*i*]tricyclo[6.2.1.0^{1,5}]undecane (II)

C(4)–C(1)–C(2)	108.7 (1)	C(11)–C(1)–C(2)	102.5 (2)
C(11)–C(1)–C(4)	114.9 (2)	C(12)–C(1)–C(2)	109.8 (2)
C(12)–C(1)–C(4)	100.2 (2)	C(12)–C(1)–C(11)	120.5 (2)
C(3)–C(2)–C(1)	104.7 (2)	C(35)–C(2)–C(1)	113.8 (2)
C(35)–C(2)–C(3)	118.7 (1)	C(6)–C(3)–C(2)	100.6 (1)
C(18)–C(3)–C(2)	115.9 (2)	C(18)–C(3)–C(6)	113.6 (2)
C(5)–C(4)–C(1)	102.2 (2)	C(17)–C(5)–C(4)	99.8 (1)
C(24)–C(5)–C(4)	108.9 (2)	C(24)–C(5)–C(17)	119.1 (2)
C(30)–C(5)–C(4)	107.3 (2)	C(30)–C(5)–C(17)	105.9 (2)
C(30)–C(5)–C(24)	114.4 (2)	C(7)–C(6)–C(3)	128.4 (2)
C(11)–C(6)–C(3)	111.6 (2)	C(11)–C(6)–C(7)	119.9 (2)
C(8)–C(7)–C(6)	119.1 (2)	C(9)–C(8)–C(7)	120.6 (2)
C(10)–C(9)–C(8)	120.7 (2)	C(11)–C(10)–C(9)	118.8 (2)
C(6)–C(11)–C(1)	110.5 (2)	C(10)–C(11)–C(1)	128.6 (2)
C(10)–C(11)–C(6)	120.9 (2)	C(13)–C(12)–C(1)	129.6 (2)
C(17)–C(12)–C(1)	109.2 (2)	C(17)–C(12)–C(13)	120.9 (2)
C(14)–C(13)–C(12)	118.7 (2)	C(15)–C(14)–C(13)	120.5 (2)
C(16)–C(15)–C(14)	120.8 (2)	C(17)–C(16)–C(15)	119.3 (2)
C(12)–C(17)–C(5)	109.0 (2)	C(16)–C(17)–C(5)	131.2 (2)
C(16)–C(17)–C(12)	119.6 (2)	C(19)–C(18)–C(3)	119.9 (2)
C(23)–C(18)–C(3)	122.5 (2)	C(23)–C(18)–C(9)	117.5 (2)
C(20)–C(19)–C(18)	121.2 (2)	C(21)–C(20)–C(19)	120.0 (2)
C(22)–C(21)–C(20)	119.7 (2)	C(23)–C(22)–C(21)	120.2 (2)
C(22)–C(23)–C(18)	121.3 (2)	C(25)–C(24)–C(5)	123.7 (2)
C(29)–C(24)–C(5)	118.3 (2)	C(29)–C(24)–C(25)	117.7 (2)
C(26)–C(25)–C(24)	121.0 (2)	C(27)–C(26)–C(25)	120.3 (2)
C(28)–C(27)–C(26)	119.6 (2)	C(29)–C(28)–C(27)	120.0 (2)
C(28)–C(29)–C(24)	121.3 (2)	C(31)–C(30)–C(5)	121.7 (2)
C(35)–C(30)–C(5)	119.2 (2)	C(35)–C(30)–C(31)	118.9 (2)
C(32)–C(31)–C(30)	121.1 (2)	C(33)–C(32)–C(31)	119.8 (2)
C(34)–C(33)–C(32)	120.0 (2)	C(35)–C(34)–C(33)	121.1 (2)
C(30)–C(35)–C(2)	121.6 (2)	C(34)–C(35)–C(2)	119.2 (2)
C(34)–C(35)–C(30)	119.0 (2)		

approximate mirror plane. The mirror plane contains the unique phenyl ring, the primary carbon atom, and the unique hydrogen atom. The C_5 ring and the phenyl substituents of C_5Ph_5H are each planar to within 0.013 and 0.009 Å, respectively. The C–C–C angles of the alkenyl carbons inside the C_5 ring are equal within experimental error (109.2 (2)°). The corresponding angle at the sp^3-hybridized carbon C(5) is 103.1 (1)°. The corresponding angles in tetraphenylcyclopentadiene are 108.9 and 104.3°.[63] The average of all of the C–C bond lengths in the C_5 ring is 1.443 (3) Å, similar to those observed in metal complexes of this ligand.[10,12,17,21,23-25,31,32] Of these bonds, the two bonds to the sp^3-hybridized carbon, C(5) (1.516 (3) Å), are significantly longer than the other C_5-ring C–C bonds. The same trend was seen for tetraphenylcyclopentadiene—the intra-ring C–C bonds to the sp^3-hybridized carbon averaging 1.496 (7) Å.[63] The slightly longer bond length (at the 2σ confidence limit) in pentaphenylcyclopentadiene may be due to the demanding steric effect of the phenyl substituent at C(5) of pentaphenylcyclopentadiene relative to a hydrogen at the corresponding position in tetraphenylcyclopentadiene. The angles C(3)–C(4)–C(24) and C(2)–C(1)–C(6) are 128.8 (2) and 128.7 (2)°, respectively, in I compared to the corresponding angles in tetraphenylcyclopentadiene of 130.2 (4) and 129.6 (4)°. The slightly smaller angles for pentaphenylcyclopentadiene (I) are also presumably due to the steric pressure exerted by the unique phenyl ring. The ipso carbons of each of the alkenyl substituted phenyl rings are located out of the C_5 plane by 0.04–0.16 Å. The ipso carbon bonded to the sp^3-hybridized carbon lies 1.10 Å out of the plane of the C_5 ring, and this phenyl ring is almost perpendicularly disposed to the C_5 ring (86.9°). The remaining phenyl rings are canted at angles of 32.2, 65.2, 70.4, and 30.8° with respect to the C_5 ring. The average angle of this tilt for the five phenyl rings is 57.1°. These values compare with those observed in complexes such as [Fe(η^5-C_5Ph_5)$(CO)_2$Br] (average 58.7°),[10] [Fe(η^5-C_5Ph_5)(toluene)]$^+$ (average 51.4°),[12] and [Co(η^5-C_5Ph_5)$(CO)_2$] (average 55.8°).[17] The near identical canting angles for chemically equivalent phenyl rings generates an effective mirror plane through the molecule so that it is close to C_s symmetry.

(ii) 4,8-Diphenyltribenzo[*b*,*f*,*i*]tricyclo[6.2.1.0^{1,5}]undecane (II). The molecular structure of II (Figure 3) reveals a substantial rearrangement of the phenyl groups by comparison with its isomer, I, and the starting ligand. The C_5 ring is cleaved, and three of the five phenyl rings are cycloannelated onto the carbon chain derived from the C_5 ring. The five carbons of the cyclopentadiene ring of the precursor are circled in structure I. Three new, linked rings are formed each of which has a phenyl group providing one edge. The aromatic C–C bond lengths are all normal. The other C–C bonds are typical of sp^3-hybridized carbon atoms but range up to 1.585 (3) Å, indicative of a large amount of steric strain. This strain is also reflected in the bond angles at the sp^3 carbons, which range from 99.8 (1) to 120.5 (2)°.

Although II is obtained only in low yield, its isolation is significant. This compound is not obtained when $P(OEt)_3$ and C_5Ph_5H or C_5Ph_5Br or $[C_5Ph_5]^-Li^+$ are combined under similar conditions. Irradiation of [Fe(η^5-C_5Ph_5)(η^6-C_6H_6)]$^+$ in CH_2Cl_2 in the absence of $P(OEt)_3$ generates the linkage isomer of decaphenylferrocene, [Fe(η^5-C_5Ph_5)(η^6-$C_6H_5C_5Ph_4$)],[11] in low yield, and II is not detected in this reaction. Compound II is not obtained

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by combining $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+$ and $P(OEt_3)$ in the dark under otherwise similar conditions. Thus, the isomerization of the pentaphenylcyclopentadienyl ligand to the skeleton of II requires both the metal complex and triethyl phosphite and probably involves photoisomerization of $[C_5Ph_5]^-$ or the radical at the metal center.

Photolytic ligand-exchange reactions of $[Fe(\eta^5\text{-}C_5H_5)(\text{arene})]^+$ complexes are well-known,[40,44,47,48,50,52] and photoinduced loss of arene from $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-arene})]^+$ cations appears to be important in the generation of catalysts for photoimaging systems.[58,59] It was demonstrated recently that the nature of the cyclopentadienyl substituents is important in determining the rates of arene exchange, with electron-withdrawing substituents facilitating the photoreaction but destabilizing the solvated intermediates.[51,54] Thus, for example, sunlight is sufficient to initiate arene exchange of $[Fe(\eta^5\text{-}C_5H_5)(\text{arene})]^+$ cations in CH_2Cl_2.[39,40,41,43] Likewise, irradiation of the acyl-substituted derivative $[Fe(\eta^5\text{-}C_5H_4COR)(\eta^6\text{-}C_6H_6)]^+PF_6^-$ with 24 equiv of trimethyl phosphite in CH_2Cl_2 at 0 °C (conditions similar to those of the present experiment) produces $[Fe(\eta^5\text{-}C_5H_4COR)\{P(OMe)_3\}_3]^+PF_6^-$ in 73% (R = Me) or 77% (R = Ph) yield in 1 h.[54] By contrast, $[Fe(\eta^5\text{-}C_5Me_5)(\text{arene})]^+$ cations are photolabile only in the presence of a sensitizer, such as acetone or anthracene.[51] The compounds $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-arene})]^+[BPh_4]^-$ are, however, recrystallized from acetone. Additionally, $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+[BPh_4]^-$ was stirred in acetone in the presence of 20 equiv of triethyl phosphite. No reaction was observed in the dark. Irradiation of the solution with visible light yielded unchanged $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+[BPh_4]^-$ (ca. 80%) and C_5Ph_5H (ca. 20%).

Pentaphenylcyclopentadiene was not detected as a coproduct of II from the irradiation of $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+[BPh_4]^-$ in the presence of $P(OEt)_3$ in CH_2Cl_2. Pentaphenylcyclopentadiene has only limited solubility in CH_2Cl_2 but is unchanged on irradiation in CH_2Cl_2 in the presence of 20 equiv of triethyl phosphite, and thus it is unlikely that II is generated from free pentaphenylcyclopentadiene.

Because of the low yield of II, we are unable to speculate on the course of the reaction. However, the generation of $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_5C_5Ph_4)]$ by photolysis of $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+$ in CH_2Cl_2 demonstrates that photoinduced arene exchange can occur in this system. Moreover, several crystal structure determinations have established that, at least in the solid state, the phenyl groups of the $[C_5Ph_5]^-$ ligand are sterically constrained from assuming coplanarity with the C_5 ring and appear to act as electron-donating substituents.[64] The low yield of II is then consistent with the low photolability of complexes with electron-donating substituents on the C_5 ring.

Thermal or acid-induced rearrangements of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol have been reported.[65-67] However, we have not detected any of the products of these reactions following the $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+[BPh_4]^-/P(OEt)_3/CH_2Cl_2$ photolysis.

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Supplementary Material Available: Listings of atom coordinates, anisotropic thermal parameters, details of least-squares planes calculations, and torsion angles (20 pages); tables of observed and calculated structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

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Contribution from the Anorganisch-chemisches Institut der
Technischen Universität München, Lichtenbergstrasse 4, W-8046 Garching, Germany

Auration of an Aryltris[(triarylphosphine)aurio(I)]phosphonium(+) Cation To Give a Hypercoordinate Aryltetrakis[(triarylphosphine)aurio(I)]phosphonium(2+) Dication

Hubert Schmidbaur,* Edgar Zeller, Gabriele Weidenhiller, Oliver Steigelmann, and Holger Beruda

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Treatment of (2-methylphenyl)phosphine with tris[(triphenylphosphine)aurio(I)]oxonium(+) tetrafluoroborate(−) affords colorless, air-stable (2-methylphenyl)tris[(triphenylphosphine)aurio(I)] phosphonium(+) tetrafluoroborate(−): $(2\text{-}MeC_6H_4)[Ph_3PAu]_3P^+BF_4^-$ (**1**); Me = methyl, Ph = phenyl. The crystal structure features tetrahedral cations with a central phosphorus atom surrounded by three gold atoms and one carbon atom. With the Au–P–Au angles showing only slight deviations from the tetrahedral value and the P–Au–P angles close to linear, the Au···Au distances are too long to allow bonding metal–metal interactions. An analogous arsenic compound $(2\text{-}MeC_6H_4)[(Ph_3PAu]_3As^+BF_4^-$ (**3**) is available from (2-methylphenyl)arsine and shows similar properties. Reaction of **1** with $[Ph_3PAu]^+BF_4^-$ gives high yields of the colorless, crystalline, air-stable species $(2\text{-}MeC_6H_4)[Ph_3PAu]_4P^{2+}(BF_4^-)_2$ (**2**). The dications have a square-pyramidal structure with phosphorus at the center, the *o*-tolyl group at the apex, and the four gold atoms forming the base with short Au···Au contacts (ca. 3.0 Å). These short distances are held responsible for the ease of formation and stability of this novel hypercoordinate unit. An analogous arsenic compound could not be prepared. Crystal data for **1**: $a = 13.341$ (3) Å, $b = 15.363$ (3) Å, $c = 16.369$ (3) Å, $\alpha = 107.88$ (1)°, $\beta = 98.17$ (1)°, $\gamma = 103.09$ (1)°, triclinic, space group $P\bar{1}$, $Z = 2$. Crystal data for $\mathbf{2}\cdot 4C_6H_6$: $a = 13.712$ (2) Å, $b = 17.873$ (3) Å, $c = 20.748$ (2) Å, $\alpha = 95.04$ (1)°, $\beta = 104.58$ (1)°, $\gamma = 96.08$ (1)°, triclinic, space group $P\bar{1}$, $Z = 2$.

Introduction

Recent work has demonstrated that a pair, trio, or quartet of gold(I) atoms clustered at or around a main group element like carbon, nitrogen, phosphorus, arsenic, oxygen, sulfur, and selenium shows a pronounced tendency to attract additional units LAu^+ to form novel hypercoordinate species.[1] For carbon,[2] the trigonal-bipyramidal cations $C(AuL)_5^+$ and octahedral dications $C(AuL)_6^{2+}$ are the prototypes for this new type of clustering phenomenon for closed-shell atoms [d^{10} for Au(I), L = tertiary

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