Synthesis and Structure of Dinuclear Diphosphine-Bridged Palladium(II) Complexes

Michael A. Zhuravel and David S. Glueck*

6128 Burke Laboratory, Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

Christopher D. Incarvito and Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received May 20, 1999

Summary: *The dinuclear dicationic complexes [(Pd(dppe)(R))$_2$(μ-diphos)]X$_2$ (diphos = dppe; R = Ph (**1**), R = Me (**2**), diphos = dppp, R = Ph (**3**)) were prepared by the addition of a bidentate diphosphine to [Pd(dppe)(R)(PMes$_2$H)]$^+$, by treatment of [Pd(dppe)(R)(X)] (X = Cl, I) with Ag$^+$ and a bidentate diphosphine, or by reaction of [Pd(dppe)(Ph)(X)] (X = Br, I) and dppe. NMR and crystal structure data show that the structure of **1** is the same in solution and in the solid state and allow structural and spectroscopic comparison of chelate and bridging dppe ligands at the same metal center.*

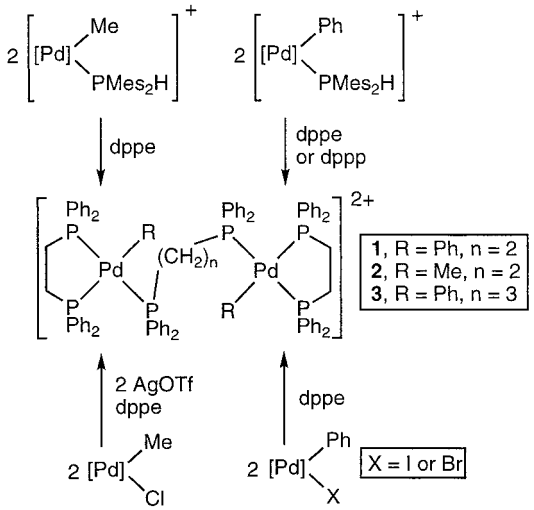
Introduction

Dinuclear metal complexes with bridging bidentate diphosphines are well-known. For example, complexes of copper,[1] vanadium,[2] gold,[3] iron,[4] chromium,[5] rhodium,[6] nickel,[7] and platinum[8] have been reported. Analogous diphosphine-bridged complexes of Pd(0) and Pd(II) have been identified as intermediates in catalytic reactions,[9] making characterization of this bonding mode in palladium complexes of particular interest. We report here synthesis of the dppe and dppp-bridged Pd(II) dinuclear complexes [(Pd(dppe)(R))$_2$(μ-diphos)]$^{2+}$ (diphos = dppe ($Ph_2PCH_2CH_2PPh_2$) or dppp ($Ph_2PCH_2CH_2CH_2PPh_2$)) and their spectroscopic and crystallographic characterization, including direct comparison of dppe as a bridging and a chelate ligand at a Pd(II) center.

Results and Discussion

The dinuclear diphosphine-bridged complex [(Pd(dppe)(Ph))$_2$(μ-dppe)]X$_2$ (**1**, X = OTf, BF_4) was initially prepared by the addition of dppe to a dichloromethane solution of [Pd(dppe)(Ph)(PMes$_2$H)]X.[10a] While no dissociation of the PMes$_2$H is observed in the absence of coordinating species, dppe readily displaces the bulky secondary phosphine. Complex **1** can also be prepared more conveniently from the neutral halide complexes [Pd(dppe)(Ph)(Br)] and [Pd(dppe)(Ph)(I)]. Addition of dppe to [Pd(dppe)(Ph)(Br)] in toluene leads to the formation of **1** over several days, while reaction of [Pd(dppe)(Ph)(I)] with dppe in CH_2Cl_2 produced **1** in good yield, providing the most rational synthesis of **1**. The synthesis of complex **1** is summarized in Scheme 1.

Scheme 1[a]



[a] [Pd] = Pd(dppe).

Complex **1** (X = OTf) was characterized spectroscopically. The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) shows three multiplets consistent with the AA′BB′CC′ spin system, which can be reproduced by simulation[11] (Figure 1; see Table 1 for atom labeling and chemical shift and coupling constant information). The bridging phosphorus nuclei give rise to a multiplet at δ 17.8 with the large *trans* coupling constant $^2J_{PP}$ = 362 Hz, which is consistent with observations for the mononuclear pre-

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(10) (a) Prepared by the reaction of Pd(dppe)(R)(I) (R = Me, Ph) with AgOTf and PMes$_2$H. Details of the synthesis and characterization will be reported separately: Zhuravel, M. A., Grewal, N. S.; Glueck, D. S. Manuscript in preparation. (b) Prepared similarly using PHPh$_2$: Zhuravel, M. A.; Glueck, D. S. Manuscript in preparation.

(11) Simulation with gNMR v. 3.6 (Cherwell Scientific).

10.1021/om990378+ CCC: $18.00
Publication on Web 09/29/1999

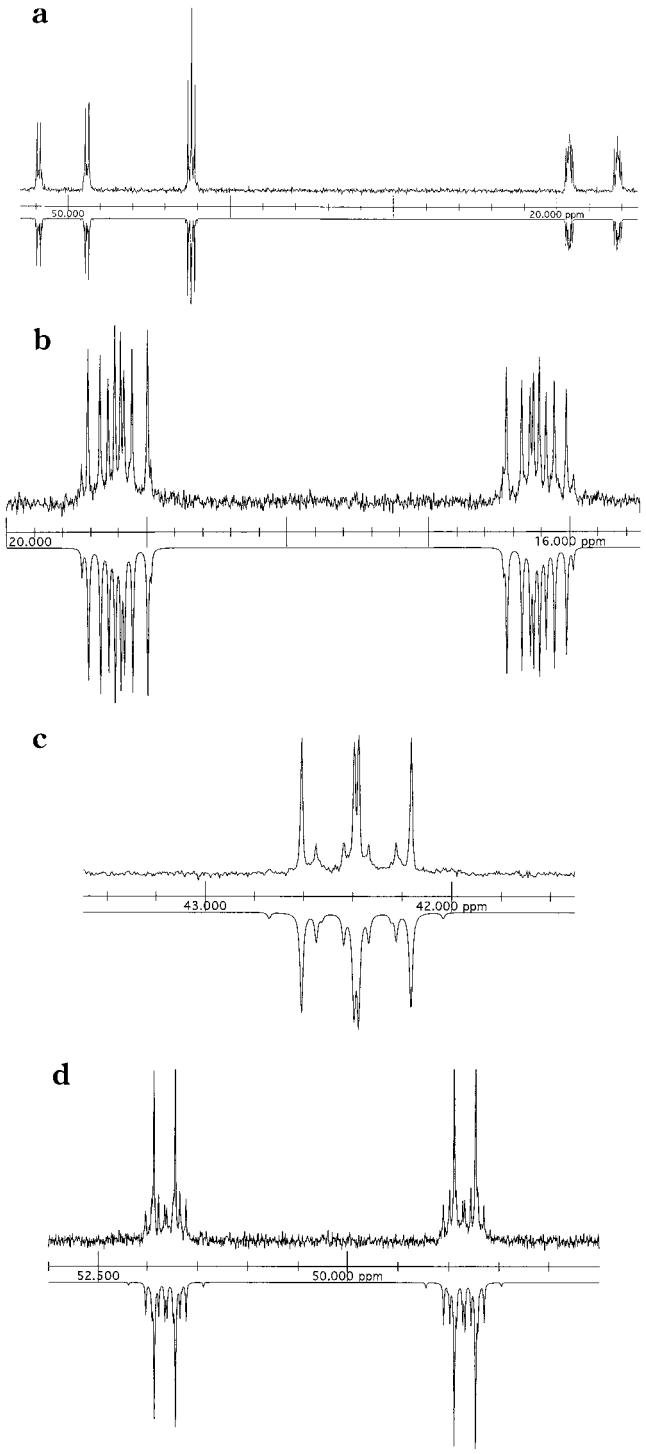


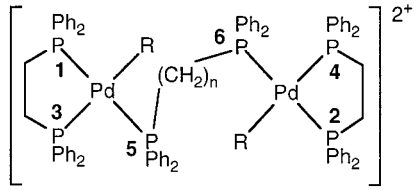
Figure 1. Experimental (top) and simulated (bottom) $^{31}P\{^1H\}$ NMR spectrum of **1**$[OTf]_2$ in CD_2Cl_2: (a) full spectrum; (b−d) expansions.

cursors $[Pd(dppe)(R)(PHMes_2)]^+$.[10a] Signals due to the chelating dppe phosphorus nuclei are multiplets at δ 50.3 and 42.4. The difference in ^{31}P NMR chemical shifts between the chelated and bridging dppe P nuclei is consistent with literature precedent.[12] Contributions from through-backbone and through-metal couplings have been suggested to account for J_{PP} values in metal complexes of chelate diphosphines.[13] Direct comparison of the P−P coupling constants observed for dppe in **1** (26 Hz, chelate, and 23 Hz, bridging) is difficult, however, because of the differing conformations of these ligands.[14]

In the ^1H NMR spectrum of **1** (CD_2Cl_2) the CH_2 protons of the chelate dppe appear as a multiplet at δ 2.15, in good agreement with the observation for the mononuclear complexes $[Pd(dppe)(R)(PR'_2H)]^+$.[10] The CH_2 protons of the bridging dppe, however, appear as a broad singlet at δ 1.02 with no apparent P−H coupling.

The crystal structure of **1** as the bromide salt is shown in Figure 2. Data collection and structure refinement are summarized in Table 2, and selected bond lengths

Table 1. Atom Labeling and ^{31}P NMR Data for Complexes 1−3[a]



	1	2	3
R	Ph	Me	Ph
bridging ligand	dppe	dppe	dppp
δ P(1,2)	50.3	57.4	52.7
δ P(3,4)	42.4	40.8	45.1
δ P(5,6)	17.8	20.3	17.0
J_{13}	26	33	25
J_{15}	362	369	360
J_{25}	2	1	0
J_{35}	28	27	29
J_{56}	23	21	0

[a] Solvent: CD_2Cl_2 for **1**, **2**, CD_3CN for **3**; ^{31}P NMR chemical shift reference: external 85% H_3PO_4; coupling constants in Hz.

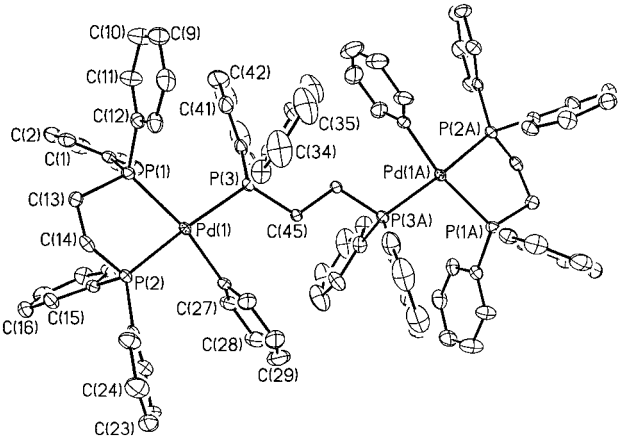


Figure 2. ORTEP diagram of **1**·2THF. For clarity, bromide counterions, solvent molecules, and hydrogen atoms are not shown. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Pd(1)−P(1) 2.360(2), Pd(1)−P(2) 2.281(2), Pd(1)−P(3) 2.336(2), Pd(1)−C(32) 2.047(4), P(3)−C(45) 1.824(6), C(45)−C(45)′ 1.53(1), P(1)−Pd(1)−P(2) 83.01(7), P(2)−Pd(1)−P(3) 174.86(7), P(3)−Pd(1)−P(1) 100.95(7), C(32)−Pd(1)−P(1) 169.6(1), C(32)−Pd(1)−P(2) 86.8(1), C(32)−Pd(1)−P(3) 89.3(1).

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Table 2. Crystallographic Data for [(Pd(dppe)(Ph))$_2$(μ-dppe)]Br$_2$ (1)·2THF

formula	$C_{98}H_{98}Br_2O_2P_6Pd_2$
fw	1866.20
space group	$P\bar{1}$
a, Å	11.700(4)
b, Å	12.461(4)
c, Å	16.762(7)
α, deg	84.60(2)
β, deg	82.26(2)
γ, deg	63.86(2)
V, Å^3	2172.4(2)
Z	1
cryst color, habit	colorless block
D(calc), g/cm^3	1.426
μ(MoKα), cm^{-1}	14.93
temp, K	264(2)
diffractometer	Siemens P4
radiation	Mo Kα (λ = 0.71073 Å)
$R(F)$, %[a]	5.31
$R(wF^2)$, %[a]	12.77

[a] Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$.

and angles appear in the figure caption. Additional details are given in the Experimental Section and the Supporting Information. The geometry around each palladium center is distorted square planar, and the Pd−P bond lengths are similar. The longest of these (2.360(2) Å) is *trans* to the Ph group, while the other Pd−P bond lengths are 2.281(2) Å (*trans* to μ-dppe) and 2.336(2) Å (*trans* to chelating dppe), respectively. The P−CH_2 and C−C bond lengths in the bridging dppe (1.824(6) and 1.53(1) Å) are consistent with the data for free dppe[15] (1.829(3) and 1.521(7) Å). The C−C−P angles are also very similar: 114.5(6)° (in **1**) and 110.9(4)° (free dppe), indicating that the bridging dppe is not sterically constrained.

The solution ^{31}P NMR spectrum of **1** is consistent with its crystal structure. In contrast, the solid-state structures of several known μ-diphosphine complexes differ from their (sometimes dynamic) solution structures. For example, the crystal structure of [Ni(dppe)(NO)]$_2$(μ-dppe)[7] shows distorted tetrahedral coordination at nickel, but no P−P coupling is observed in the ^{31}P NMR spectrum at room temperature. In the solid-state structure of [Pd(dippe)]$_2$(μ-dippe)[16] (dippe = (i-Pr)$_2$PCH$_2$CH$_2$P(i-Pr)$_2$), the P nuclei of a chelating dippe are inequivalent, which would give rise to an [ABC]$_2$ spin system. In solution, however, a simpler [AB$_2$]$_2$ spin system is observed, which was ascribed to facile rotation of the Pd(dippe) fragment around the remaining Pd−P bond. Finally, the bridging dmpe observed by X-ray crystallography for [Rh$_2$(dmpe)$_4$(μ-dmpe)][Cp]$_2$[6] (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$, Cp = $C_5H_5^-$) dissociates in solution, and [Pt(dfepe)(CO)]$_2$(μ-dfepe)[8b] (dfepe = (C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$) disproportionates in solution.

The substitution of PMes$_2$H with a chelating diphosphine is a general reaction. Addition of 0.5 equiv of dppe to a solution of [Pd(dppe)(Me)(PMes$_2$H)]OTf[10a] in CH_2Cl_2 results in the formation of the insoluble complex [(Pd(dppe)(Me))$_2$(μ-dppe)][OTf]$_2$ (**2**), which was characterized by elemental analysis and IR spectroscopy. The solubility of **2** in common solvents is not high enough for NMR spectroscopy; however, the ^{31}P NMR spectrum of the reaction mixture confirms the loss of PMes$_2$H. Stirring **2** with 2 equiv of K(BAr′$_4$) (Ar′ = 3,5-(CF$_3$)$_2$C$_6$H$_3$) produces the soluble BAr′$_4$ salt of **2**. The second-order ^{31}P NMR spectrum of **2**[BAr′$_4$]$_2$ (CD_2Cl_2) is very similar to that of **1** (Table 1), as expected. The ^{1}H NMR spectrum ($CDCl_3$) includes peaks due to Pd−Me (m, δ 0.30) and dppe CH_2 resonances (δ 2.45−1.90 (m, chelate dppe); 0.7 (m, μ-dppe)) similar to those in **1**.

Similarly, reaction of [Pd(dppe)(Ph)(PMes$_2$H)]OTf with dppp gives the dppp-bridged dication [(Pd(dppe)(Ph))$_2$(μ-dppp)][OTf]$_2$ (**3**) in excellent yield. As expected, since the longer bridge of dppp reduces the long-range couplings,[9b,16] the ^{31}P NMR spectrum of **3** (CD_3CN) is much simpler than those of **1** and **2** (Table 1). The bridging dppp gives rise to a doublet of doublets at δ 17.0 with a large *trans* (360 Hz) and a small *cis* (29 Hz) coupling constant, and peaks due to dppe appear as two doublets of doublets at δ 52.7 and 45.1. As in the dppe-bridged complexes, the μ-dppp CH_2 ^{1}H NMR signals are a broad multiplet at δ 0.76 (acetone-d_6).

We have not explored the generality of these phosphine substitution reactions with ligands less bulky than PHMes$_2$ in detail. However, although complex **1** forms rapidly when dppe is added to [Pd(dppe)(Ph)(PHMes$_2$)]$^+$ in THF, the analogous diphenylphosphine complex[10b] [Pd(dppe)(Ph)(PHPh$_2$)]$^+$ does not react with dppe in THF under similar conditions.

In conclusion, the dinuclear diphosphine-bridged complexes [(Pd(dppe)(R))$_2$(μ-diphos)]$^{2+}$ form readily when the cationic complexes [Pd(dppe)(R)(PMes$_2$H)]X are treated with diphos or by substitution of the halide X in [Pd(dppe)(R)(X)]. NMR and crystal structure data for **1** confirm that the diphosphine-bridged solid-state structure is maintained in solution and reveal similar bonding characteristics for chelate and μ-dppe ligands.

Experimental Section

General Experimental Details. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at 20 °C in a drybox or using standard Schlenk techniques. Petroleum ether (bp 38−53 °C), ether, THF, and toluene were dried and distilled before use by employing Na/benzophenone. CH_2Cl_2 was distilled from CaH_2. Acetone and acetonitrile were degassed by purging with N_2 and stored over molecular sieves.

Unless otherwise noted, all NMR spectra were recorded by using a Varian 300 MHz spectrometer. ^{1}H or ^{13}C NMR chemical shifts are reported vs Me_4Si and were determined by reference to the residual ^{1}H or ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported vs H_3PO_4 (85%) used as an external reference. Coupling constants are reported in hertz (Hz). Unless otherwise noted, peaks in NMR spectra are singlets. Infrared spectra were recorded on KBr pellets on a Perkin-Elmer 1600 series FTIR machine and are reported in cm^{-1}. Elemental analyses were provided by Schwarzkopf Microanalytical Laboratory. Low-resolution FAB mass spectroscopy was performed by S. L. Mullen on a VG ZAB-SE instrument at the University of Illinois.

Unless otherwise noted, reagents were from commercial suppliers. The following compounds were made by the literature procedures: [Pd(dppe)(Ph)(I)],[17] [Pd(dppe)(Me)(Cl)],[18]

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K(BAr′$_4$).[19] [Pd(dppe)(Ph)(Br)] was prepared as for [Pd(dppe)(Ph)(I)] by treatment of [*trans*-Pd(PPh$_3$)$_2$(Ph)(Br)][20] with dppe.

[(Pd(dppe)(Ph))$_2$(μ-dppe)]X$_2$ (X = BF$_4$, OTf, Br, I) (1). Method 1. [Pd(dppe)(Ph)(PMes$_2$H)]OTf (108 mg, 0.11 mmol) was dissolved in 2 mL of CH_2Cl_2. Dppe (22 mg, 0.06 mmol) was added to the yellow solution as a solid, and the mixture was allowed to stir for 20 min, after which precipitation of white solid started. Diethyl ether was added, and cooling to −25 °C afforded the product as 81 mg (81% yield) of off-white solid. Anal. Calcd for $C_{92}H_{82}F_6O_6P_6Pd_2S_2$: C, 59.40; H, 4.44. Found: C, 59.48; H, 4.79. The tetrafluoroborate salt of **1** was prepared in a similar fashion.

^{1}H NMR (CD_2Cl_2): δ 7.56−7.26 (m, 28H, Ph), 7.14−6.98 (m, 24H, Ph), 6.78−6.43 (m, 18H, Ph), 2.30−2.00 (m, 8H, CH_2), 1.02 (broad, 4H, CH_2). IR: 3053, 1563, 1482, 1436, 1268, 1222, 1149, 1102, 1029, 997, 878, 820, 692, 636. FAB MS (Magic Bullet): *m*/*z* 979.2 (Pd(dppe)$_2$Ph), 902.2 (Pd(dppe)$_2$), 581.1 (Pd(dppe)Ph), 553.0, 504.0 (Pd(dppe)), 475.1, 427.0, 399.9, 367.0, 290.9, 263.1, 212.9, 183.1.

Method 2. [Pd(dppe)(Ph)(I)] (74 mg, 0.1 mmol) was dissolved in 1 mL of CH_2Cl_2. Dppe (21 mg, 0.05 mmol) was added to the yellow solution as a solution in 1 mL of CH_2Cl_2, and the reaction mixture was stirred for 20 min. The solution was filtered and crystallized by adding Et_2O and cooling to −25 °C. The crude product was obtained as 64 mg (68% yield) of yellow solid. The bromide salt of **1** was prepared in a similar way and used for X-ray crystallography.

[(Pd(dppe)(Me))$_2$(μ-dppe)]X$_2$ (X = OTf, BAr′$_4$) (2) Method 1. [Pd(dppe)(Me)(PMes$_2$H)]OTf[10a] (77 mg, 0.08 mmol) was dissolved in 2 mL of CH_2Cl_2. Dppe (17 mg, 0.04 mmol) was added to the yellow solution as a solid, and the reaction mixture was allowed to stir for 20 min. Precipitation of white solid started immediately after the addition of the dppe. The solution was decanted, and the solid residue was washed with Et_2O (4 × 5 mL) and dried in a vacuum to give the product as 51 mg (71% yield) of insoluble off-white solid. Anal. Calcd for $C_{82}H_{78}F_6O_6P_6Pd_2S_2$: C, 56.73; H, 4.53. Found: C, 57.01; H, 4.65. IR: 3054, 2966, 2895, 1482, 1436, 1272, 1223, 1150, 1102, 1030, 748, 696, 636.

Method 2. To a solution of [Pd(dppe)(Me)(Cl)] (111 mg, 0.20 mmol) in 3 mL of CH_2Cl_2 was added AgOTf (52 mg, 0.20 mmol). The solution was allowed to stand for 5 min and filtered, and then dppe (40 mg, 0.10 mmol) was added. After an additional 5 min, a white solid precipitated. The solution was decanted, and the solid residue was washed with 3 × 10 mL of Et_2O and dried. Then K(BAr′$_4$) (361 mg, 0.40 mmol) was added as a solution in 3 mL of THF. The slurry was stirred for 2 days and filtered. Petroleum ether was added, and cooling to −25 °C gave the crude product as a yellow oil, which could not be obtained analytically pure by recrystallization. ^{1}H NMR ($CDCl_3$): δ 7.80−6.80 (m, 70H), 2.40−1.95 (m, 8H, CH_2), 0.65 (m, 4H, CH_2), 0.30 (m, 6H, Me).

[(Pd(dppe)(Ph))$_2$(μ-dppp)][OTf]$_2$ (3). [Pd(dppe)(Ph)(PMes$_2$H)]OTf[10a] (88 mg, 0.09 mmol) was dissolved in 2 mL of CH_2Cl_2. Dppp (19 mg, 0.05 mmol) was added to the yellow solution as a solid, and the reaction mixture was allowed to stir for 20 min. The solution was filtered, Et_2O was added, and cooling to −25 °C afforded the product as 81 mg (99% yield) of off-white solid. Anal. Calcd for $C_{93}H_{84}F_6O_6P_6Pd_2S_2$: C, 59.59; H, 4.52. Found: C, 59.76; H, 4.74. ^{1}H NMR ((CD$_3$)$_2$CO): δ 7.61−7.05 (m, 55H, Ph), 6.88−6.81 (m, 7H, Ph), 6.64−6.59 (m, 2H, Ph), 6.41−6.36 (m, 3H, Ph), 6.24−6.18 (m, 3H, Ph), 2.36−2.22 (br m, 8H, CH_2), 0.76 (br m, 6H, CH_2). IR: 3059, 3024, 2922, 2849, 1600, 1492, 1452, 1028, 906, 756, 697.

Crystallographic Structural Determination. A summary of the crystallographic data is given in Table 2. A suitable crystal was selected and mounted in a nitrogen-flushed, thin-walled glass capillary. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($15° \leq 2\theta \leq 25°$). No evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data. *E*-statistics suggest the centrosymmetric space group option, $P\bar{1}$, which yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix, least-squares procedures. No absorption corrections were required because there was less than 10% variation in the integrated ψ-scan intensities. The molecule lies on a crystallographic inversion center and cocrystallized with two molecules of THF. All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were treated as idealized contributions. All phenyl rings were refined as rigid planar bodies to conserve a reasonable data-to-parameter ratio. All software and sources of the scattering factors are contained in the SHELXTL (5.10) program library.[21]

Acknowledgment. We thank the NSF Career Program, DuPont, and Union Carbide (Innovation Recognition Program) for partial support, and the Department of Education for a GAANN fellowship for M.A.Z. The University of Delaware thanks the NSF (CHE-9628768) for their support of the purchase of the CCD-based diffractometer.

Supporting Information Available: Details of the crystal structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990378+

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