Synthesis and Structure of a New Type of Sandwich-Like Yttrium Complex Derived from Tetraphenylethylene: [Na(THF)$_6$][Y(Ph$_2$CCPh$_2$)$_2$]

Dmitrii M. Roitershtein,*,[1] Joseph W. Ziller, and William J. Evans*

Contribution from the Department of Chemistry, University of California, Irvine, Irvine, California 92697-2025

Received April 27, 1998

Abstract: Yttrium trichloride reacts with both Na$_2$[Ph$_2$CCPh$_2$] and K$_2$[Ph$_2$CCPh$_2$], made from Ph$_2$C=CPh$_2$ and sodium and potassium mirrors, respectively, to form complexes of general formula [M(THF)$_x$][Y(Ph$_2$-CCPh$_2$)$_2$] (M = Na, **1**; K, **2**; x = 4−6). Complex **2** undergoes cation exchange with NaBPh$_4$ in THF to form crystals of [Na(THF)$_6$][Y(Ph$_2$CCPh$_2$)$_2$](THF)$_2$, **3**, suitable for X-ray diffraction. The anionic unit in **3**, [Y(Ph$_2$CCPh$_2$)$_2$]$^-$, has a sandwich-like structure in which each (Ph$_2$CCPh$_2$)$^{2-}$ dianion has six carbon atoms oriented toward the metal center with Y−C distances ranging from 2.518(6) to 2.689(7) Å.

Although the organometallic chemistry of yttrium and the f-elements is dominated by sandwich complexes in which the metal is located between two polyhapto ligands, the number of *types* of ligands involved is rather narrow.[2−4] The most common ligands are cyclopentadienide and cyclooctatetraenide and their substituted derivatives.[2] A few sandwich compounds are known with noncyclic pentadienyl ligands[5] and with tris-*tert*-butylbenzene,[6] and recently a pentalene complex has been reported.[7,8] We report here a new type of yttrium sandwich complex derived from the dianion of tetraphenylethylene which displays unusual coordination features both in the solid state and in solution.

Experimental Section

The complexes described below are extremely air- and moisture-sensitive. Therefore, the syntheses and manipulations of these compounds were conducted under nitrogen with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. The methods for drying solvents were described previously.[11] YCl$_3$(THF)$_3$

was prepared from YCl$_3$(H$_2$O)$_x$ and SOCl$_2$ in THF according to the literature,[12] and tetraphenylethylene (Aldrich) was purified by recrystallization from dioxane. ^{13}C and ^{1}H NMR analyses were carried out on Bruker DRX-400 and Bruker DRX-500 NMR spectrometers. UV analyses were carried out on a Shimadzu UV-600 spectrometer in THF solution.

Bulk Synthesis of Na$_2$(Ph$_2$CCPh$_2$) and K$_2$(Ph$_2$CCPh$_2$). A piece of sodium metal (ca. 1 g, 5-fold excess) was placed into a 100 mL round-bottom flask, and the flask was capped with a high-vacuum stopcock adapter. The vessel was attached to the vacuum line and evacuated. The alkali metal was heated to the melting point with a torch and an alkali metal mirror formed on the walls of the flask. In the glovebox, tetraphenylethylene (1.268 g, 3.8 mmol) was placed in the flask with 90 mL of THF along with a stir bar, and the reaction mixture was stirred for 2 days. The resulting dark purple solution of disodium tetraphenylethenide was used for further reactions. Dark purple solutions of the dipotassium tetraphenylethenide were prepared in a similar way.

NMR-Scale Synthesis of Na$_2$(Ph$_2$CCPh$_2$). A piece of sodium metal (0.2 g, 300-fold excess) was placed in a Schlenk tube which had an NMR tube attached to it as well as a high-vacuum stopcock adapter. The system was attached to the vacuum line and evacuated. Sodium was sublimed to the upper part of the Schlenk tube, and the bottom part of the system containing unsublimed sodium was isolated with a torch and detached. The system was taken into a glovebox, and tetraphenylethylene (0.010 g, 0.03 mmol) and 0.5 mL of THF-d_8 were added. The system was attached to a vacuum line and evacuated, and the Schlenk tube was sealed with a torch. The solution was kept over the sodium mirror for 3 days and then transferred to the NMR tube and sealed. ^{1}H NMR (THF-d_8) δ 5.61 (t, 4H), 6.51 (t, 8H), 6.98 (d, 8H). ^{13}C{^{1}H} NMR (THF-d_8) δ 94.9, 107.4, 116.6, 129.0, 147.3.

[Na(THF)$_4$][Y(Ph$_2$CCPh$_2$)$_2$], 1. In a glovebox, a solution of Na$_2$(Ph$_2$CCPh$_2$) in 90 mL of THF obtained from tetraphenylethylene (1.268 g, 3.8 mmol) and a sodium mirror was added to a stirred suspension of YCl$_3$(THF)$_3$ (0.786 g, 1.9 mmol) in 15 mL of THF. After the reaction mixture was stirred overnight, the orange-brown solution was separated from a precipitate by centrifugation. Since the product is not very soluble, the precipitate was extracted with THF (3 × 150

(1) Present location: Karpov Institute of Physical Chemistry, Moscow, Russia.

(2) Schumann, H. *Chem. Rev.* **1995**, *95*, 865.

(3) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982, Chapter 21. Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1995; Vol. 4, Lappert, M. F., Ed., Chapter 2. Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2466−2488.

(4) Bochkarev, M. N.; Zakharov, L. N.; Kalinina, G. S.*Organoderivatives of Rare Earth Elements*; Kluwer: Dordrecht, 1995.

(5) Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1982**, *1*, 708. Sieler, J.; Simon, A.; Peters, K.; Taube, R.; Geitner, M. *J. Organomet. Chem.* **1989**, *362*, 297. Zielinski, M. B.; Drummond, D. K.; Iyer, P. S.; Leman, J. T.; Evans, W. J. *Organometallics* **1995**, *14*, 3724−3731. Kunze, K.; Arif, A. M.; Ernst, R. D. *Bull. Soc. Chim. Fr.* **1993**, *130*, 708−711.

(6) Cloke, F. G. N. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1995; Vol. 4, Lappert, M. F., Ed., Chapter 1.

(7) Cloke, F. G. N.; Hitchcock, P. B. *J. Am. Chem. Soc.* **1997**, *119*, 7899.

(8) Sandwich compounds with inorganic ligands are also known e.g. with polypyrazolylborate[9] and carboranyl anions.[10]

(9) Santos, I.; Marques, N. *New J.Chem.* **1995**, *19*, 551.

(10) Manning, M. J.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1988**, *110*, 4458.

(11) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423.

(12) Herrmann, W. A. In *Synthetic Methods of Organometallic and Inorganic Chemistry (Herrmann/Brauer). Vol. 6. Lanthanides and Actinides*; Edelmann, F. T., Ed.; Verlag: Stuttgart, 1997; pp 34−35.

Table 1. Experimental Data for the X-ray Diffraction Study of {[Na(THF)₆][Y(Ph₂CCPh₂)₂]}(THF)₂, **3**

formula	$C_{84}H_{104}NaO_8Y$	c (Å)	12.5615(5)
FW	1353.57	volume (Å³)	7552.1(8)
temp (K)	296	Z	4
crystal system	orthorhombic	D_{calcd} (Mg/m³)	1.19
space group	*Pnna*	μ(Cu Kα), mm⁻¹	1.562
a (Å)	23.616(2)	$R1$,^{a} [$I > 2\sigma(I)$]	0.0752
b (Å)	25.4578(10)		

^{a} $R1 = [\sum||F_o| - |F_c||/\sum|F_o|]$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]]^{1/2}$.

mL). These extracts were combined with the original solution, and the solvent was removed by rotary evaporation. This left a brown solid which was recrystallized from hot THF and dried under dynamic vacuum at room temperature for 2 h to yield **1** as dark brown-violet crystals (1.20 g, 62%). Anal. Calcd for the tetrasolvate [Na(THF)₄]-[Y(Ph₂CCPh₂)₂]: C, 76.67; H, 6.81; Y, 8.35; Na, 2.16. Found: C, 75.01; H, 7.49; Y, 8.26; Na, 2.02. UV λ_{max}(nm, THF) 405, 530 sh. When heated in the sealed glass capillary, condensation of a liquid in the upper part of the tube was observed at around 150 °C, and complete decomposition occurred at 245−255 °C.

[K(THF)₄][Y(Ph₂CCPh₂)₂], 2. Complex **2** (0.420 g, 48%) was synthesized as described above for **1** from YCl₃(THF)₃ (0.333 g, 0.81 mmol). Anal. Calcd for the tetrasolvate [K(THF)₄][Y(Ph₂CCPh₂)₂]: Y, 8.22. Found: Y, 8.02.

[Na(THF)₆][Y(Ph₂CCPh₂)₂], 3. In a glovebox, 5 mL of a saturated solution of [K(THF)₄][Y(Ph₂CCPh₂)₂] in THF was added to a 5 mL saturated solution of NaBPh₄ in THF. Large, brown-purple, well-shaped hexagonal single crystals of **3** deposited overnight at room temperature as well as KBPh₄ as a colorless precipitate. The crystals of **3** were washed with THF to remove residual KBPh₄ and sealed in a glass capillary for X-ray investigation. Attempts to examine the crystals at low temperature using Paratone oil without sealing in capillary were unsuccessful since the crystals cracked at low temperature.

X-ray Data Collection, Structure Determination, and Refinement for [Na(THF)₆][Y(Ph₂CCPh₂)₂]. A brown-purple crystal of approximate dimensions 0.27 × 0.40 × 0.46 mm was sealed into a glass capillary under nitrogen in an inert atmosphere box and transferred to a Siemens P4 diffractometer. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out according to standard procedures.[13] Intensity data were collected at 296 K using a $2\theta/\omega$ scan technique with Cu Kα radiation. Details are given in Table 1.

The raw data were processed with a local version of CARESS[14] which employs a modified version of the Lehman−Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. Subsequent calculations were carried out using the SHELXTL program.[15] All 6306 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was *mmm*, and the systematic absences are consistent with the centrosymmetric space group *Pnna*.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis.[16] The yttrium and sodium atoms are located on 2-fold rotation axes and were each assigned site-occupancy factors of 1/2. The carbon atoms of the THF molecules associated with O(2) and O(3) are disordered. Each was included with two components with SOF = 1/2. There are two disordered THF solvent molecules present per formula unit. All five atoms (O and C) were included with two components and SOF = 1/2. Hydrogen atoms associated with ordered and disordered carbon atoms were included using a riding model. At convergence, $wR2 = 0.2631$ and GOF = 1.015 for 378 variables refined against all 6306 unique

(13) XSCANS Software Users Guide, Version 2.1, Siemens Industrial Automation, Inc.; Madison, WI, 1994.

(14) Broach, R. W. Argonne National Laboratory, Illinois, 1978.

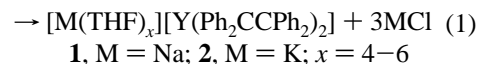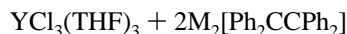(15) Sheldrick, G. M. Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994.

(16) *International Tables for X-ray Crystallography, Vol. C*; Kluwer: Dordrecht, 1992.
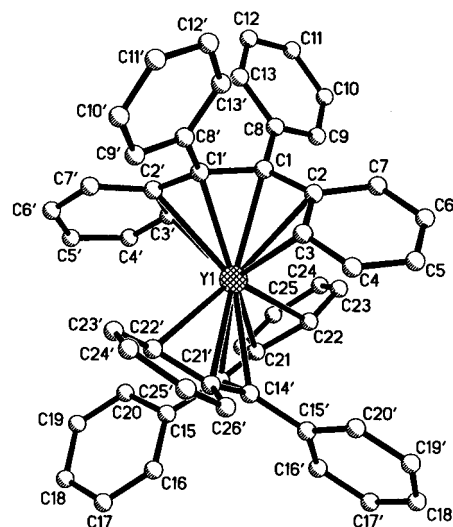
Figure 1. Ball and stick diagram of the organometallic anion in [Na-(THF)₆][Y(Ph₂CCPh₂)₂](THF)₂, **3**.

data (as a comparison for refinement on *F*, $R1 = 0.0752$ for those 3302 data with with $F > 4.0\sigma(F)$). The high residuals are probably due to a combination of weak diffraction data, room-temperature data collection (necessary due to crystal cracking at low temperature), and the disordered THF molecules.

Results and Discussion

Synthesis. Tetraphenylethylene, like other aryl-substituted olefins and polycyclic aromatic compounds, undergoes a two-electron reduction to make a dianion.[17] The sodium and potassium salts of this dianion react with YCl₃ in THF to form new organoyttrium complexes according to eq 1. The highly

$$YCl_3(THF)_3 + 2M_2[Ph_2CCPh_2]$$
$$\rightarrow [M(THF)_x][Y(Ph_2CCPh_2)_2] + 3MCl \quad (1)$$
$$\textbf{1}, M = Na; \textbf{2}, M = K; x = 4{-}6$$

air-sensitive **1** and **2** are moderately soluble in THF and DME, slightly soluble in dioxane, and insoluble in toluene and hexane. The solubility of **1** is significantly lower than that of **2**, which is in contrast to the higher solubility of disodium tetraphenyl-ethylene compared to dipotassium tetraphenylethylene.

Attempts to fully characterize **1** and **2** obtained according to eq 1 by X-ray crystallography were unsuccessful. However, a cation exchange reaction between **2** and NaBPh₄ led to crystals of [Na(THF)₆][Y(Ph₂CCPh₂)₂], **3**, which provided an X-ray crystal structure.

Solid-State Structure. As shown in Figure 1, the two (Ph₂CCPh₂)²⁻ dianions in the monoanionic [Y(Ph₂CCPh₂)₂]⁻ unit form a sandwich-like structure with the yttrium. The anionic complex has S_4 symmetry overall, and in each dianionic (Ph₂CCPh₂)²⁻ ligand only half of the atoms are crystallographically unique.

The Y−C distances in **3**, Table 2, can be compared with typical Y−C(C₅H₅) distances in yttrocene complexes, which are in the range 2.63−2.68 Å,[2,18−20] and with the average Y−(μ-CH₃) distance in [(C₅H₅)₂Y(μ-CH₃)]₂,[18] which is 2.545(11) Å. The primary yttrium−hydrocarbyl interactions in **3** are delocalized over six carbon atoms in each (Ph₂CCPh₂)²⁻ component which fall into three categories. Yttrium approaches closest to

(17) Szwarc, M. *Carbanions. Living Polymer and Electron-Transfer Processes*; Interscience: New York, 1968.

(18) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54.

11344   *J. Am. Chem. Soc., Vol. 120, No. 44, 1998*

Roitershtein et al.

Table 2. Selected Bond Distances (Å) and Angles (deg) for {[Na(THF)$_6$][Y(Ph$_2$CCPh$_2$)$_2$]}(THF)$_2$, **3**[a]

Y(1)−C(1)	2.518(6)	Y(1)−C(14)	2.529(6)
Y(1)−C(22)	2.607(7)	Y(1)−C(3)	2.612(6)
Y(1)−C(2)	2.677(6)	Y(1)−C(21)	2.689(7)
C(1)−C(2)	1.436(9)	C(1)−C(1)#1	1.494(13)
C(1)−C(8)	1.504(9)	C(2)−C(7)	1.417(10)
C(2)−C(3)	1.418(9)	C(3)−C(4)	1.371(9)
C(4)−C(5)	1.381(11)	C(5)−C(6)	1.334(12)
C(6)−C(7)	1.378(11)	C(8)−C(9)	1.391(10)
C(8)−C(13)	1.386(10)	C(9)−C(10)	1.387(10)
C(10)−C(11)	1.344(13)	C(11)−C(12)	1.371(13)
C(12)−C(13)	1.368(11)	C(14)−C(21)	1.415(9)
C(14)−C(15)	1.482(10)	C(14)−C(14)#1	1.515(14)
C(15)−C(20)	1.398(10)	C(15)−C(16)	1.399(10)
C(16)−C(17)	1.386(11)	C(17)−C(18)	1.372(14)
C(18)−C(19)	1.396(14)	C(19)−C(20)	1.374(12)
C(21)−C(26)	1.437(9)	C(21)−C(22)	1.445(9)
C(22)−C(23)	1.402(10)	C(23)−C(24)	1.364(11)
C(24)−C(25)	1.389(13)	C(25)−C(26)	1.389(11)
Na(1)−O(1)	2.386(7)	Na(1)−O(2)	2.410(8)
Na(1)−O(3)	2.435(8)		
C(1)−Y(1)−C(1)#1	34.5(3)	C(1)−Y(1)−C(14)	156.4(2)
C(1)#1−Y(1)−C(14)	155.0(2)	C(14)−Y(1)−C(14)#1	34.9(3)
C(1)−Y(1)−C(22)	102.0(2)	C(1)#1−Y(1)−C(22)	134.3(2)
C(14)−Y(1)−C(22)	58.1(2)	C(14)#1−Y(1)−C(22)	67.9(2)
C(22)−Y(1)−C(22)#1	123.4(3)	C(1)−Y(1)−C(3)	58.0(2)
C(1)#1−Y(1)−C(3)	68.3(2)	C(14)−Y(1)−C(3)	134.9(2)
C(14)#1−Y(1)−C(3)	101.2(2)	C(22)−Y(1)−C(3)	104.7(2)
C(22)#1−Y(1)−C(3)	101.1(2)	C(3)−Y(1)−C(3)#1	123.8(3)
C(1)−Y(1)−C(2)	31.9(2)	C(1)#1−Y(1)−C(2)	57.5(2)
C(14)−Y(1)−C(2)	146.6(2)	C(14)#1−Y(1)−C(2)	123.4(2)
C(22)−Y(1)−C(2)	92.5(2)	C(22)#1−Y(1)−C(2)	130.1(2)
C(3)−Y(1)−C(2)	31.1(2)	C(3)#1−Y(1)−C(2)	99.9(2)
C(2)−Y(1)−C(2)#1	86.9(3)	C(1)−Y(1)−C(21)	125.4(2)
C(1)#1−Y(1)−C(21)	145.4(2)	C(14)−Y(1)−C(21)	31.3(2)
C(14)#1−Y(1)−C(21)	56.9(2)	C(22)−Y(1)−C(21)	31.6(2)
C(22)#1−Y(1)−C(21)	99.0(2)	C(3)−Y(1)−C(21)	133.5(2)
C(3)#1−Y(1)−C(21)	90.2(2)	C(2)−Y(1)−C(21)	123.8(2)
C(2)#1−Y(1)−C(21)	120.6(2)	C(21)−Y(1)−C(21)#1	85.6(3)
O(1)−Na(1)−O(1)#2	175.0(5)	O(1)−Na(1)−O(2)	91.3(3)
O(1)#2−Na(1)−O(2)	85.2(3)	O(2)#2−Na(1)−O(2)	91.3(4)
O(1)−Na(1)−O(3)	86.5(3)	O(1)#2−Na(1)−O(3)	97.2(3)
O(2)#2−Na(1)−O(3)	171.3(3)	O(2)−Na(1)−O(3)	91.4(3)
O(3)−Na(1)−O(3)#2	87.2(4)		

[a] Symmetry transformations used to generate equivalent atoms: #1, x, $-y + 1/2$, $-z + 3/2$; #2, $-x - 1/2$, $-y$, z.

the former double bond carbon atoms C(1) and C(14) with 2.518(6) Å Y−C(1) and 2.529(6) Å Y−C(14) bond distances. Ortho carbons C(3) and C(22) are the next closest with 2.612(6) Å Y−(3) and 2.607(7) Å Y−C(22) distances. The ipso carbon atoms of the coordinated phenyl rings are next with 2.677(6) Å Y−C(2) and 2.689(7) Å Y−C(21) lengths. Since all of the interactions are within the range of Y−C(C$_5$H$_5$) lengths, each (Ph$_2$CCPh$_2$)$^{2-}$ ligand in **3** can be considered to be hexahapto.

The most closely related crystallographically characterized complexes in the literature which can be used for the evaluation of the bond distances and angles within the (Ph$_2$CCPh$_2$)$^{2-}$ anions in **3** are {Na[Na(Et$_2$O)$_2$](Ph$_2$CCPh$_2$)}$_n$, **4**,[21] and [Cs(diglyme)]$_2$(Ph$_2$-

(19) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45. Evans, W. J.; Dominguez, R.; Levan, K. R.; Doedens, R. J. *Organometallics* **1985**, *4*, 1836. Evans, W. J.; Sollberger, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 6095. Evans, W. J.; Hanusa, T. P.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1987**, *6*, 295−301. Evans, W. J.; Hozbor, M. A.; Bott, S. G.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 1990. Alvarez, D., Jr.; Caulton, K. G.; Evans, W. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 5674. Evans, W. J.; Sollberger, M. S.; Shreeve, J. L.; Olofson, J. M.; Hain, J. H., Jr.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 2492. Evans, W. J.; Boyle, T. J.; Ziller, J. W. *Organometallics* **1993**, *12*, 3998.

(20) Rogers, R. D.; Atwood, J. L.; Emad, A.; Sikora, D. J.; Rausch, M. D. *J. Organomet. Chem.* **1981**, *216*, 383.

CCPh$_2$), **5**.[22] However, each of these complexes has metal ligand coordination environments which differ from that in **3**. In polymeric **4**, only the bis(diethyl ether)-solvated sodium has a metal−(Ph$_2$CCPh$_2$)$^{2-}$ interaction similar to that in **3**; the other sodium atom interacts only with η^6-arene rings of two different (Ph$_2$CCPh$_2$)$^{2-}$ anions. The pattern of M−C(arising from double bond) < M−C(ortho) < M−C(ipso) in **3** is like that found for the bis(ether)-solvated sodium atom in **4** except that the sodium is not symmetrically interacting with each side of the (Ph$_2$CCPh$_2$)$^{2-}$ dianion. Each of the three types of Na−C bond lengths on one side of **4** is 0.06 Å shorter than the analogous Na−C distances on the other side. In **3**, both sides have identical bond lengths due to symmetry. In **5**, the diglyme-solvated cesium interacts primarily with three aryl rings. Despite this coordinative difference, the internal structures of the (Ph$_2$CCPh$_2$)$^{2-}$ dianions can be compared.

The C(1)−C(1′) and C(14)−C(14′) bonds which were double bonds of length 1.36 Å[23] in the starting tetraphenylethylene have lengthened to 1.494(13) and 1.515(14) Å in **3** compared to 1.49 Å in **4** and 1.51 Å in **5**. The twist angles between the two (CPh$_2$)$^-$ units [i.e., the dihedral angles between planes defined by C(1), C(2), and C(8) and C(1′), C(2′), and C(8′) and between C(14), C(15), and C(21) and C(14′), C(15′), and C(21′)] are 68.3 and 65.6°, respectively, compared to 56° in **4** and 76° in **5**. The phenyl rings are out of the C(1)−C(2)−C(8) and C(14)−C(15)−C(21) planes by 7−47° compared to a 10−40° range in **4**. The 122.0(6)° C(2)−C(1)−C(8) and 123.4(6)° C(15)−C(14)−C(21) angles are opened up compared to the 114° angle in the parent hydrocarbon just as in **4** which has an analogous angle of 122°.

The phenyl rings involved in the yttrium interactions do not have bonding parameters significantly differ from the distal phenyl rings except that the C(ipso carbon)−C(former double bond carbon) distances are shorter in the interacting rings: 1.436(9) Å C(1)−C(2) and 1.415(9) Å C(14)−C(21) vs 1.504(9) Å C(1)−C(8) and 1.482(10) Å C(14)−C(15). A similar trend is observed in **4**, 1.430 and 1.441 Å vs 1.462 and 1.463 Å, but the magnitude is smaller. This may be because every ring in this polymer interacts to some extent with a metal atom.

Solution Structure. To determine if the solid-state structure of **3** is retained in solution, a series of NMR experiments was conducted. Since the solubility of **2** is higher than **1**, which is only slightly soluble in THF, these experiments were performed with the potassium salt. The NMR spectrum of the sodium derivative Na$_2$(Ph$_2$CCPh$_2$) in THF was also obtained for comparison.

The NMR data on **3** indicate that, in THF solution at room temperature, two different types of phenyl rings are present as is seen in the solid-state structure. The ^{1}H NMR spectrum of **2** (Figure 2) contains eight different signals belonging to the protons of the phenyl rings. The ^{1}H COSY spectrum of this complex (Figure 3) shows that these eight signals fall into two different separate sets, one containing three phenyl signals and one containing five resonances. The signals at δ 6.55 (t, 2H), 6.87 (t, 4H), and 7.13 (d, 4H) correspond, respectively, to the para, meta, and ortho protons of one type of ring, and the resonances at δ 4.60 (m, 2H), 6.06 (t, 2H), 6.68 (t, 2H), 6.81 (t, 2H), and 7.54 (dd, 2H) correspond to the *e*, *c*, *b*, *d*, and *a* protons, respectively, of a second type of ring as indicated in Chart 1. It can be seen from the ^{1}H COSY spectrum that all of the splitting observed in the proton spectrum is the result of
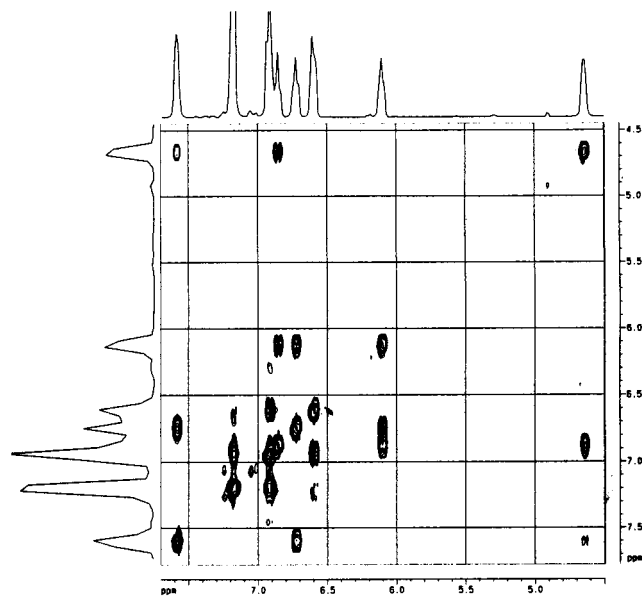
(21) Bock, H.; Ruppert, K.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1685.

(22) Bock, H.; Hauck, T.; Näther, C. *Organometallics* **1996**, *15*, 1527.

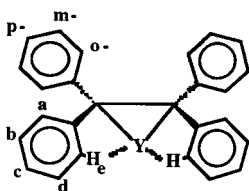(23) Hoekstra, A.; Vos, A. *Acta Crystallogr.* **1975**, *B31*, 1722.
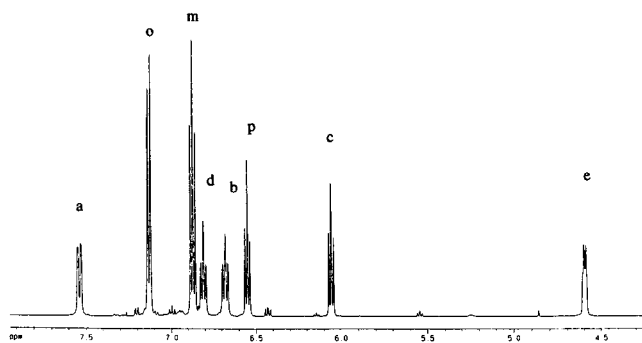
Figure 2. 400 MHz ^{1}H NMR spectrum of complex **2** in THF-d_8 (298 K) in the phenyl region.

Figure 3. ^{1}H enhanced gradient COSY spectrum of complex **2** in THF-d_8 (298 K) in the phenyl region.

**Chart 1.** Labeling Scheme for the Tetraphenylethenide Ligand Coordinated to Yttrium

Table 3. 100 MHz ^{13}C{^{1}H} NMR Data for Complex **2**

	carbon	chemical shift (δ, ppm)		carbon	chemical shift (δ, ppm)
1	Ph₂C–CPh₂	88.3 (J_{Y-C} = 8.4Hz)	7	para	120.9
2	e	99.6	8	meta	127.4
3	c	111.5	9	ortho	129.2
4	a	120.1	10	C-ipso	139.0
5	d	131.2	11	C-ipso	145.9
6	b	138.9			

spin−spin interactions within each set of protons; i.e., there are no interactions between protons of the two different sets. Therefore, these two sets of protons can be identified as belonging to two different types of phenyl rings. The ^{13}C NMR data on **2** (Table 3) are also in good agreement with these assignments. Eight different signals for aromatic carbons with the attached proton can be found in the spectrum, and two different signals for ipso-aromatic protons are present. The
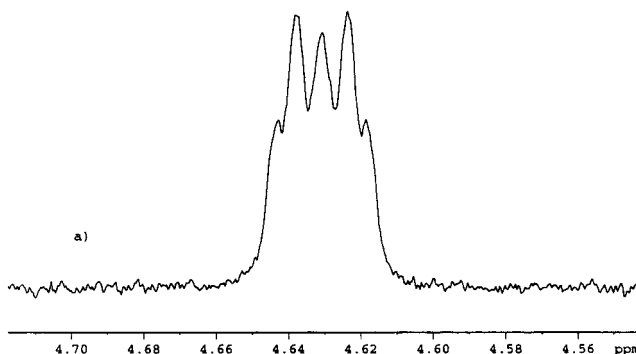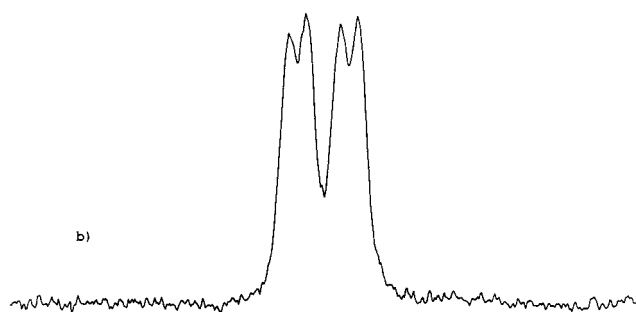
Figure 4. Expansion of the 500 MHz ^{1}H NMR signal for the *e* ortho hydrogen interacting with yttrium: (a) regular spectrum, (b) ^{1}H−{^{89}Y} spectrum.

assignment of the ^{13}C NMR signals was made using the 2D heteronuclear correlation spectrum (Supporting Information). The J_{Y-C} coupling constants for the former double bond carbons are 8.4 Hz. The coupling constants for ipso and ortho carbons were not observed presumably due to low values. Nevertheless, it should be mentioned that the signal of ortho carbon *e* is broadened ($\Delta\nu_{1/2}$ = 4.1 Hz) probably due to the coupling with the 100% natural abundance spin 1/2 ^{89}Y nucleus.

One additional feature of **2** concerning the ortho protons is revealed from the room temperature NMR spectra. The short contacts between yttrium and the ortho carbons of the phenyl rings in the solid state apparently are also accompanied by larger than expected Y···H coupling. The resonance of the ortho proton *e* at 4.60 ppm is observed not as a doublet of doublets which is observed for H$_a$, but as a quintet. This coupling pattern is due to additional coupling to the ^{89}Y nucleus. This was confirmed with an NMR experiment with broad-band ^{1}H−{^{89}Y} decoupling. The expanded spectrum in the region of the H$_e$ resonance signal before and after decoupling is presented in Figure 4. The spectrum with ^{1}H−{^{89}Y} decoupling in the region of H$_e$ contains a doublet of doublets with J_{H-H} = 7.3 and 2.4 Hz, analogous to that for H$_a$. Comparison of the coupled and decoupled spectra allows the J_{Y-H} constant to be calculated. The 3.5 Hz value obtained is close to the values of J_{Y-C-H} in the literature[18,24] found for hydrogens on carbon *directly* bonded to yttrium. For example, in [(C₅H₅)₂Y(μ-CH₃)]₂,[18] the methyl hydrogens have J_{Y-C-H} = 3.6 Hz and the methyl carbon has a J_{Y-C} = 25 Hz. In the case of **2**, where ortho carbon J_{Y-C} splitting could not be observed due to the low value of the

(24) Evans, W. J.; Dominguez, R.; Levan, K. R.; Doedens, R. J. *Organometallics* **1985**, *4*, 1836. den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, B. R.; Huis, R. *Organometallics* **1986**, *5*, 1726. Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 263. Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Doedens, R. J. *Organometallics* **1987**, *6*, 2279. Evans, W. J.; Boyle, T. J.; Ziller, J. W. *J. Organomet. Chem.* **1993**, *46*, 141. Evans, W. J.; Broomhall-Dillard, R. N. R.; Ziller, J. W. *Organometallics* **1996**, *15*, 1351.

Table 4. 400 MHz ^{1}H and 100 MHz ^{13}C{^{1}H} NMR Data for Na$_2$[Ph$_2$CCPh$_2$]

	carbon	chemical shift (δ, ppm)	
		^{1}H	^{13}C^a
1	meta	6.51 (t, 8H)	129.0
2	para	5.61 (t, 4H)	107.4
3	ortho	6.98 (d, 8H)	116.6
4	quaternary		147.3
5	Ph$_2$C$-$CPh$_2$		94.9

^{a} Assignment made on the basis of the ^{1}H$-^{13}$C heteronuclear correlation spectrum data.

coupling constant, the yttrium splitting must be due to a J_{Y-H} through space constant, not a $J_{Y-C-C-C-H}$ constant through four bonds.

The fact that the solution NMR spectrum matches the solid-state structure indicates that aryl ring rotation is frozen at room temperature. In contrast, in the case of disodium tetraphenylethenide, all four phenyl rings are equivalent as can be observed from the ^{1}H and ^{13}C NMR data (Table 4). Therefore, the coordination of the tetraphenylethylene dianion with yttrium results in increased rigidity of the ligand.

To investigate the dynamics of this system, high-temperature NMR studies were conducted. The high-temperature NMR experiments (Figure 5) were performed in dioxane-d_8 solution due to the higher boiling point of this solvent. Since the signals of the ortho *a* and *e* and meta *b* and *d* protons broadened at 323 K and coalesced at 373 K, it appears that at higher temperature the coordinated (Ph$_2$CCPh$_2$)$^{2-}$ ligands become more flexible and the phenyl rings closest to yttrium are able to rotate. Nevertheless, even at 368 K, the difference between the two kinds of phenyl rings (those oriented toward the yttrium and those oriented out of the coordination sphere) is still retained. This indicates that the sandwich-like coordination of the tetraphenylethylene dianions with the yttrium cation remains unchanged in solution even at higher temperature.

Conclusion

The number of organic dianions which will complex yttrium to make (ligand)$_2$M sandwich complexes has been extended to include the (Ph$_2$CCPh$_2$)$^{2-}$ ion. The effects of this new ligand environment on the reaction chemistry of yttrium are under investigation.
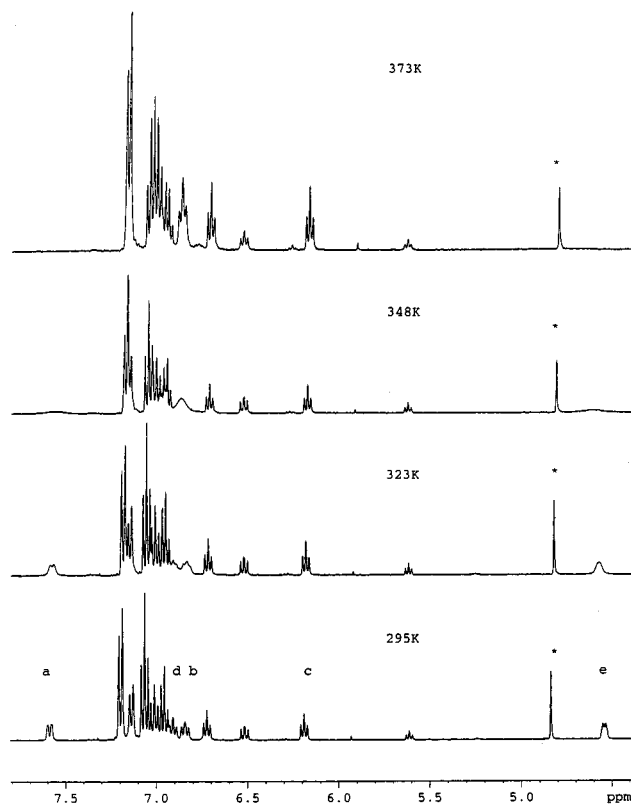
Figure 5. Variable temperature 400 MHz ^{1}H NMR spectrum of **2**.

Supporting Information Available: 2D ^{13}C$-^1$H enhanced gradient heteronuclear correlation spectrum of complex **2** and tables of atomic coordinates, atomic displacement parameters, and bond distances and angles (19 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9814321