Formation of a Chelate Bis(phosphino)[3]ferrocenophane Ligand and Its Use in Palladium-Catalyzed Alternating CO/Ethene Copolymerization

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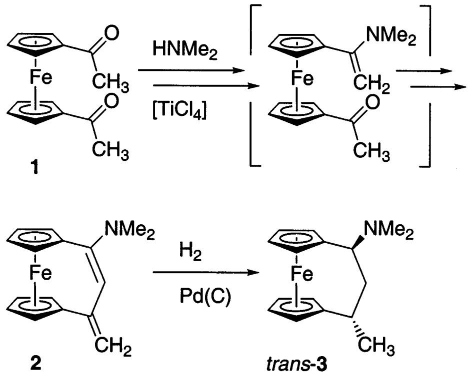
Received January 31, 2003

Treatment of 1,1′-diacetylferrocene (**1**) with dimethylamine, catalyzed by titanium tetrachloride, proceeded in a Mannich-type C−C coupling reaction to yield the unsaturated [3]ferrocenophane **2**. Subsequent catalytic hydrogenation gave the saturated [3]ferrocenophane derivative [($C_5H_4CHMeCH_2CH(NMe_2)C_5H_4$)Fe] (*trans*-**3)**. Directed Cp metalation of *trans*-**3** was carried out by treatment with *n*-BuLi, followed by reaction with $ClPPh_2$ to yield the "ortho-phosphorylated" *P*,*N*-[3]ferrocenophane chelate ligand **4**. Its treatment with $HPPh_2$ in acetic acid resulted in a clean substitution of the $-NMe_2$ group by $-PPh_2$ with overall stereochemical retention to yield the *P*,*P*-[3]ferrocenophane ligand **5**. The stereochemical pathway of such substitution reactions at the [3]ferrocenophane framework, which proceed cleanly by a double-inversion route with participation of the metal center, was modeled by computational chemistry and its reactive cationic intermediate **14** characterized by a DFT calculation. Reaction of **4** with (cod)$PdCl_2$ gave the chelate complex **6**. The analogous reaction of **5** with (cod)$PdCl_2$ furnished the *P*,*P*-[3]ferrocenophane−$PdCl_2$ chelate complex **7**. Both the complexes **6** and **7** and the ligand **5** were characterized by X-ray diffraction. Treatment of **7** with $AgBF_4$ in dichloromethane or alternatively of **5** with palladium acetate, followed by BF_3 addition, gave very active catalyst systems for alternating carbon monoxide/ethene copolymerization.

We have recently found a novel, very convenient synthetic pathway to functionalized [3]ferrocenophane derivatives[1] and related compounds.[2] For example, in a one-pot procedure 1,1′-diacetylferrocene (**1**) is treated with a secondary amine in the presence of titanium tetrachloride. Under these typical conditions of enamine formation[3] the corresponding intermediate is not stable but undergoes a $TiCl_4$ Lewis acid catalyzed Mannich-type condensation reaction to directly yield the unsaturated [3]ferrocenophane derivative **2** (see Scheme 1). A subsequent catalytic hydrogenation then yields 1,1′-[1-(dimethylamino)-1,3-butanediyl]ferrocene (**3**).[4] This very efficient two-step procedure yields the respective cis- and trans-disubstituted [3]ferrocenophanes (i.e. *cis*-**3** and *trans*-**3**) in a ca. 1:7 diastereomeric ratio. The pure *trans*-**3** isomer was obtained isomerically pure after one recrystallization.[4]

Scheme 1



The [3]ferrocenophane moiety has been utilized as a rather rigid framework for the construction of chelate ligands, especially bis(phosphine) chelate ligands.[5] In a beautiful series of papers especially Weissensteiner et al.[6] have developed this chemistry, including enantiomerically pure derivatives,[7] starting from conventional entries into [3]ferrocenophane chemistry. We have now developed some novel synthetic entries to chelate bis(donor ligand)[3]ferrocenophane systems that were based on our simple two-step preparative pathway to α-functionalized [3]ferrocenophanes, and we have found that such ligands can probably play a significant role in the development of new active catalyst variations

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[†] X-ray crystal structure analyses.

[‡] DFT calculations.

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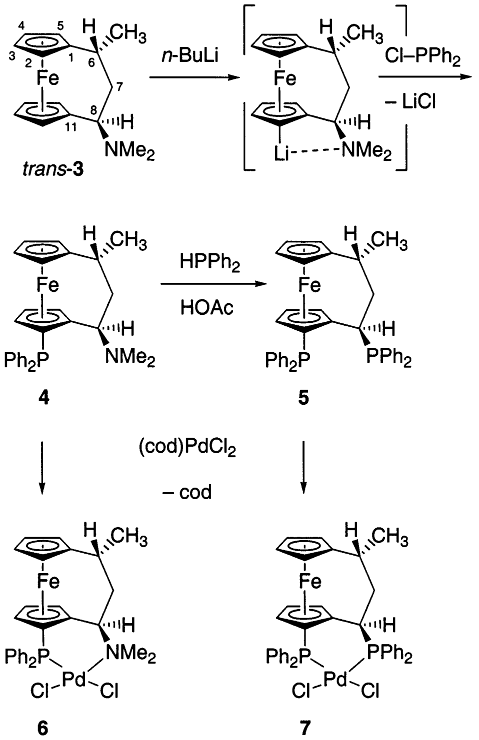
Scheme 2



for applications in catalytic alternating carbon monoxide/olefin polymerization reactions.[8]

Results and Discussion

Synthesis of the Doubly Functionalized [3]Ferrocenophane Derivatives. The (dimethylamino)[3]-ferrocenophane compound *trans*-**3**[4] was subjected to a directed metalation[9] by treatment with *n*-butyllithium. After 3 h phosphorylation was carried out by treatment with chlorodiphenylphosphine to yield **4** (see Scheme 2). Next, the dimethylamino group was exchanged for $-PPh_2$. This was achieved by treatment of **4** with $HPPh_2$ in acetic acid solution.[10] The chelate ligand system **5** was isolated in ca. 65% yield.

The mono(phosphine) **4** shows a characteristic set of four ^{13}C NMR Cp methine signals at δ 67.5, 68.6, 70.2, and 72.2, corresponding to the C_5H_4 ring of the ferrocene system (*ipso*-C at δ 93.3), and another set of three methine resonances at δ 68.9, 73.9, and 74.1 (*ipso*-C at δ 91.4) of the C_5H_3(P) unit. The C(P) ^{13}C NMR resonance of the latter ring is observed at δ 75.2 with a coupling constant of $^1J(P,C) = 12$ Hz. The ^{1}H NMR signals of the substituted butane-1,3-diyl bridge of the single isomer of the [3]ferrocenophane system **4** are detected at δ 2.31, 3.16 (7-H,H′ (CH_2)), 2.68 (8-H), 2.84 (6-H), 1.22 (6-CH_3), and 1.79 (8-NMe_2). The subsequent substitution reaction of the NMe_2 group has taken place by complete retention of configuration. This was revealed by the characteristic set of NMR resonances of the obtained single, isomerically pure product (**5**; for details see the Experimental Section), and the relative stereochemical assignment was secured by an X-ray crystal structure analysis of **5** (see below). The relative stereochemical positioning of the $-NMe_2$ and $-PPh_2$ groups in **4** and the pair of $-PPh_2$ groups in **5** makes both of these compounds suitable chelate ligands for $PdCl_2$ coordination.

The N,P-chelate ligand **4** reacts readily with (cyclooctadiene)$PdCl_2$[11] by replacement of the cod ligand and formation of the N,P-chelate-$PdCl_2$ complex **6** (see Scheme 2). Chelate ring formation has made the $-N(CH_3)_2$ groups in **6** diastereotopic (^{1}H NMR: δ 2.81, 3.18), and the ^{31}P NMR resonance was shifted from δ -21.7 in **4** to δ 12.9 in **6**. The reaction of (cod)$PdCl_2$ with **5** required several hours at room temperature to go to completion and to yield the sparingly soluble P,P-chelate$-PdCl_2$ complex **7** (ca. 90% isolated yield). It shows a pair of ^{31}P NMR signals at δ 16.0 (AX, $J(P,P) = 5.2$ Hz) and δ 57.4 that is characteristically shifted from the corresponding ^{31}P NMR resonances of the free ligand (**5**: δ -22.4, -7.9, $J(P,P) = 80$ Hz).

X-ray Crystal Structure Analyses. Single crystals suitable for a structural characterization by X-ray diffraction were obtained from the P,P-ligand system **5** and both of the palladium complexes **6** and **7**. A view of the molecular structure of **5** is depicted in Figure 1. It shows a projection of the [3]ferrocenophane framework in its characteristic conformation with the pair of attached $-PPh_2$ functional groups. The metallocene nucleus is only slightly distorted by the attachment of the bridging C_3 chain. The two substituted Cp rings are only marginally tilted toward the connecting bridge. This leads to a small but typical shortening of the Fe$-$C1 (2.021(2)Å) and Fe$-$C11 (2.010(2)Å) linkages of the metal to the *ipso*-C(Cp) atoms. The adjacent metal$-$carbon bonds are longer (Fe$-$C5/C2 = 2.033(2)/2.037(2) Å; Fe$-$C12/C15 = 2.035(2)/2.038(2) Å) and the distal Fe$-$C(Cp) bonds are even slightly longer (Fe$-$C3/C4 = 2.053(2)/2.055(2) Å; Fe$-$C14/C13 = 2.048(2)/2.058(2) Å).[13]

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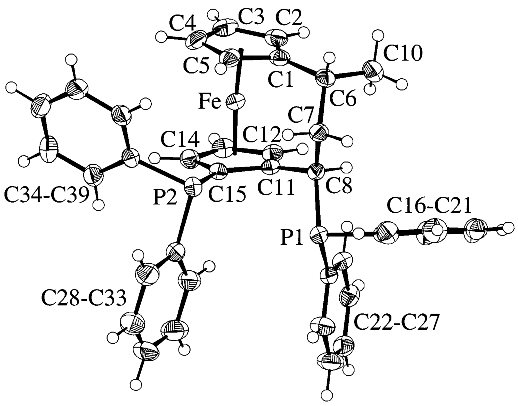

Figure 1. Molecular geometry of the *P*,*P*-[3]ferrocenophane ligand **5**. Selected bond lengths (Å) and angles (deg): Fe−C1 = 2.021(2), Fe−C11 = 2.010(2), Fe−C2 = 2.037(2), Fe−C12 = 2.035(2), Fe−C3 = 2.053(2), Fe−C13 = 2.058(2), Fe−C4 = 2.055(2), Fe−C14 = 2.048(2), Fe−C5 = 2.033(2), Fe−C15 = 2.038(2), C1−C6 = 1.512(2), C6−C7 = 1.543(2), C6−C10 = 1.531(3), C7−C8 = 1.551(2), C8−C11 = 1.510(2), C8−P1 = 1.872(2), P1−C16 = 1.842(2), P1−C22 = 1.837(2), C15−P2 = 1.830(2), P2−C28 = 1.840(2), P2−C34 = 1.847(2); C1−C6−C7 = 112.6(1), C1−C6−C10 = 112.2(2), C10−C6−C7 = 111.8(2), C6−C7−C8 = 115.6(1), C7−C8−C11 = 114.3(1), C7−C8−P1 = 108.7(1), C11−C8−P1 = 110.2(1), C8−P1−C16 = 100.0(1), C8−P1−C22 = 103.3(1), C16−P1−C22 = 100.1(1), C15−P2−C28 = 101.5(1), C15−P2−C34 = 100.4(1), C28−P2−C34 = 99.6(1).

The ansa bridge is strongly folded. The C5−C1−C6−C7−C8−C11−C15 unit of seven carbon atoms is boat-shaped, similar to a corresponding seven-membered carbocyclic ring system with C7 attaining the “tip” position.[14] This leads to a pronounced spatial distinction of the substituents at the C6 to C8 bridge: the methyl substituent at C6 attains a pseudoaxial position at the metallacyclic ring system, whereas the bulky −PPh$_2$ substituent attached at C8 is oriented pseudoequatorially. The corresponding dihedral angles at the bridging unit amount to 68.4(2)° (C1−C6−C7−C8), −65.8(2)° (C6−C7−C8−C11), −59.0(2)° (C10−C6−C7−C8), and 170.6(1)° (C6−C7−C8−P1). The Ph$_2$P(2) group is attached at the C11 to C15 Cp ring with its C15−P2 vector (1.830(2) Å) lying in the Cp plane. The angle between the C15−P2 and the C8−P1 vectors amounts to 53.3°. The bond angles at both phosphorus atoms are found within a narrow range between 103.3(1) and 99.6(1)°. Both phosphorus centers have their attached phenyl groups arranged so that they are pointing away from each other toward the outside of the molecule (see Figure 1), leaving the inside between the two phosphorus centers available for bonding.[15] The P1−P2 distance in **5** amounts to 3.633 Å.

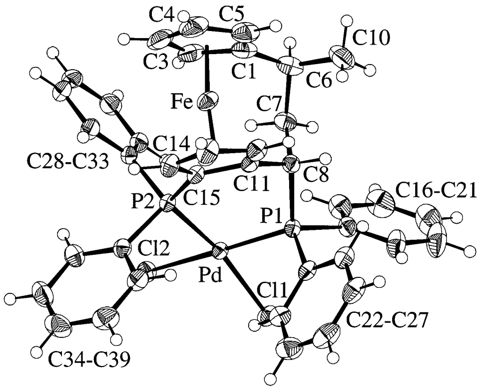

Figure 2. View of the molecular structure of the palladium complex **7**. Selected bond lengths (Å) and angles (deg): Fe−C1 = 2.019(2), Fe−C11 = 2.010(2), Fe−C2 = 2.040(2), Fe−C12 = 2.039(2), Fe−C3 = 2.057(2), Fe−C13 = 2.063(2), Fe−C4 = 2.060(2), Fe−C14 = 2.057(2), Fe−C5 = 2.043(2), Fe−C15 = 2.038(2), C1−C6 = 1.513(3), C6−C7 = 1.553(3), C6−C10 = 1.532(3), C7−C8 = 1.545(3), C8−C11 = 1.503(3), C8−P1 = 1.857(2), P1−Pd = 2.252(1), P1−C16 = 1.821(2), P1−C22 = 1.812(2), C15−P2 = 1.799(2), P2−C28 = 1.816(2), P2−C34 = 1.818(2), P2−Pd = 2.252(2), Pd−Cl1 = 2.361(1), Pd−Cl2 = 2.364(1); C1−C6−C7 = 112.4(2), C1−C6−C10 = 112.9(2), C10−C6−C7 = 111.1(2), C6−C7−C8 = 115.3(2), C7−C8−C11 = 115.1(2), C7−C8−P1 = 111.1(1), C11−C8−P1 = 108.2(1), C8−P1−Pd = 115.5(1), C8−P1−C16 = 104.5(1), C8−P1−C22 = 103.6(1), Pd−P1−C16 = 110.7(1), Pd−P1−C22 = 112.9(1), C16−P1−C22 = 109.0(1), C15−P2−C28 = 108.7(1), C15−P2−C34 = 102.9(1), C15−P2−Pd = 116.7(1), C28−P2−Pd = 116.3(1), C34−P2−Pd = 104.5(1), C28−P2−C34 = 106.1(1), P1−Pd−P2 = 94.30(2), P1−Pd−Cl1 = 88.81(2), P1−Pd−Cl2 = 176.22(2), P2−Pd−Cl1 = 167.80(2), P2−Pd−Cl2 = 87.46(2), Cl1−Pd−Cl2 = 90.16(2).

The X-ray crystal structure analysis of **7** revealed now ideally the coordination geometry of the ligand system **5** was to accommodate the PdCl$_2$ unit (Figure 2).[15] The essential structural features of the ligand system in complex **7** are almost identical with those of the free ligand. As expected, the Pd(II) center is (distorted) square planar coordinated (∑° = 360.7°) inside the chelate framework, with both Pd−P bond lengths amounting to 2.252(1) Å. The cis bonding angles around Pd are in a range between 87.46(2) and 94.30(2)°. The trans bond angles at palladium were found at 167.80(2) and 176.22(2)°. Bonding of the phosphorus atoms to the metal has resulted in a slight decrease of the adjacent C15−P2 (1.799(2) Å) and C8−P1 (1.857(2) Å) bond lengths. The C11−C8−P1 angle has become slightly smaller (108.2(1)°; for **5**, 110.2(1)°) and the adjacent angles at C8 have increased slightly (C11−C8−C7 = 115.1(1)° (**7**), 114.3(1)° (**5**); C7−C8−P1 = 111.1(1)° (**7**), 108.7(1)° (**5**)). Both phosphorus centers in **7** are pseudotetrahedrally coordinated, with bond angles at P1 ranging between 115.5(1)° (C8−P1−Pd) and 103.6(1)° (for P2, the range is 116.7(1)° (C15−P2−Pd) to 102.9(1)°). The angle between the C15−P2 and C8−P1 vectors in **7** amounts to −43.0°; the distance between P1 and P2 in **7** is 3.302 Å.

The structure of the P,N-chelate [3]ferrocenophane palladium complex **6** is very similar (Figure 3). The C8−N9 bond length is 1.519(3) Å, and the N9−Pd bond length amounts to 2.148(2) Å (Pd−P = 2.259(1) Å). The Pd−Cl bond lengths in **6** are 2.302(1) Å (Pd−Cl2) and 2.357(1) Å (Pd−Cl1). Again, the Pd atom is pseudo square planar coordinated (∑° = 359.8°) with the cis bond angles at Pd ranging from 85.4(1) to 94.8(1)° and the trans bond angles being 177.7(1) and 172.1(1)°. The C12−P and C8−N9 vectors form an angle of −41.1°, and the P···N9 separation in complex **6** is 3.246 Å.

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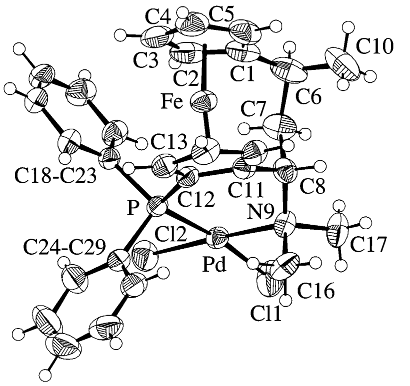
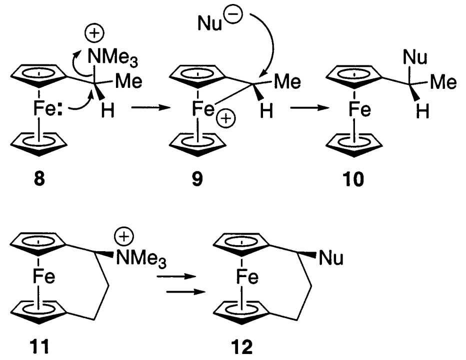


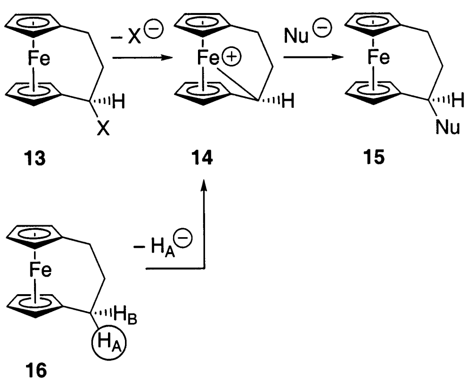
Figure 3. Molecular structure of **6**. Selected bond lengths (Å) and angles (deg): Fe−C1 = 2.028(3), Fe−C11 = 2.007(3), Fe−C2 = 2.038(3), Fe−C12 = 2.027(3), Fe−C3 = 2.056(3), Fe−C13 = 2.053(3), Fe−C4 = 2.053(3), Fe−C14 = 2.057(3), Fe−C5 = 2.039(3), Fe−C15 = 2.040(3), C1−C6 = 1.506(5), C6−C7 = 1.541(4), C6−C10 = 1.528(5), C7−C8 = 1.545(4), C8−C11 = 1.501(4), C8−N9 = 1.519(3), N9−Pd = 2.148(2), N9−C16 = 1.489(4), N9−C17 = 1.499(3), C12−P = 1.795(3), P−C18 = 1.816(2), P−C24 = 1.829(2), P−Pd =2.259(1), Pd−Cl1 = 2.357(1), Pd−Cl2 = 2.302(1); C1−C6−C7 = 111.7(3), C1−C6−C10 = 113.1(3), C10−C6−C7 = 112.5(3), C6−C7−C8 = 114.8(3), C7−C8−C11 = 114.5(2), C7−C8−N9 = 109.7(2), C11−C8−N9 = 111.4(2), C8−N9−Pd = 114.1(2), C8−N9−C16 = 109.7(2), C8−N9−C17 = 107.1(2), Pd−N9−C16 = 106.6(2), Pd−N9−C17 = 113.8(2), C16−N9−C17 = 105.1(2), C12−P−C18 = 105.6(1), C12−P−C24 = 103.6(1), C12−P−Pd = 112.9(1), C18−P−Pd = 118.0(1), C24−P−Pd = 110.1(1), C18−P−C24 = 105.5(1), N9−Pd−P = 94.8(1), N9−Pd−Cl1 = 91.9(1), N9−Pd−Cl2 = 177.7(1), P−Pd−Cl1 = 172.1(1), P−Pd−Cl2 = 85.4(1), Cl1−Pd−Cl2 = 87.7(1).

Scheme 3



Computational Evaluation of the Stereoselective Substitution Pathway. It is well-known that nucleophilic substitution in the α-position at a ferrocene side chain proceeds with retention of the configuration. In the open-chain system this was attributed by Ugi et al.[16] to a two-step reaction mechanism involving the metal atom: thus, by a typical double-inversion pathway such as that shown in Scheme 3. Tainturier, Gautheron,[7] and later Weissensteiner et al.[6] have shown that the analogous nucleophilic substitution reaction at [3]ferrocenophanes also proceeds with overall stereochemical retention (e.g. **11** → **12** in Scheme 3).

Scheme 4



The structural characterization of the systems **5**−**7** (and earlier structural work by us[4] and by Weissensteiner et al.[6]) has shown that the positioning of the −X substituent at the [3]ferrocenophane bridge is pseudoequatorial. This orientation would be ideally suited from a stereochemical point of view to allow participation of the metal atom by an internal nucleophilic attack (proceeding with inversion at the stereogenic center). The following external attack of a nucleophile would cleave the metal−carbon bond of the cationic intermediate and finish the double-inversion pathway to give the observed product (e.g. **15** from **13** in Scheme 4).

A computational study has now shown that the alleged intermediate of this pathway (**14**) can indeed be formed readily, although it contains a rather distorted bridging framework. In the DFT study[17] we started from the unfunctionalized [3]ferrocenophane **16**. The investigation showed that abstraction of a pseudoequatorial hydride (H^-) proceeds in a facile manner to yield the intermediate **14** (see Figure 4).

The DFT-calculated structure of **16** is analogous to the framework experimentally observed for the substituted [3]ferrocenophane derivatives. The connecting C1−C6 linkage is found in the calculation at 1.505 Å, and the corresponding C1−C6 vector is only tilted marginally out the Cp plane by 4.0° (see Figure 4). In the calculated structure of the cationic intermediate **14** there is a strong Fe−C8 interaction (2.206 Å), and both the ferrocene unit and the connecting bridge are distorted. Inside the metallocene framework the Fe−C11 bond is rather short at 1.966 Å. The C11−C8 linkage is short at 1.414 Å, and the C11−C8 vector is considerably bent outside the adjacent averaged Cp plane by ca. 43°.[18]

Behavior of the Palladium Complexes 6 and 7 in Alternating CO/Ethene Copolymerization. Che-

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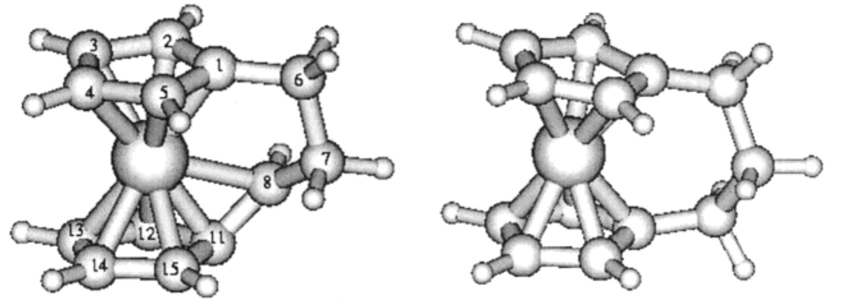
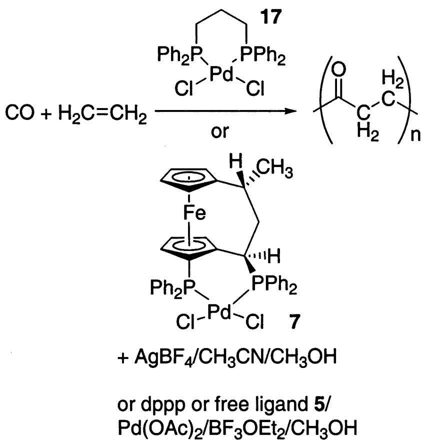


Figure 4. Views of the DFT-calculated structures of the neutral parent [3]ferrocenophane **16** (right) and the cationic [3]ferrocenophane derivative **14** (left). Selected bond lengths (Å) of **14** (**16**): C(Cp)−Fe = 1.966−2.155 (2.028−2.068), C1−C6 = 1.518 (1.505), C6−C7 = 1.550 (1.545), C7−C8 = 1.508 (1.545), C8−C11 = 1.414 (1.505), C8−Fe = 2.206 (3.102). The out-of-plane bending angle C8−C11−ring is 42.90° (4.00°).

Scheme 5



late phosphine ligands have been used successfully for generating very active Pd(II) catalysts for alternating CO/alkene copolymerization.[8,19] As a reference system we have carried out CO/ethene copolymerization using the (dppp)PdCl$_2$ (**17**) catalyst precursor (Scheme 5).[20] It was activated by treatment with AgBF$_4$ in dichloromethane solution that contained a small quantity of acetonitrile. Methanol was added and then the system pressurized with ethene (30 bar) and then CO (ca. 30 bar). After the reaction was allowed to proceed overnight at ambient temperature, the CO/ethene alternating copolymer was obtained after the usual workup (catalyst activity a = 157 g/mmol of [Pd]) (Table 1). In an alternative procedure, a dichloromethane solution of the free diphosphine dppp and Pd(OAc)$_2$ was treated with boron trifluoride etherate and activated with methanol. Again, the system was pressurized with ethene (30 bar) and CO (30 bar) and allowed to react at ambient temperature overnight. After workup the copolymer could be obtained (catalyst activity a = 68 g/mmol of [Pd]).

We have tried to carry out the CO/ethene copolymerization reaction under analogous conditions using the *P*,*N*-[3]ferrocenophane−PdCl$_2$ complex **6** and the free ligand **4**/Pd(OAc)$_2$ as catalyst precursors, but these systems turned out to be close to inactive.[21] However, the corresponding *P*,*P*-[3]ferrocenophane−PdCl$_2$ chelate complex **7** gave a very active catalyst after AgBF$_4$ treatment. Under the applied conditions a catalyst activity of ca. 100 g of alternating CO/ethene copolymer/mmol of [Pd] was obtained. An even higher activity was obtained when the active catalyst was prepared in situ. For this, the free ligand **5** was reacted with palladium acetate and boron trifluoride etherate. The polymers were characterized by ^{13}C NMR (signals at δ 212.9 (C=O) and δ 35.6 (CH$_2$)) and by IR (ν 1716 (C=O) and 2920 (CH$_2$) cm^{-1}). We are hopeful that the catalyst activity can further be improved by optimizing the reaction conditions and variations at the ligand framework, and we will investigate the potential of enantiomerically pure variants of this catalyst system in asymmetric CO/1-alkene copolymerization reactions.[22]

Table 1. Alternating CO/Ethene Copolymerization Catalyzed with Chelate Ligand Palladium Complexes

complex	amt of complex, mg/μmol	amt of copolym, g	act^c
17^a	41/69.5	10.9	157
17^b	30/51.6	2.9	68
6^a	36/55.6	0.1	
7^a	39/43.0^d	4.1	94
7^{a,e}	39/43.0^d	4.6	107
5^b	32/51.6	10.3	239
5^{b,e}	32/51.6	11.2	260
4^b	24/51.6		

[a] Conditions: activated with AgBF$_4$/CH$_3$CN/CH$_3$OH in CH$_2$Cl$_2$; reaction at room temperature; ca. 30 bar of CO/30 bar of ethene. [b] Conditions: 1.2 equiv of ligand; 43 μmol of Pd(OAc)$_2$; activated with BF$_3$·OEt$_2$/CH$_3$OH in CH$_2$Cl$_2$; reaction at room temperature; ca. 30 bar of CO/30 bar of ethene. [c] Catalyst activities in g of polymer/mmol of [Pd]. [d] Calcd + 1.5 equiv of CH$_2$Cl$_2$ in the crystal. [e] Second experiment under analogous conditions.

Experimental Section

Technical Details of the Quantum-Chemical Calculations. The calculations have been performed with the TURBOMOLE suite of programs.[17a] The structures of **14** and **16** have been fully optimized without any symmetry restrictions at the density functional (DFT) level employing the BP86 functional,[17b,c] a large Gaussian AO basis of valence-triple-ζ quality with two sets of polarization functions (TZV2P: C [5s3p2d], Fe [6s5p3d], H [3s2p]),[17d] and the resolution-of-the-identity (RI) approximation to represent the Coulomb operator.[17e] The final structure of the neutral complex **16** has C_s symmetry. For **14**, several different starting geometries in the

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optimization have been tested (including the optimized neutral molecule), which always converged to the Fe−C-bridged structure shown. For both compounds further calculations of the analytical second derivatives were carried out, yielding only real vibrational frequencies.

Technical Details of the X-ray Structure Analysis. Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a Nonius FR591 rotating anode generator. Programs used: data collection COLLECT (Nonius BV, 1998), data reduction Denzo-SMN,[25] absorption correction SORTAV,[26] structure solution SHELXS-97,[27] structure refinement SHELXL-97,[28] graphics DIAMOND.[29]

General Procedures. All manipulations involving air-sensitive materials were carried out using standard Schlenk type glassware (or a glovebox) under an atmosphere of argon. Solvents were dried with the procedure reported by Grubbs[23] or distilled from appropriate drying agents. The palladium complex (cycloocta-1,5-diene)$PdCl_2$[11] and the ferrocenophane **3**[4] were prepared as previously described. For additional general information, including a list of instrumentation used for the physical characterization of the new compounds, see ref 4. Most NMR assignments were received by various 2D NMR measurements.[24]

1-(Diphenylphosphino)-2,1′-[(1-dimethylamino)butane-1,3-diyl]ferrocene (4). A solution of **3** (0.71 g, 2.52 mmol) in 10 mL of diethyl ether was cooled to 4 °C and treated with a 1.6 M solution of *n*-butyllithium in hexane (1.9 mL, 3.02 mmol, 1.2 equiv). The cooling bath was removed and the solution stirred for 3 h, during which time the color changed from light orange to dark orange. Afterward, the mixture was cooled to 4 °C and chlorodiphenylphosphine (0.54 mL, 3.02 mmol, 1.2 equiv) was added dropwise. The cooling bath was removed and the resulting suspension stirred at room temperature overnight. To this mixture was added saturated $NaHCO_3$ solution (10 mL), and the aqueous phase was extracted with pentane (3 × 10 mL). The combined organic phases were washed with water and brine and dried over $MgSO_4$. After evaporation of the solvent the residue was purified by column chromatography on silica (pentane/ethanol 6/1) to afford a yellow solid (0.55 g, 46%). Mp: 156 °C (DSC). ^1H NMR (599.9 MHz, $CDCl_3$): δ 1.22 (d, $J_{HH} = 7.3$ Hz, 3H, CH_3), 1.79 (s, 6H, NCH_3), 2.31 (m, 1H, CH_2(trans)), 2.68 (pd, 1H, NCH), 2.84 (m, 1H, CH), 3.16 (m, 1H, CH_2(cis)), 3.68 (m, 2H, C_5H_4, C_5H_3), 3.85 (m, 1H, C_5H_4), 4.11 (m, 1H, C_5H_4), 4.14 (m, 2H, C_5H_3), 4.41 (m, 1H, C_5H_4), 7.22−7.47 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (150.8 MHz, $CDCl_3$): δ 16.7 (CH_3), 27.7 (CH), 44.2 (NCH_3), 45.3 (CH_2), 59.1 (NCH), 67.5, 68.6, 70.2, 72.2 (C_5H_4), 68.9, 73.9, 74.1 (C_5H_3), 75.2 (d, $J_{PC} = 12$ Hz, C_5H_3(P)), 91.4 (br, C_5H_3(i)), 93.3 (C_5H_4(i)), 127.5, 127.7, 128.1, 133.1, 133.4 (d, $J_{PC} = 19$ Hz), 134.2 (d, $J_{PC} = 19$ Hz), 138.9, 139.4 (all broad, Ph). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ −21.7. Anal. Calcd for $C_{28}H_{30}NFeP$ (467.4): C, 71.96; H, 6.47; N, 3.00. Found: C, 71.74; H, 6.07; N, 2.96.

1-(Diphenylphosphino)-2,1′-[(1-diphenylphosphino)-butane-1,3-diyl]ferrocene (5). To a solution of **4** (1.58 g, 3.38 mmol) in freshly distilled acetic acid (29 mL) was added diphenylphosphine (0,65 mL, 3.72 mmol, 1.1 equiv). The solution was stirred at 100 °C for 19 h, during which time the formation of a yellow precipitate was observed. The reaction mixture was cooled to room temperature, and CH_2Cl_2 (30 mL) and a saturated $NaHCO_3$ solution (30 mL) were added (vigorous evolution of CO_2). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed until neutral with saturated $NaHCO_3$ solution followed by water and brine and dried over $MgSO_4$. After evaporation of the solvent the residue was purified by column chromatography on silica ($CHCl_3$) to afford a yellow solid (1.34 g, 65%). Single crystals suitable for an X-ray crystal structure analysis were grown by a slow evaporation of a CH_2Cl_2/ethanol solution. Mp: 205 °C dec (DSC). ^1H NMR (599.9 MHz, CD_2Cl_2): δ 1.10 (d, $J_{HH} = 7.2$ Hz, 3H, CH_3), 1.91 (m, 1H, CH_2(trans)), 2.59 (m, 1H, CH), 3.13 (dd, $J_{HH} = 4.2$ Hz, $J_{HH} = 12.9$ Hz, 1H, NCH), 3.19 (m, 1H, CH_2(cis)), 3.40 (m, 1H, C_5H_4), 3.71 (m, 1H, C_5H_3), 3.83 (m, 1H, C_5H_4), 4.12 (m, 1H, C_5H_3), 4.14 (m, 1H, C_5H_4), 4.27 (m, 1H, C_5H_3), 4.31 (m, 1H, C_5H_4), 7.04−7.54 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2): δ 15.9 (CH_3), 26.0 (d, $J_{PC} = 10.6$ Hz, CH), 29.3 (dd, $J_{PC} = 2.7$ Hz, $J_{PC} = 12.9$ Hz, PCH), 45.3 (dd, $J_{PC} = 10.2$ Hz, $J_{PC} = 23.5$ Hz, CH_2), 68.0, 69.2, 70.3, 72.4 (d, $J = 4.8$ Hz) (C_5H_4), 69.8 (C_5H_3), 73.9 (d, $J_{PC} = 15.5$ Hz, C_5H_3(P)), 74.6 (C_5H_3), 76.6 (dd, $J_{PC} = 2.6$ Hz, $J_{PC} = 5.1$ Hz, C_5H_3), 91.1 (dd, $J_{PC} = 17.2$ Hz, $J_{PC} = 21.5$ Hz, C_5H_3(i)), 92.9 (C_5H_4(i)), 127.7, 128.1 (3x), 128.7 (2x) (d, $J_{PC} = 7.7$ Hz), 129.0, 129.3, 133.2 (d, $J_{PC} = 18.0$ Hz), 133.7 (d, $J_{PC} = 4.0$ Hz), 133.8 (d, $J_{PC} = 2.3$ Hz), 135.5 (d, $J_{PC} = 21.0$ Hz) (Ph), 138.2 (d, $J_{PC} = 16.1$ Hz, Ph(i)), 139.2 (dd, $J_{PC} = 5.4$ Hz, $J_{PC} = 12.6$ Hz, Ph(i)), 140.2 (dd, $J_{PC} = 3.2$ Hz, $J_{PC} = 20.7$ Hz, Ph(i)), 141.2 (d, $J_{PC} = 8.2$ Hz, Ph(i)). $^{31}P\{^1H\}$ NMR (242.5 MHz, CD_2Cl_2): δ −22.4 (d, $J_{PP} = 79.6$ Hz, P(C_5H_3)). −7.9 (d, $J_{PP} = 79.6$ Hz, PCH). Anal. Calcd for $C_{38}H_{34}FeP_2$ (608.5): C, 75.01; H, 5.63. Found: C, 74.80; H, 5.37.

X-ray crystal structure analysis of **5**: formula $C_{38}H_{34}FeP_2$, $M_r = 608.44$, yellow crystal 0.40 × 0.20 × 0.20 mm, $a = 11.313(1)$ Å, $b = 11.886(1)$ Å, $c = 12.452(1)$ Å, $\alpha = 94.27(1)°$, $\beta = 113.80(1)°$, $\gamma = 95.75(1)°$, $V = 1512.1(2)$ Å^3, $\rho_{calcd} = 1.336$ g cm^{-3}, $\mu = 6.31$ cm^{-1}, empirical absorption correction ($0.787 \leq T \leq 0.884$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.710\,73$ Å, $T = 198$ K, ω and φ scans, 19 774 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.67$ Å^{-1}, 7440 independent ($R_{int} = 0.041$) and 6045 observed reflections ($I \geq 2\sigma(I)$), 371 refined parameters, R1 = 0.036, wR2 = 0.084, maximum (minimum) residual electron density 0.57 (−0.35) e Å^{-3}, hydrogens calculated and refined as riding atoms.

{1-(Diphenylphosphino)-2,1′-[(1-dimethylamino)butane-1,3-diyl]ferrocene}$PdCl_2$ (6). To a solution of (cycloocta-1,5-diene)$PdCl_2$ (0.50 g, 1.74 mmol, 1.01 eq.) in CH_2Cl_2 (20 mL) was added **4** (0.81 g, 1.72 mmol), and the solution was stirred at room temperature for 16 h. The solvent was evaporated and the remaining solid washed with THF (3 × 50 mL) to yield a red powder (0.77 g, 69%). Single crystals suitable for an X-ray crystal structure analysis were grown by slow diffusion of pentane vapor into a $CHCl_3$ solution. Mp: 264 °C dec (DSC). ^1H NMR (599.9 MHz, CD_2Cl_2): δ 1.19 (d, $J_{HH} = 7.3$ Hz, 3H, CH_3), 2.20 (m, 1H, 2-H), 2.68 (m, 2H, CH, CH_2(trans)), 2.76 (m, 1H, NCH), 2.80 (m, 1H, CH_2(cis)), 2.81 (s, 3H, NCH_3), 3.18 (s, 3H, NCH_3), 3.73 (m, 1H, 3-H), 3.87 (m, 1H, 4-H), 4.16 (m, 1H, 5-H), 4.27 (m, 1H, 13-H), 4.41 (m, 1H, 14-H), 4.48 (m, 1H, 15-H), 7.33−8.27 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2): δ 16.4 (6-CH_3), 27.5 (C-6), 50.0 (d, $J_{PC} = 3.9$ Hz, C-7), 52.8 (NCH_3), 56.8 (NCH_3), 66.0 (d, $J_{PC} = 3.6$ Hz, C-8), 67.6 (d, $J_{PC} = 46.5$ Hz, C-12), 69.1 (C-4), 69.9 (C-5), 70.9 (d, $J_{PC} = 6.8$ Hz, C-14), 71.9 (C-3), 72.4 (d, $J_{PC} = 8.2$ Hz, C-15), 73.9 (C-2), 75.4 (C-13), 88.6 (d, $J_{PC} = 19.1$ Hz, C-11), 93.7 (C-1), 128.1 (d, $J_{PC} = 11.6$ Hz, Ph(o,m)), 128.5 (d, $J_{PC} = 11.7$ Hz, Ph(m)), 130.8 (d, $J_{PC} = 3.3$ Hz, Ph(p)), 131.7 (d, $J_{PC} = 66.0$ Hz, Ph(i)), 132.1 (d, $J_{PC} = 2.7$ Hz, Ph(p)), 133.4 (d, $J_{PC} = 9.4$ Hz, Ph(o/m)), 134.6 (d, $J_{PC} = 65.2$ Hz, Ph(i)), 136.7 (d, $J_{PC} = 11.4$ Hz, Ph(o)). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 12.9. Anal. Calcd for $C_{28}H_{30}NFePPdCl_2$ (644.7): C, 52.17; H, 4.69; N, 2.17. Found: C, 51.64; H, 4.40; N, 2.02.

X-ray crystal structure analysis of **6**: formula $C_{28}H_{30}Cl_2FeNPPd$, $M_r = 644.65$, red crystal 0.35 × 0.30 × 0.15 mm, *a*

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= 11.584(1) Å, b = 16.517(1) Å, c = 13.831(1) Å, β = 102.95(1)°, V = 2579.0(3) Å^3, ρ_{calcd} = 1.660 g cm^{-3}, μ = 15.47 cm^{-1}, empirical absorption correction ($0.614 \leq T \leq 0.801$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.710 73 Å, T = 293 K, ω and φ scans, 11 087 reflections collected ($\pm h$, $\pm k$, $\pm l$), (sin θ)/λ = 0.66 Å^{-1}, 6129 independent (R_{int} = 0.023) and 4958 observed reflections ($I \geq 2\sigma(I)$), 310 refined parameters, R1 = 0.032, wR2 = 0.072, maximum (minimum) residual electron density 0.75 (−0.63) e Å^{-3}, hydrogens calculated and refined as riding atoms.

{1-(Diphenylphosphino)-2,1′-[(1-diphenylphosphino)-butane-1,3-diyl]ferrocene}PdCl$_2$ (7). To a solution of [(cycloocta-1,5-diene)PdCl$_2$] (0.22 g, 0.77 mmol, 1.1 equiv) in CH$_2$Cl$_2$ (20 mL) was added a solution of **5** (0.43 g, 0.70 mmol) in CH$_2$Cl$_2$ (10 mL). Without stirring, the reaction flask was placed in a larger vessel containing 10 mL of pentane and allowed to stand at room temperature overnight. Red crystals (0.28 g, 50%) could be collected that were washed with CH$_2$Cl$_2$ and dried. Mp: 231 °C (DSC). A second crop could be obtained by treating the mother liquor with pentane, washing the red amorphous precipitate with CH$_2$Cl$_2$, and drying (0.21 g, 38%). Single crystals suitable for an X-ray crystal structure analysis were grown by letting the reaction mixture stand at room temperature overnight. ^{1}H NMR (599.9 MHz, CD$_2$Cl$_2$): δ 0.90 (d, J = 7.2 Hz, 3H, CH$_3$), 2.23 (m, 1H, C$_5$H$_4$), 2.28 (m, 1H, CH$_2$), 2.41 (m, 1H, NCH), 2.47 (m, 1H, CH), 3.03 (m, 1H, CH$_2$), 3.57 (m, 1H, C$_5$H$_4$), 3.86 (m, 1H, C$_5$H$_4$), 4.07 (m, 2H, C$_5$H$_3$, C$_5$H$_4$), 4.22 (m, 1H, C$_5$H$_3$), 4.47 (m, 1H, C$_5$H$_3$), 6.82−8.28 (m, 20H, Ph H). ^{31}P{^{1}H} NMR (242.5 MHz, CD$_2$Cl$_2$): δ 16.0 (d, J_{PP} = 5.2 Hz, P(C$_6$H$_5$)$_2$), 57.4 (br, P(C$_6$H$_5$)$_2$). Due to the poor solubility in common solvents, no interpretable ^{13}C NMR spectra could be recorded. Anal. Calcd for C$_{38}$H$_{34}$FeP$_2$PdCl$_2$·CH$_2$Cl$_2$ (870.7): C, 53.80; H, 4.17. Found: C, 53.67; H, 3.88.

X-ray crystal structure analysis of **7**: formula C$_{38}$H$_{34}$Cl$_2$FeP$_2$Pd·2CH$_2$Cl$_2$, M_r = 955.59, orange crystal 0.45 × 0.20 × 0.15 mm, a = 13.081(1) Å, b = 18.692(1) Å, c = 16.507(1) Å, β = 98.99(1)°, V = 3986.5(4) Å^3, ρ_{calcd} = 1.592 g cm^{-3}, μ = 13.27 cm^{-1}, empirical absorption correction ($0.587 \leq T \leq 0.826$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 198 K, ω and φ scans, 37 674 reflections collected ($\pm h$, $\pm k$, $\pm l$), (sin θ)/λ = 0.66 Å^{-1}, 9485 independent (R_{int} = 0.033) and 8108 observed reflections ($I \geq 2\sigma(I)$), 452 refined parameters, R1 = 0.028, wR2 = 0.062, maximum (minimum) residual electron density 0.76 (−0.75) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Polymerization Procedure and Polymer Characterization. Polymerizations were conducted in CH$_2$Cl$_2$ in a 300 mL steel autoclave with glass insert. In a typical procedure, 43 μmol of the catalyst precursor was suspended in CH$_2$Cl$_2$ (10 mL). One drop of CD$_3$CN was added, followed by AgBF$_4$ (0.5 mmol, 93.7 mg). The reaction mixture was stirred at room temperature for 10 min. A gradual color change from red to brown to green and the formation of a white precipitate could be observed. The mixture was filtered and the solution injected into the autoclave under an argon atmosphere. After this, CH$_2$Cl$_2$ (40 mL) and MeOH (0.25 mL) were added. In an alternative procedure, Pd(OAc)$_2$ (43 μmol, 10.0 mg) and the free ligand (52 μmol, 1.2 equiv) were dissolved in CH$_2$Cl$_2$ (40 mL). Then, BF$_3$·OEt$_2$ solution (20 μL, 50 wt %, 86 μmol, 2.0 equiv) was added followed by MeOH (0.25 mL). In the case of ligand **5**, the initially yellow solution appeared orange after addition of the boron trifluoride. A further change toward red occurred after MeOH addition. The autoclave was pressurized with 30 bar of ethene and stirred for 1 min, during which the pressure dropped to 17 bar. Then, the autoclave was pressurized with CO to a total pressure of 60 bar. The polymerization mixture was stirred at room temperature for 16 h. Quenching was done by release of the CO/ethene pressure and the resulting polymer isolated by filtration, washed with MeOH and ether, and dried. For ^{13}C NMR spectra, 50 mg of the polymer was suspended in 1.8 mL of hexafluoro-2-propanol (HFIP) and 0.2 mL of C$_6$D$_6$. Of this saturated, viscous solution, 1 mL was used. ^{13}C{^{1}H} NMR (50.3 MHz, HFIP/C$_6$D$_6$ 9/1): δ 35.6 (CH$_2$), 212.9 (C═O). IR (KBr): $\tilde{\nu}$ = 1716 (C═O), 2920 (CH$_2$) cm^{-1}.

Acknowledgment. Financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We thank Professor Bernhard Rieger for helping us with the polymerization reactions.

Supporting Information Available: Tables giving detailed information about the X-ray crystal structure analyses of **5**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030076E