Palladium Chemistry of 2-Ferrocenyl-1,10-phenanthroline Ligand

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The synthesis of the 2-ferrocenyl-1,10-phenanthroline ligand **1** has been improved, and its reactivity toward palladium is described. This study allows evidencing that **1** can coordinate to the metal center in an N−N bidentate fashion or undergo *ortho* metalation, thus acting as a terdentate N−N−C pincer ligand. Examples of the former coordination mode include complexes [Pd(Cl)(Me)(**1**)] (**2**) and [Pd(Me)(NCMe)(**1**)][PF_6] (**3**), whereas cyclometalation is observed in [Pd(**1**)(O_2CCF_3)] (**5**), [Pd(**1**)(MeCN)][PF_6] (**6**), and [Pd(**1**)(PPh_3)][O_2CCF_3] (**7**). These cyclometalated adducts are chiral, racemic compounds. X-ray crystal structures of compounds **5**, **6**, and **7** have been determined, confirming the presence of a five-membered palladacycle and evidencing that in the solid state packing occurs through weak $\pi-\pi$ interactions between the phenanthroline rings of the ligands. The reactivity of the racemic mixture of **5** with the enantiopure phosphine (*R*)-Ph-BINEPINE (**8**) affords a kinetic dynamic resolution leading, after two recrystallizations, to the isolation of only one of the two possible diastereoisomers.

Introduction

Palladacycles represent a class of compounds of remarkable importance that have found a number of applications in the field of organometallic chemistry. These complexes have been widely used in catalysis,[1] especially for C−C bond formation, as resolving agents,[2] and studied for their luminescence properties,[3] their capability of interacting with DNA,[4] or as building blocks for molecular architectures of higher complexity.[5] A wide variety of tridentate ligands have been exploited for the preparation of palladacycles. Among these, N−C−N pincer ligands have received particular attention,[6] and they are encountered much more frequently than their N−N−C counterparts.[7]

Chiral ferrocenyl-based ligands have been extensively used in homogeneous enantioselective catalysis.[8] Nevertheless, palladacycles arising from the N-supported metalation at the sp^2 carbon atom of a cyclopentadienyl ring of a pincer ferrocenyl ligand are surprisingly few,[9] and even less are the derivatives of this type that have been tested in catalytic reactions.[10]

In this paper we report on the synthesis and characterization of different palladium complexes containing the 2-ferrocenyl-1,10-phenanthroline (**1**) moiety, a ligand that can bind the metal either in N−N bidentate or in N−N−C tridentate fashion. In the latter case, the intramolecular metalation of the *ipso* cyclopentadienyl ring generates a chiral N−N−C pincer palladacycle featuring a stereogenic plane as the unique chiral element. While optically active pincer palladacycles with stereogenic carbon atom(s) in the ligand backbone are not rare, pincer palladacycles with planar chirality are almost unprecedented.

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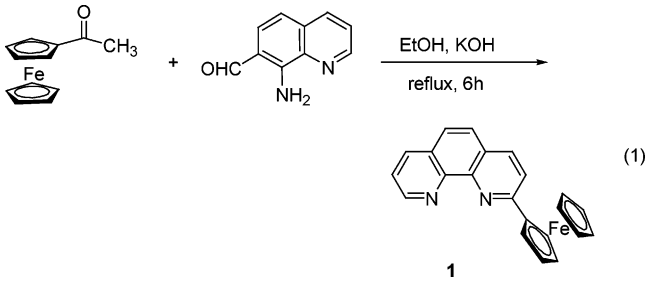
Results and Discussion

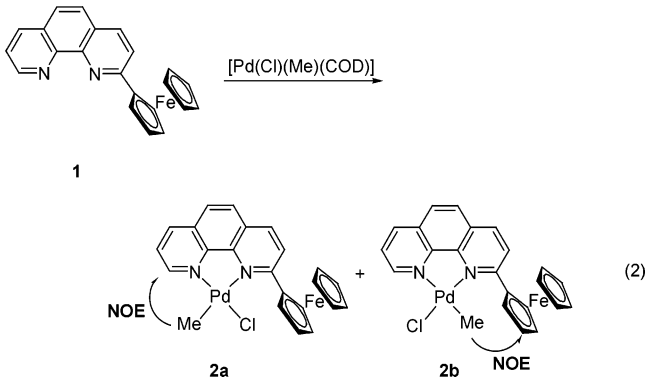
Synthesis of 2-Ferrocenyl-1,10-phenanthroline, 1. The preparation of 2-ferrocenyl-1,10-phenanthroline (**1**) has been readily accomplished through the Friedlander condensation of ferrocenyl methyl ketone with 8-amino-7-quinoline carboxyaldehyde (eq 1). The reaction is performed in ethanolic KOH and



(1)

is completed in 6 h reflux. This methodology, modeled on a procedure recently established for the preparation of alkyl-substituted phenanthrolines,[11] affords the desired ligand in 65% isolated yield and is by far better yielding than the previously reported preparation of **1** from 2-chlorophenanthroline and ferrocenyl lithium.[12]

Palladium Chemistry. Reaction of **1** with [Pd(Cl)(Me)-(COD)] (COD = 1,5-cyclooctadiene) leads to the formation of a dark red product **2**. Its ^{1}H NMR spectrum provides evidence of the presence in solution of the two possible isomers due to the unsymmetrical nature of the ligand. Two singlets for the Pd−Me group, one for each of the two isomers, are present at 1.07 (major product) and 0.33 (minor product) ppm in a 3:2 ratio. NOE experiments allow us to assign the former to the isomer **2a**, having the Cl ligand *cis* to the aromatic ring bearing the ferrocenyl moiety and thus the latter one to the isomer **2b** (eq 2). The NOE experiment also indicates that the two isomers

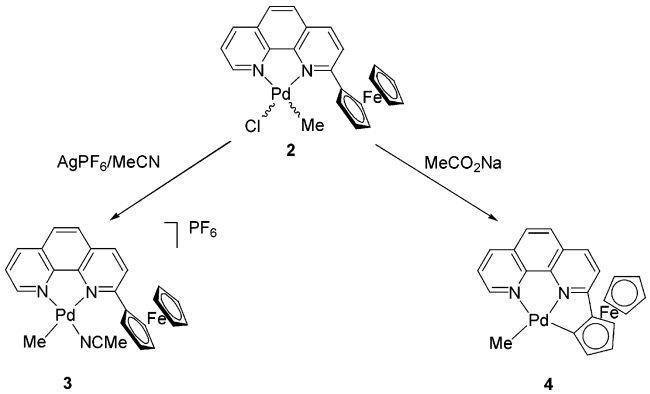


(2)

are in equilibrium. At room temperature, the rate of this equilibrium is low on the NMR time scale. All the aromatic protons were attributed with a 2D homonuclear correlation experiment (COSY). Chemical shifts of all the protons are very similar to those reported previously for the complex [$PdCl_2$-(**1**)].[9a] In particular, in the dichloro derivative, a value of 9.34 ppm is observed, comparable to that of H^9 in **2b** (9.27 ppm). In the case of **2a**, the absence of a *cis*-chloro ligand leads the H^9 proton to resonate at 8.87 ppm, in agreement with the fact that the Pd−Cl significantly shifts to higher frequency the resonance of the proton *cis* to it.[13] This provides further support to the attribution of the structure of the two isomers made on the basis of the NOE experiments.

When **2** is reacted with $AgPF_6$ in the presence of acetonitrile, the cationic complex **3** is formed (Scheme 1). It is interesting to note that, unlike the neutral precursor, in this case just one isomer is obtained even when starting from a mixture of **2a** and **2b**. The NOE between the H^9 proton of the phenanthroline and the Pd−Me at 1.15 ppm shows that in this complex the coordinated acetonitrile sits in *cis* position to the ferrocenyl group of the ligand.

Scheme 1. Reactivity of 2 with $AgPF_6$ or with $MeCO_2Na$



The bidentate coordination displayed by ligand **1** in the adducts **2** and **3** is identical to that previously observed in the complex [$PdCl_2$(**1**)] prepared from ligand **1** and [$PdCl_2$(COD)]. Notably, in this latter reaction, the corresponding 6-ferrocenyl-2,2′-bipyridine analogue of **1** undergoes direct cyclometalation at the *ipso* cyclopentadienyl ring, leading to the formation of [PdCl(6-ferrocenyl-2,2′-bipyridine)], where the 6-ferrocenyl-2,2′-bipyridine acts as a monoanionic tridentate ligand.[9a] The

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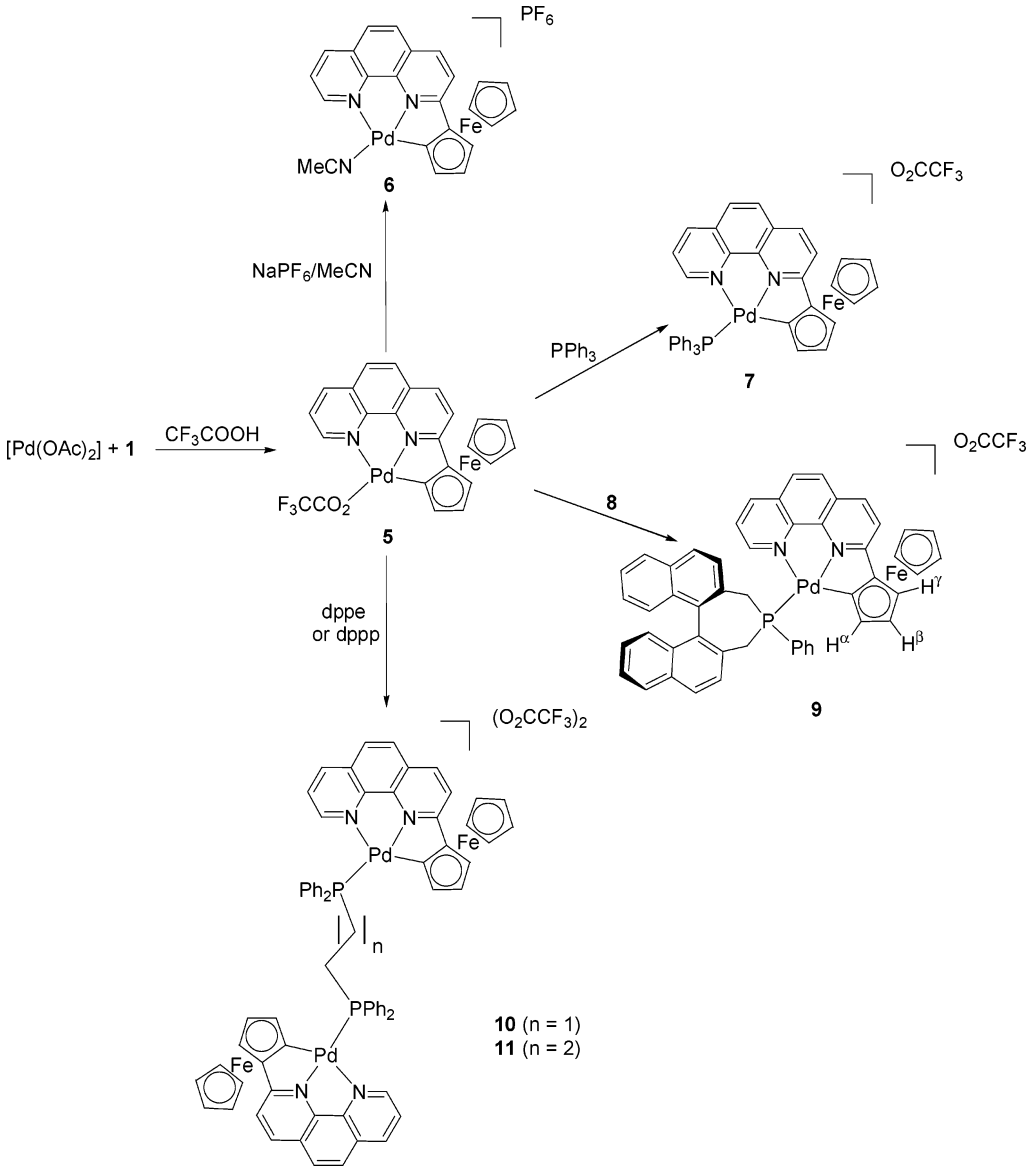
Scheme 2. Reactivity of 1 with [Pd(OAc)$_2$] and Further Reactions



preparation of the analogous phenanthroline complex [PdCl(**1**)] could be achieved by reaction of **1** with $K_2[PdCl_4]$.[9j]

We have observed that an analogous cyclopalladated complex **4**, where deprotonated **1** acts as an anionic tridentate N−N−C pincer ligand, is obtained by reacting the adduct **2** with sodium acetate. Apparently, the presence of a base, even a weak one, is necessary for **2** to undergo the intramolecular cyclometalation to **4** (Scheme 1) as reported in some cases of cyclopalladation processes.[1e,7a,9b−d,f−i,m−o,10f] Note that the conversion of **2** is complete and that no traces of unreacted **2b**, which does not possess the appropriate geometry for the substitution to occur, are observed at the end of the reaction. This behavior is in agreement with the equilibration between **2a** and **2b**.

Direct cyclopalladation of **1** is also observed on the attempted preparation of the bis-trifluoroacetate adduct [Pd(O$_2$CCF$_3$)$_2$(**1**)] from [Pd(OAc)$_2$]. This reaction was performed by adding ligand **1** to a methanolic solution of [Pd(OAc)$_2$] according to a procedure devised by us for the synthesis of similar N−N chelate complexes.[14] Addition of trifluoroacetic acid to the red solution, probably containing the adduct [Pd(OAc)$_2$(**1**)], resulted in the separation of a dark blue solid, **5** (Scheme 2), characterized both in the solid state (by X-ray diffraction; see below and Figure 1) and in solution by ^{1}H NMR spectroscopy. As in

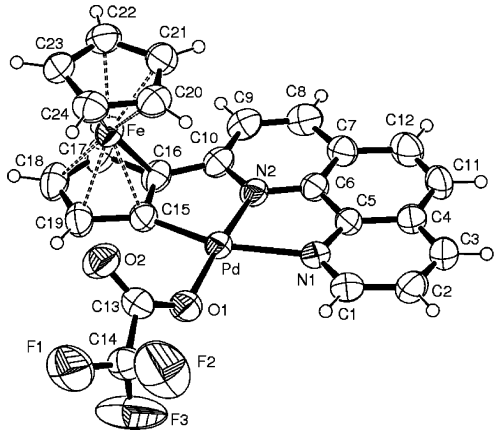


Figure 1. Molecular structure of complex **5** (ORTEP drawing with 40% probability ellipsoids).

the case of **4**, the ^{1}H NMR spectrum of the isolated solid evidences the presence of a metalated ferrocene cyclopentadienyl

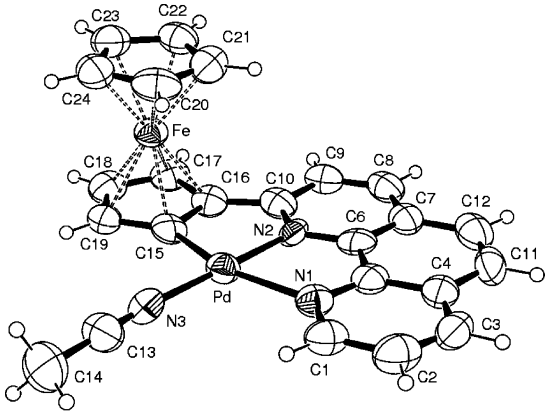


Figure 2. Molecular structure of the cation of **6** (ORTEP drawing with 40% probability ellipsoids).

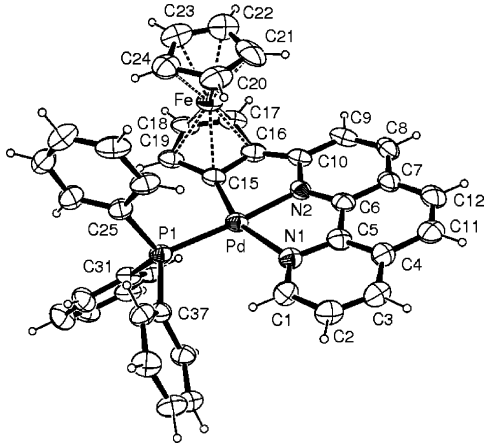


Figure 3. Molecular structure of the cation of **7** (ORTEP drawing with 30% probability ellipsoids). Only the *ipso* C atoms of the phenyl rings are labeled for clarity.

ring. Three different signals, each one integrating for one proton, are observed for the cyclopentadienyl ring bonded to palladium. Coupling constants together with two-dimensional homonuclear correlation experiments (COSY) confirm that the cyclometallation occurs exclusively at the *ipso* carbon atom of the cyclopentadienyl ring, generating a five-membered palladacycle, according to Cope's rule.

Complex **5** was used as the starting material for the synthesis of other cyclometalated complexes (Scheme 2). Its reaction with $NaPF_6$ in the presence of acetonitrile leads to the formation of the cationic complex **6**. In its ^{1}H NMR spectrum a singlet at 2.58 ppm, characteristic of the coordinated acetonitrile, is observed. The spectrum presents three very broad signals for the cyclometalated cyclopentadienyl ring when recorded in acetone-d_6, whereas when CD_2Cl_2 is the solvent, they are not observed at room temperature and start to be visible at −70 °C.

Reaction of **5** with 1 equiv of PPh_3 leads slowly to the formation of the cationic complex **7**, the reaction being completed after one night, at room temperature. Coordination of the phosphine is confirmed by the singlet at 35.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum, while the ^{1}H NMR evidences the retention of the cyclometalated structure. Unlike in the case of **6**, the signals of the protons in the NMR spectrum of **7** are well resolved, allowing the observation of the multiplicity for the three resonances of the palladated cyclopentadienyl ring. In the aromatic region, apart from the expected signals for the phenyl groups of the phosphine, the seven protons of the phenanthroline backbone are observed. Remarkable in this case is the high upfield shift of the signal of H^9 (6.85 ppm), with respect to the same frequency in both the free ligand **1** (9.21 ppm) and in **5** (8.80 ppm). A similar shift is observed for the signal of one of the protons of the cyclopentadienyl ring bound to palladium (3.55 ppm) and for the singlet due to the five protons of the Cp ring (3.81 ppm). This is attributed to the shielding effect of the phenyl rings of the coordinated phosphine.

The crystal structures of **6** and **7** were resolved by X-ray diffraction (see below and Figures 2, 3) on single crystals. This structural analysis provides further evidence of the terdentate coordination mode of the 2-ferrocenyl-1,10-phenanthroline ligand **1** in these complexes.

The reaction of **5** with 1 equiv of the enantiopure (*R*)-Ph-BINEPINE, the axially chiral monodentate phosphine **8**,[15] leads to complex **9** (Scheme 2). $^{31}P\{^1H\}$ NMR monitoring of the reaction points out that, unlike the case of triphenylphosphine, with this ligand the reaction is almost instantaneous since no signal corresponding to the free phosphine **8** at 6.5 ppm is observed in the spectrum recorded immediately after the dissolution of the reagents. Since in the case of **9** the generation of the stereogenic plane inherent with the cyclometalation implies the removal of one pair of diastereotopic protons, two diastereomers are expected from this reaction. Accordingly, the two resonances in 2:1 ratio observed in $^{31}P\{^1H\}$ NMR at 42.0 and 42.5 ppm are attributed to the two diastereoisomers (R,S_P) and (R,R_P) that can result from the reaction of racemic **5** with the enantiopure (*R*)-Ph-BINEPINE, **8**. The $^{31}P\{^1H\}$ chemical shifts of the two isomers of **9** are similar to those observed in other palladium complexes with this ligand and confirm the phosphine binding to palladium.[15] The coordination-induced downfield shift is also comparable to that observed in the case of the reaction with PPh_3. In the case of **9**, again, the cyclometalated structure is maintained, as can be evidenced in the ^{1}H NMR spectrum by the resonances of the cyclopentadienyl ring bound to both the phenanthroline backbone and the palladium center. The signals of some protons of the cyclopentadiene rings are a probe of the presence of the two diastereoisomers. In particular, in the major diastereoisomer both the singlet of the protons of the cyclopentadienyl ring (3.69 ppm) not bound to palladium and the broad signal of H^α (4.26 ppm) are remarkably shifted to lower frequency than the same signals both in **5** and in the minor diastereoisomer (4.28 ppm for the 5H of Cp and 4.70 ppm for H^α in **5**; 4.22 ppm for the 5H of Cp and 4.59 ppm for H^α in the minor diastereoisomer), thus suggesting that in the major diastereoisomer the cyclopentadienyl moiety is more affected by the presence of **8** than in the minor isomer.

Addition of diethyl ether to a chloroform solution of this mixture afforded a crop of crystals where the isomer ratio improved up to 5:1. One further crystallization gave a sample of the pure diastereoisomer featuring $^{31}P\{^1H\}$ NMR at 42.0 ppm. The optical activity of a chloroform solution of the solid isolated after the second crystallization process has been measured (see Experimental Section), confirming that the complex is optically active. $^{31}P\{^1H\}$ NMR inspection of the filtrate from these crystallizations points out that the diastereomeric ratio in solution is 2:1 and that this value is constant with time.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) and Geometrical Parameters of the Ferrocenyl Moiety for Compounds 5, 6, and 7

	5 (X = O(1))	**6** (X = N(3))	**7** (X = P(1))
Pd−N(1)	2.173(3)	2.173(7)	2.197(8)
Pd−N(2)	1.965(3)	1.984(7)	2.014(8)
Pd−C(15)	1.980(4)	1.986(9)	1.979(10)
Pd−X	2.043(3)	1.984(9)	2.249(3)
Fe−C(Cp)	2.024(4)−2.064(4)	2.032(9)−2.058(10)	1.990(12)−2.095(17)
Fe−Cp centroid	1.660, 1.652	1.666, 1.640	1.672, 1.635
N(1)−Pd−N(2)	79.29(13)	80.2(3)	78.5(3)
N(1)−Pd−C(15)	160.05(14)	160.6(3)	158.0(4)
N(2)−Pd−C(15)	80.77(14)	80.4(3)	79.6(4)
N(1)−Pd−X	97.71(12)	100.9(3)	107.9(2)
N(2)−Pd−X	175.72(11)	178.9(3)	173.5(3)
C(15)−Pd−X	102.24(15)	98.5(3)	94.0(3)
C(19)−C(15)−Pd	141.7(3)	141.9(8)	142.2(8)
C(13)−X−Pd	129.6(3)	174.7(8)	
Cp1/Cp2	3.2(2)	1.6(4)	4.61(8)
twist angle Cp1/Cp2	5.2	10.7	8.8
phen/C(15−19) ring	3.8(2)	0.9(5)	7.93(5)

These results indicate not only that the axially chiral (*R*)-PhBINEPINE (**8**) can be successfully exploited as a resolving agent for the chiral palladacycle reported in this work but also that the cationic complex **9** is configurationally labile and that the two diastereoisomers, in solution, undergo an interconversion process until they reach the equilibrium concentration 2:1, at room temperature. For this equilibration to occur, opening of the palladacycle ring followed by rotation around the C−C bond connecting the phenanthroline to the cyclopentadienyl ring is required.

The configuration of these isomers, however, could not be cleared and all attempts to grow crystals suitable for X-ray diffraction were unsuccessful.

When 2 equiv of **5** are reacted with a diphosphine such as 1,2-bis(diphenylphosphino)ethane (dppe) or 1,3-bis(diphenylphosphino)propane (dppp), a quantitative immediate reaction takes place, affording the hetero-tetrametallic complexes **10** and **11**, respectively (Scheme 2). $^{31}P\{^1H\}$ NMR spectra display, in both cases, two very close resonances due to the formation of diastereoisomers, as expected from the reaction of the diphosphine with the racemic mixture of **5**. Their chemical shifts are indicative of the coordination of the phosphorus donor atoms to palladium. ^1H NMR spectra show two sets of three rather broad resonances for the protons of the cyclometalated cyclopentadienyl rings, evidencing the retention of the cyclometalated structure. However, at room temperature the protons of the free Cp rings give only one large signal, which is split into two distinct signals when the measurement is performed at temperatures below −20 °C for **11** and around 0 °C for **10**. Lowering the temperature did not allow observing a better resolution of the spectra, all signals still being broad at −60 °C. The signals for the H^9 protons of the phenanthroline backbones are, as observed in **7**, upfield shifted, though this effect is less pronounced than in the case of the complex containing the triphenylphosphine (e.g., 7.21 ppm in **10** vs 6.85 ppm in **7**). In the aromatic region the presence of the signals of the phenyl rings of the diphosphine and the presence of a large number of signals for the phenanthroline protons render difficult the complete assignment for all of them. As a general comment, signals are broader in the case of **11** than for **10**. NMR measurements were performed at higher temperature, in dmso-d_6. Signals become better resolved at 100 °C. In the $^{31}P\{^1H\}$ NMR spectra, no significant change was observed in the studied range of temperature. Integration of the ^1H NMR spectrum of **11** evidences the presence of two palladacycle units for one diphosphine, supporting a bridging coordination mode of the diphosphine. This observation, together with the quantitative consumption of the reagents in a 2:1 ratio, allows us to rule out the formation of mononuclear species with a chelating diphosphine around the palladium center. Such a behavior of bidentate phosphines toward cyclometalated complexes, which occurs through opening of a chelate ring via dissociation of one nitrogen atom of the ligand, has been reported in some cases.[7h,8i]

Structure Description. Single crystals suitable for X-ray analysis were obtained upon crystallization from dichloromethane/diethyl ether for complexes **5** and **7**, whereas they were directly isolated from the crude reaction mixture for **6**.

The molecular structures of complexes **5**, **6**, and **7** with the atom-numbering scheme are shown in Figures 1, 2, and 3, respectively. In all the structures the palladium atom displays a distorted square planar geometry, being chelated by the terdentate ferrocenyl ligand and having the monocoordinated trifluoroacetate-O (**5**), acetonitrile-N (**6**), or phosphine-P (**7**) as fourth ligand. A selection of bond distances, angles, and geometrical parameters is reported in Table 1.

These data indicate comparable values of the bond distances and angles in the coordination sphere, with the exception of the values relative to the N(2)−Pd−X fragment. In fact the Pd−N(2) bond length *trans* to the trifluoroacetate appears slightly shorter, 1.965(3) Å, with respect to the values measured in the monocationic **6** and **7** derivatives (1.984(7) and 2.014(8) Å, respectively). Moreover, a comparison of the N−Pd−X and C−Pd−X bond angles reveals slightly different values within a few degrees in **5**, **6**, and **7**. As expected the Pd−N(1) bond distance is significantly longer in comparison with the Pd−N(2), the former phen nitrogen being located *trans* to the ferrocene C atom. In all the complexes the donors of the coordination sphere are coplanar with the palladium atom. Both the five-membered rings formed by the terdentate ferrocenyl ligand have coordination bond angles N(1)−Pd−N(2) and N(2)−Pd−C(15) close to 79−80° in all the complexes. In the palladate compounds, the formation of a σ (Pd−C_{sp2} ferrocene) bond is expected to modify the ring current in the ferrocenyl moiety and the redox behavior of the iron center. However geometrical data in the solid state indicate that the terdentate N−N−C ligands are rigid, the coordination geometry being rather unaffected by the electronic and steric properties of the fourth ligand at Pd. This is also indicated by comparable Pd−Fe distances, of 3.505 (for **5**), 3.550 (**6**), and 3.591 Å (**7**), which exclude any interaction between the metals. To our knowledge, only two examples of Pd−Cl complexes with a metalated ferrocenyl-phen[9j] and ferrocenyl-bipy[9a] have been reported. The

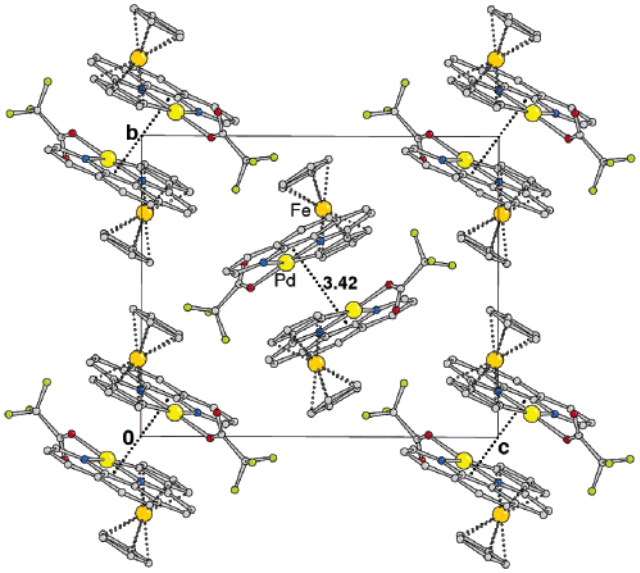

Figure 4. Packing arrangement of complex **5** viewed down axis *a*.

geometry of the terdentate ligand in these chlorine derivatives agrees well with those presented here. The ferrocene moieties are similar in all complexes, and the greater variations in the geometry are observed in complex **7**, mainly ascribed to the less accurate geometrical data but also to the presence of the bulky phosphine ligand. In all complexes the cyclopentadienyl rings are parallel, the largest interplanar angle being 4.61(8)° observed in the phosphine complex, and they deviate by 5.2°, 10.7°, and 8.8° in **5**, **6**, and **7**, respectively, from the ideal eclipsed conformation. The Fe−C bond lengths fall in a range from 1.990(12) to 2.095(17) Å, with the iron atom slightly displaced toward the metalated ring (ca. 1.67 vs 1.64 Å). The C−C bond length associated to the chelating ring (C(15)−C(16) of ca. 1.45 Å) appears the longest inside the cyclopentadienyl rings. Finally, the phenanthroline mean plane is essentially coplanar with the substituted cyclopentadienyl ring in **5** and **6**, while the calculated dihedral angle in **7** is 7.93(5)°.

In the crystal these systems are efficiently packed through the establishment of weak interactions between parallel planar phenanthroline ligands. In **5** and **7** the complexes are associated in pairs, forming *head-to-tail* dimers related by a crystallographic symmetry center in such a way that the facing phen ligands give rise to $\pi-\pi$ interactions. In the neutral complex **5** the centroids of the five-membered rings Pd/N1/C5/C6/N2 are separated by 3.42 Å, so that each nitrogen N(2) lies over the Pd ion of the symmetry-related complex at 3.560 Å, approximately located at the apical position of the square coordination plane (Figure 4). The pairing of structural complex units was also found in the isomorphous Pt and Pd compounds containing a terdentate [$C_{(sp2}$, ferrocene)−N−S] ligand.[8o] In complex **7** the *face-to-face* alignment leads the two phen fragments to be at a mean distance of 3.43 Å between the symmetry-related py ring centroids (Figure 5). The $CF_3CO_2^-$ anions and CH_2Cl_2 solvent molecules do not evidence any unusual close contact with the metal complexes.

On the other hand, compound **6** shows a different crystal packing with Cp rings that contribute, beside the phen ligands, to $\pi-\pi$ intermolecular interactions. The molecules are pillared in columns, running parallel to the crystallographic axis *a*, as illustrated in Figure 5c. This arrangement of molecules resembles the packing found in the neutral [PdCl(**1**)] species,[9j] and both can be favored by the presence of the less bulky monocoordinated MeCN and Cl[9j] ligand in comparison to the $CF_3CO_2^-$ (for **5**) and PPh_3 one (for **7**).

Some authors have postulated that the π-stacking of the terdentate ligand in Pd and Pt complexes and the M−M separation are relevant for photoluminiscent properties.[3b,c,16] The Pd−Pd intradimer distances in **5** and **7** are 4.323(1) and 6.872(2) Å, respectively, while the shortest Pd−Pd separation in **6** is 4.527(2) Å; all these values are larger than the sum of the van der Waals metal ion radii, thus excluding any metal−metal interactions.[8o]

Catalytic Tests. Complex **3** was tested in the CO/styrene copolymerization in 2,2,2-trifluoroethanol, in the presence of 1,4-benzoquinone ([BQ]/[Pd] = 5) at 30 °C under an atmospheric pressure of carbon monoxide. After 8 h, only traces of copolymers were obtained. The same complex has also been tested in the benchmark Heck reaction of iodobenzene with methyl acrylate. The reaction has been run for 14 h at 110 °C at a substrate-to-Pd ratio of 10^3 using DMF as solvent and triethylamine as base. The reaction affords methyl *trans*-cinnamate with a 98% conversion. No apparent precipitation of palladium was noticed during the reaction.

Further investigations on the catalytic behavior of the palladacycles described in this work are currently in progress in our laboratories.

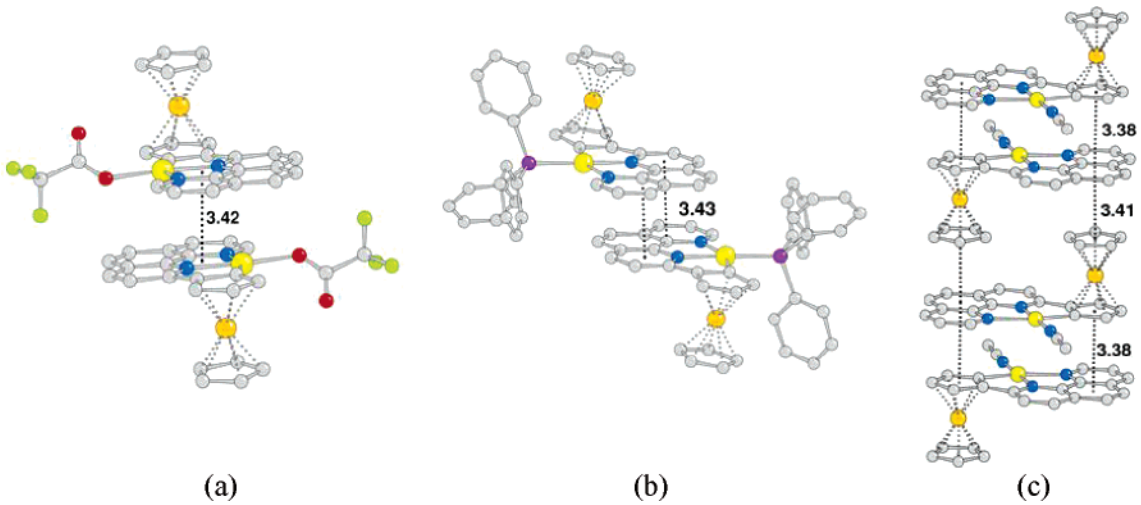

Figure 5. View of the *head-to-tail* dimer of **5** (a) and **7** (b) related by an inversion center. (c) Crystal packing of complex **6** pillared along axis *a*.

Conclusion

In the course of this investigation we have devised practical procedures for the preparation of racemic Pd complexes featuring as a unique chiral element a stereogenic plane arising from the N−N−C terdentate coordination of 2-ferrocenyl-1,-10-phenanthroline ligand **1**. Both neutral and cationic complexes of this kind are accessible by a two-step procedure involving the intermediate isolation of the N−N chelate adducts followed by reaction with a suitable base. Alternatively, the same compounds can be straightforwardly obtained in a single-pot reaction when using Pd derivatives with poorly coordinative anions as precursors. A suitable procedure for the resolution of the enantiomers of the cationic cyclopalladated fragment has been established by using the axially chiral monodentate phosphine (*R*)-Ph-BINEPINE (**8**) as chiral resolving agent. Some traits of the catalytic activity and of the supramolecular structure in the solid state of these Pd complexes have been pointed out. Further work aimed at clearing the optical properties and the utility of these derivatives in asymmetric catalysis is in progress.

Experimental Section

The dichloromethane used for the synthesis of complexes was purified through distillation over $CaCl_2$ and stored under an inert atmosphere. Other solvents (Carlo Erba, Fluka) were used as received. $[Pd(OAc)_2]$ was a gift from Engelhard Italia. Carbon monoxide (CP grade, 99.9%) was supplied by SIAD.

^{1}H NMR spectra were recorded at 400 MHz, on a JEOL EX 400 spectrometer; the resonances were referenced to the solvent peak versus TMS ($CDCl_3$ at 7.26 δ, CD_2Cl_2 at 5.33 δ, CD_3CN at 1.94 δ, dmso-d_6 at 2.50 δ, acetone-d_6 at 2.05 δ). Attribution of the resonances for all the complexes was made on the basis of two-dimensional homonuclear correlation spectra (COSY) obtained with the automatic program of the instrument. The NOE experiments were run with a ^{1}H pulse of 90° of 12.3 μs. ^{31}P{^{1}H} NMR spectra were recorded on a JEOL EX 400 at 161.8 MHz and on a JEOL 270 at 109.25 Hz and referenced to an H_3PO_4 external standard. Elemental analyses (C, H, N), performed at Dipartimento di Scienze Chimiche (Università di Trieste), were in perfect agreement with the proposed stoichiometry. PPh_3, 1,2-bis(diphenylphosphino)ethane (dppe), and 1,3-bis(diphenylphosphino)propane (dppp) are commercial and were used as received.

[Pd(Cl)(Me)(COD)] was prepared from $[Pd(OAc)_2]$ in three steps according to published procedures.[13,17] Phosphine **8** was prepared according to a published procedure.[15]

2-ferrocenyl-1,10-phenanthroline, 1. A mixture of 8-amino-7-quinolinecarbaldehyde (1.09 g, 6.33 mmol), ferrocenyl methyl ketone (1.44 g, 6.33 mmol), and saturated ethanolic KOH (2 mL) in absolute EtOH (65 mL) was introduced into a 100 mL round-bottom flask, equipped with a condenser, a magnetic stirrer, and a serum cap, under an atmosphere of nitrogen, and the solution was refluxed for 6 h. The reaction was followed by TLC on neutral alumina eluting with EtOAc. After cooling, the mixture was concentrated and diluted with water to produce a white precipitate, which was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phase was washed with water (2 × 20 mL) and dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography with $EtOAc/CH_2Cl_2$, 1:1. Crystallization from diethyl ether gave the pure compound (1.5 g; 65% yield); mp 198−200 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 4.08 (s, 5H, Cp), 4.49 (d, $^3J_{H,H}$ = 1.8 Hz, 1H, H$^\beta$ of C_5H_4), 4.50 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H$^\beta$ of C_5H_4), 5.23 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H$^\alpha$ of C_5H_4), 5.24 (d, $^3J_{H,H}$ = 1.8 Hz, 1H, H$^\alpha$ of C_5H_4), 7.60 (dd, $^3J_{H,H}$ = 8.1 Hz and $^3J_{H,H}$ = 4.5 Hz, 1H, H^8), 7.74−7.78 (m, 2H, H^5 and H^6), 7.83 (d, $^3J_{H,H}$ = 8.4 Hz, 1H, H^3 or H^4), 8.14 (d, $^3J_{H,H}$ = 8.4 Hz, 1H, H^3 or H^4), 8.23 (dd, $^3J_{H,H}$ = 8.1 Hz and $^4J_{H,H}$ = 1.8 Hz, 1H, H^7), 9.21 (dd, $^3J_{H,H}$ = 4.5 Hz and $^4J_{H,H}$ = 1.8 Hz, 1H, H^9). ^{13}C NMR ($CDCl_3$): δ 160.1 (C^2), 150.1 (C^9), 145.9, 145.8, 136.0 (C^7), 135.5 (C^4), 129.1, 126.8, 126.6 (C^5 or C^6), 125.2 (C^5 or C^6), 122.6 (C^8), 121.3 (C^3), 84.2 (C ipso of C_5H_4), 70.3 (C$^\alpha$ of C_5H_4), 69.7 (C of Cp), 68.6 ppm (C$^\beta$ of C_5H_4). MS: *m*/*e* 364.8 (M^+), 342.0, 317.0, 301.0, 279.1, 263.1.

[Pd(Cl)(Me)(1)], 2. To a stirred solution of [Pd(Cl)(Me)(COD)] (0.070 g, 0.26 mmol) in 10 mL of CH_2Cl_2, under argon, was added **1** as a solid (0.107 g, 0.294 mmol). After 1 h, addition of diethyl ether to the dark red solution caused the precipitation of a red solid, which was filtered, washed with diethyl ether, and dried under vacuum. Yield: 80%.

2a: ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 1.07 (s, 3H, Pd−Me), 3.94 (s, 5H, Cp), 4.58 (t, $^3J_{H,H}$ = 1.95 Hz, 2H, C_5H_4), 5.36 (t, $^3J_{H,H}$ = 1.95 Hz, 2H, C_5H_4), 7.7−7.8 (m, 1H, H^8), 7.86−7.92 (m, 2H, H^5 and H^6), 8.08 (d, $^3J_{H,H}$ = 8.79 Hz, 1H, H^3 or H^4), 8.26 (d, $^3J_{H,H}$ = 8.79 Hz, 1H, H^3 or H^4), 8.49 (dd, $^3J_{H,H}$ = 7.81 Hz and $^4J_{H,H}$ = 1.47 Hz, 1H, H^7), 8.87 (1H, dd, $^3J_{H,H}$ = 5.37 Hz, H^9) ppm.

2b: ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 0.33 (s, 3H, Pd−Me), 4.01 (s, 5H, Cp), 4.61 (t, $^3J_{H,H}$ = 1.95 Hz, 2H, C_5H_4), 5.40 (t, $^3J_{H,H}$ = 1.95 Hz, 2H, C_5H_4), 7.7−7.8 (m, 1H, H^8), 7.86−7.92 (m, 2H, H^5 and H^6), 8.07 (d, $^3J_{H,H}$ = 8.30 Hz, 1H, H^3 or H^4), 8.28 (d, $^3J_{H,H}$ = 8.30 Hz, 1H, H^3 or H^4), 8.44 (dd, $^3J_{H,H}$ = 8.30 Hz and $^4J_{H,H}$ = 1.47 Hz, 1H, H^7), 9.27 (dd, $^3J_{H,H}$ = 4.88 Hz and $^4J_{H,H}$ = 1.46 Hz, 1H, H^9) ppm. Anal. Calcd for $C_{23}H_{19}ClFeN_2Pd$: C, 53.01; H, 3.67; N, 5.38. Found: C, 53.3; H, 4.09; N, 5.42.

[Pd(Me)(NCMe)(1)][PF$_6$], 3. A solution of $AgPF_6$ (0.023 g, 0.09 mmol) in 1 mL of anhydrous MeCN was added to a stirred solution of **2** (0.04 g, 0.08 mmol) in 10 mL of CH_2Cl_2, under inert atmosphere. After 30 min, the solution was filtered and diethyl ether was added, leading to the formation of a dark precipitate, which was filtered, washed with diethyl ether, and dried under vacuum. Yield: 68%.

^{1}H NMR (400 MHz, CD_3CN, 25 °C): δ 1.15 (s, 3H, Pd−Me), 2.54 (s, 3H, MeCN), 4.13 (s, 5H, Cp), 4.64 (br, 2H, C_5H_4), 5.24 (br, 2H, C_5H_4), 7.92 (dd, $^3J_{H,H}$ = 8.4 and 5.2 Hz, 1H, H^8), 8.09 (m, 2H, H^5 and H^6), 8.36 (d, $^3J_{H,H}$ = 8.5 Hz, 1H, H^3 or H^4), 8.53 (d, 1H, H^3 or H^4), 8.75 (d, 1H, H^7), 8.88 (d, 1H, H^9) ppm. Anal. Calcd for $C_{25}H_{22}F_6FeN_3PPd$: C, 44.70; H, 3.30; N, 6.26. Found: C, 44.9; H, 3.0; N, 6.72.

[Pd(Me)(1)], 4. To a stirred solution of **2** (0.03 g, 0.06 mmol) in 10 mL of methanol was added, at room temperature, an excess of sodium acetate (0.024 g, 0.30 mmol). After 2 days, the initially red solution has turned purple. It was then filtered and the volatiles were removed under reduced pressure. To the resulting solid was added dichloromethane, and the mixture was filtered over Celite. A pure sample of the desired product was obtained by flash chromatography (ethyl acetate). Yield: 57%.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 0.83 (br, 3H, Pd−Me), 4.19 (s, 5H, Cp), 4.64 (t, $^3J_{H,H}$ = 2.3 Hz, 1H, H$^\beta$ of C_5H_3), 4.71 (d, $^3J_{H,H}$ = 2.2 Hz, 1H, H$^\alpha$ of C_5H_3), 5.06 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H$^\gamma$ of C_5H_3), 7.50 (d, $^3J_{H,H}$ = 8.51 Hz, 1H, H^3 or H^4), 7.77 (m, 3H, H^5, H^6, and H^8), 8.19 (d, $^3J_{H,H}$ = 8.4 Hz, 1H, H^3 or H^4), 8.37 (dd, $^3J_{H,H}$ = 8.2 and $^4J_{H,H}$ = 1.3 Hz, 1H, H^7), 9.03 (dd, $^3J_{H,H}$ = 4.8 and $^4J_{H,H}$ = 1.3 Hz, 1H, H^9) ppm.

[Pd(1)(O$_2$CCF$_3$)], 5. $[Pd(OAc)_2]$ (0.10 g, 0.45 mmol) was stirred at room temperature in 10 mL of MeOH. After 10 min, solid **1** (0.185 g, 0.51 mmol) was added and the solution became dark red. It was then filtered and 1 mL of CF_3COOH added to the filtrate, which immediately became purple and was stirred for 30 min,

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leading to the precipitation of a solid. The latter was then filtered, washed with cold MeOH, and dried under vacuum. Crystals suitable for X-ray crystallography were obtained from CH_2Cl_2/Et_2O. Yield: 58%.

^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 4.28 (s, 5H, Cp), 4.70 (br, 1H, H$^\alpha$ of C_5H_3), 4.82 (br, 1H, H$^\beta$ of C_5H_3), 4.85 (br, 1H, H$^\gamma$ of C_5H_3), 7.51 (d, $^3J_{H,H}$ = 8.5 Hz, 1H, H^3), 7.79−7.82 (m, 3H, H^5, H^6, and H^8), 8.24 (d, $^3J_{H,H}$ = 8.78 Hz, 1H, H^4), 8.45 (d, $^3J_{H,H}$ = 8.06 Hz, 1H, H^7), 8.80 (d, $^3J_{H,H}$ = 4.64 Hz, 1H, H^9) ppm. Anal. Calcd for $C_{24}H_{15}F_3FeN_2O_2Pd$: C, 49.47; H, 2.59; N, 4.81. Found: C, 51.6; H, 2.11; N, 4.95.

[Pd(1)(NCMe)][PF$_6$], 6. To a stirred solution of **5** (0.03 g, 0.05 mmol) in 10 mL of CH_2Cl_2 was added an excess of $NaPF_6$ (0.01 g, 0.06 mmol) dissolved in 1 mL of anhydrous MeCN. It was stirred at room temperature for 3 h and filtrated. Addition of diethyl ether caused the precipitation of a solid, which was filtrated, washed with hexane, and dried under vacuum, affording a dark purple crystalline solid. Crystals suitable for X-ray crystallography were obtained directly from the synthesis.

^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ 4.40 (s, 5H, Cp), 4.85 (br, 1H, H$^\alpha$ of C_5H_3), 5.01 (br, 1H, H$^\beta$ of C_5H_3), 5.14 (br, 1H, H$^\gamma$ of C_5H_3), 7.84 (d, $^3J_{H,H}$ = 8.79 Hz, 1H, H^3), 8.05−8.12 (m, 3H, H^8, H^5, and H^6), 8.61 (d, 1H, H^4), 8.34 (d, $^3J_{H,H}$ = 7.8 Hz, 1H, H^7), 9.04 (br, 1H, H^9) ppm. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 2.58 (s, 3H, MeCN), 4.40 (s, 5H, Cp), 7.50 (d, $^3J_{H,H}$ = 8.8 Hz, 1H, H^3), 7.86 (m, 2H, H^5 and H^6), 7.90 (dd, $^3J_{H,H}$ = 8.3 and 4.8 Hz, 1H, H^8), 8.28 (d, 1H, $^3J_{H,H}$ = 8.8, H^4), 8.52 (dd, $^3J_{H,H}$ = 8.3 Hz and $^4J_{H,H}$ = 1.46, 1H, H^7), 8.84 (d, 1H, $^3J_{H,H}$ = 4.88 Hz, H^9) ppm. Anal. Calcd for $C_{24}H_{18}F_6FeN_3PPd$: C, 43.97; H, 2.77; N, 6.41. Found: C, 44.35; H, 3.09; N, 6.7.

[Pd(1)(PPh$_3$)][O$_2$CCF$_3$], 7. To a solution of **5** in $CDCl_3$ was added 1 equiv of solid PPh_3. ^{1}H and ^{31}P{^{1}H} NMR spectra recorded immediately showed the presence of free phosphine (less than 10%) and unreacted **5**. Total conversion occurred after 1 night, affording **7** as the only product observed in solution.

Synthesis: To a stirred solution of **5** (0.035 g, 0.06 mmol) in 10 mL of CH_2Cl_2 was added 1 equiv of solid PPh_3 (0.016 g, 0.06 mmol). The reaction was monitored by ^{31}P{^{1}H} NMR. When the spectrum showed complete reaction of the phosphine, the volatiles were removed under reduced pressure. The solid obtained was then washed with diethyl ether, filtrated, and dried under vacuum, affording a dark crystalline solid. Crystals suitable for X-ray crystallography were obtained from CH_2Cl_2/Et_2O at 6 °C. Yield: 81%.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.55 (d, $^3J_{H,H}$ = 2.4 Hz, 1H, H$^\alpha$ of C_5H_3), 3.81 (s, 5H, Cp), 4.46 (t, $^3J_{H,H}$ = 2.2 Hz, 1H, H$^\beta$ of C_5H_3), 4.91 (d, $^3J_{H,H}$ = 2.2 Hz, 1H, H$^\gamma$ of C_5H_3), 6.85 (d, $^3J_{H,H}$ = 4.9 Hz, 1H, H^9), 7.46 (dd, 1H, $^3J_{H,H}$ = 8.0 and 4.9 Hz, H^8), 7.55 (m, 6H, PPh_3), 7.63 (m, 3H, PPh_3), 7.74 (d, $^3J_{H,H}$ = 8.54 Hz, 1H, H^3), 7.85 (m, 6H, PPh_3), 7.98 (dd, 2H, H^5 and H^6), 8.55 (d, 1H, H^4), 8.62 (d, 1H, H^7) ppm. ^{31}P{^{1}H} NMR (109.25 MHz, $CDCl_3$, 25 °C): δ 35.3 (s) ppm. Anal. Calcd for $C_{42}H_{30}F_3FeN_2O_2PPd$: C, 59.70; H, 3.58; N, 3.32. Found: C, 59.53; H, 3.88; N, 3.18.

[Pd(1)(8)][O$_2$CCF$_3$], 9. To a stirred solution of **5** (0.02 g, 0.034 mmol) in 5 mL of CH_2Cl_2 was added under argon 1 equiv of solid **8**. After stirring at room temperature for 30 min the volatiles were removed under reduced pressure. The solid obtained was then washed with diethyl ether, filtrated, and dried under vacuum. Yield: 77%.

^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, 25 °C): δ 42.0 (s) and 42.5 (s) ppm.

Two successive recrystallizations from chloroform/diethyl ether (1:1, 3 mL for 10 mg of solid) at 6 °C afforded a pure, dark purple, solid sample of one of the two diastereoisomers.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.48 (dd, $^3J_{H,H}$ = 6.6 and $^2J_{P,H}$ = 13.6 Hz, 1H, CH_2), 3.64 (dd, $^3J_{H,H}$ = 3.9 and $^2J_{P,H}$ = 12.6 Hz, 1H, CH_2), 3.69 (s, 5H, Cp), 3.87 (d br, $^2J_{P,H}$ = 12.6 Hz, 1H, CH_2), 4.03 (d br, $^2J_{P,H}$ = 13.5 Hz, 1H, CH_2), 4.26 (d, $^3J_{H,H}$ = 2.2 Hz, 1H, H$^\alpha$ of C_5H_3), 4.63 (br, 1H, H$^\beta$ of C_5H_3), 4.89 (d, 1H, H$^\gamma$ of C_5H_3), 7.40−7.90 (series of m, aromatics and H^5, H^6), 7.68 (d, $^3J_{H,H}$ = 6.1 Hz, 1H, H^3), 7.93 (d, $^3J_{H,H}$ = 8.3 Hz, 1H, H^8), 8.50 (br, 1H, H^4), 8.52 (br, 1H, H^7), 8.87 (br, 1H, H^9) ppm. ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, 25 °C): δ 42.0 (s) ppm. $[\alpha]^{20}_D$ +1200 (5×10^{-3} g/100 mL; $CHCl_3$). Anal. Calcd for $C_{52}H_{36}F_3FeN_2O_2PPd$: C, 64.32; H, 3.74; N, 2.88. Found: C, 64.91; H, 3.27; N, 3.35.

[Pd$_2$(1)$_2$(μ-dppe)][O$_2$CCF$_3$]$_2$, 10. To a stirred solution of **5** (0.04 g, 0.07 mmol) in 10 mL of CH_2Cl_2 was added 0.5 equiv of 1,2-bis(diphenylphosphino)ethane (dppe) (0.014 g, 0.035 mmol). After stirring at room temperature for 30 min the volatiles were removed under reduced pressure. The solid obtained was then washed with diethyl ether, filtrated, and dried under vacuum. Yield: 71%.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.02 (br, 4H, CH_2), 3.69 (d, $^3J_{H,H}$ = 2.2 Hz, 1H, H$^\alpha$ of C_5H_3), 3.77 (s, 10H, Cp), 3.81 (d, $^3J_{H,H}$ = 2.2 Hz, 1H, H$^\alpha$ of C_5H_3), 4.33 (br t, 1H, H$^\beta$ of C_5H_3), 4.36 (br t, 1H, H$^\beta$ of C_5H_3), 4.62 (d, $^3J_{H,H}$ = 2.1 Hz, 1H, H$^\gamma$ of C_5H_3), 4.64 (d, $^3J_{H,H}$ = 2.3 Hz, 1H, H$^\gamma$ of C_5H_3), 7.21 (d, $^3J_{H,H}$ = 4.6 Hz, 1H, H^9), 7.33 (br, H^8), 7.38−7.68 (series of m, aromatics), 7.57 (d, 1H, H^3), 7.74−7.96 (m, 4H, H^5 and H^6), 8.24 (br, 1H, H^7), 8.43 (br, 2H, H^7 and H^4), 8.52 (d, $^3J_{H,H}$ = 8.5 Hz, 1H, H^4) ppm. ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, 25 °C): δ 26.6 (s) and 27.1 (s) ppm. Anal. Calc for $C_{74}H_{54}F_6Fe_2N_4O_4P_2Pd_2$: C, 56.84; H, 3.48; N, 3.58. Found: C, 57.4; H, 3.29; N, 3.89.

[Pd$_2$(1)$_2$(μ-dppp)][O$_2$CCF$_3$]$_2$, 11. A procedure similar to that of the synthesis of **10** was used, using 1,3-bis(diphenylphosphino)-propane (dppp) instead of dppe. Yield: 76%.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.5 and 3.40 (br, 6H, CH_2), 3.71 (br s, 1H, C_5H_3), 3.76 (s, 10H, Cp), 3.82 (br s, 1 H, C_5H_3), 4.32 (br s, 1H, C_5H_3), 4.37 (br s, 1H, C_5H_3), 4.63 (br s, 1H, C_5H_3), 4.65 (br s, 1H, C_5H_3), 7.18−8.53 (series of br m, aromatics) ppm. ^{1}H NMR (400 MHz, dmso-d_6, 100 °C): δ 2.5 (br, 2H, CH_2), 3.20 (br m, 4H, CH_2), 3.70 (d, $^3J_{H,H}$ = 2.2 Hz, 1H, H$^\alpha$ of C_5H_3), 3.72 (d, $^3J_{H,H}$ = 2.3 Hz, 1H, H$^\alpha$ of C_5H_3), 3.86 (s, 10 H, Cp), 4.38 (t, $^3J_{H,H}$ = 2.5 Hz, 1H, H$^\beta$ of C_5H_3), 4.44 (t, $^3J_{H,H}$ = 2.5 Hz, 1H, H$^\beta$ of C_5H_3), 4.87 (d, 1H, H$^\gamma$ of C_5H_3), 4.90 (d, 1H, H$^\gamma$ of C_5H_3), 7.17 (d, $^3J_{H,H}$ = 4.2 Hz, 1H, H^9), 7.21 (d, $^3J_{H,H}$ = 4.1 Hz, 1H, H^9), 7.40 (m, 2H, H^8), 7.52−7.88 (series of m, aromatics), 7.68 (d, 1H, H^3), 7.77 (d, 1H, H^3), 7.90−8.07 (m, 4H, H^5 and H^6), 8.50 (m, 3H, one H^4 and two H^7), 8.59 (d, $^3J_{H,H}$ = 8.5 Hz, 1H, H^4) ppm. ^{31}P-{^{1}H} NMR (161.8 MHz, $CDCl_3$, 25 °C): δ 26.5 (s) and 27.0 (s) ppm. Anal. Calcd for $C_{75}H_{56}F_6Fe_2N_4O_4P_2Pd_2$: C, 57.09; H, 3.58; N, 3.55. Found: C, 57.55; H, 3.74; N, 3.97.

CO/Styrene Copolymerization. The copolymerization reaction was carried out in a glass reactor (75 mL), equipped with a magnetic stirrer and a temperature controller. The catalyst (1.27×10^{-5} mol), 1,4-benzoquinone, styrene (10 mL), and 2,2,2-trifluoroethanol were placed in the reactor, CO was bubbled through the solution for 10 min, then a balloon filled with CO was connected to the reactor and the system was heated at 30 °C. At the end of the reaction, after cooling and releasing of the residual gas, the reaction mixture was poured into methanol (100 mL), causing the precipitation of the polymer, which was then filtered, washed with methanol, and dried under vacuum. A ^{13}C NMR spectrum of the polyketones obtained was recorded in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) with a small amount of $CDCl_3$ for locking purposes at 100.5 MHz.

Heck Coupling. To a 25 mL Schlenk flask were added catalyst (3×10^{-3} mmol; 0.1%), triethylamine (0.42 mL, 3.0 mmol), iodobenzene (2.0 mmol), methyl acrylate (0.27 mL, 3 mmol), and DMF (10 mL). The mixture was refluxed at 110 °C into an oil bath. After 14 h the reaction mixture was extracted with dichloromethane (5 mL) and water (10 mL). The organic layer was washed four times with 10 mL portions of water and dried with $MgSO_4$. The mixture was then filtered and the dichloromethane removed in vacuo. A pure product was obtained by flash column

Table 2. Crystal Data and Details of Refinements for Compounds 5, 6, and 7

	5	**6**·CH_2Cl_2	**7**·CH_2Cl_2
formula	$C_{24}H_{15}F_3FeN_2O_2Pd$	$C_{25}H_{20}Cl_2F_6FeN_3PPd$	$C_{43}H_{32}Cl_2F_3FeN_2O_2PPd$
M_r [g mol^{-1}]	582.63	740.56	929.83
wavelength [Å]	0.71073	1.54178	0.71073
cryst syst	monoclinic	monoclinic	Triclinic
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a [Å]	11.427(4)	10.105(3)	10.708(3)
b [Å]	12.338(4)	22.529(5)	10.965(4)
c [Å]	15.599(5)	11.948(4)	17.713(4)
α [deg]	90.0	90.0	102.76(3)
β [deg]	110.56(3)	96.86(3)	90.78(3)
γ [deg]	90.0	90.0	98.74(2)
volume [Å^3]	2059.1(12)	2700.5(13)	2002.4(10)
Z	4	4	2
D_{calcd} [g cm^{-3}]	1.879	1.821	1.542
μ [mm^{-1}]	1.631	12.639	1.038
F(000)	1152	1464	936
θ range [deg]	2.16−27.10	5.42−56.05	2.02−26.49
no. of reflns collected	32 782	11 735	16 790
no. of unique reflns	4395	3283	7015
R_{int}	0.0634	0.0419	0.0417
obsd $I > 2\sigma[I]$	3445	2593	3271
no. of params	298	389	494
goodness of fit (F^2)	1.025	1.056	0.914
R_1 [$I > 2\sigma[I]$][a]	0.0353	0.0611	0.0731
wR_2[b]	0.0942	0.1584	0.2034
$\Delta\rho$ [e Å^{-3}]	0.919, −0.643	0.791, −0.728	1.345, −0.673

[a] $R_1 = \sum ||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

chromatography on silica gel with a mixture of hexane/diethyl ether as eluent (12:1, v/v). The conversion was determined by GC and the identity of the product was confirmed by ^{1}H NMR comparison with the authentic sample.

Crystallographic Data Collection and Refinements. Data collections of complexes **5** and **7** were carried out at 293(3) K using Mo Kα radiation ($\lambda = 0.71073$ Å) on a Nonius DIP-1030H system, and that of compound **6** on a Bruker-Nonius FR591 rotating anode (Cu Kα) equipped with a KappaCCD detector. Cell refinement, indexing, and scaling of the data set were performed using the programs Mosflm,[18] Denzo, and Scalepack.[19] In **6** the equatorial PF_6^- fluorine atoms were found disordered over two positions along the F−P−F axial direction (occupancies refined to 0.70/0.30). A lattice CH_2Cl_2 molecule was detected in the ΔF map of **6** and **7**; in the latter structure the solvent is disordered over two positions (occupancies refined to 0.53/0.47, H atoms not included). All the structures were solved by direct method and successive Fourier analyses and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[20] Crystal data for the structures reported are summarized in Table 2. The calculations were performed using the WinGX System, Ver. 1.70.00.[21]

Further details of the crystal structure determination have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC numbers 614894−614896 for complexes **5**, **6**, and **7**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: ^{1}H NOE spectrum of **2** (Figure S1), comparison of the ^{1}H NMR spectra of **2**, **3**, **4**, and **5** (Figure S2), and full details of crystallographic analyses of **5**, **6**, and **7** in CIF format. This material is available free of charge via the Internet http://pubs.acs.org.

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