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Trans-Chelating Chiral Peralkyldiphosphine Ligands (*R*,*R*)-(*S*,*S*)-2,2″-Bis[1-(dialkylphosphino)ethyl]-1,1″-biferrocenes (AlkylTRAPs) and Their Transition Metal Complexes

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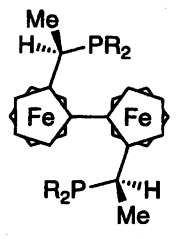
New chiral peralkyldiphosphines (*S*,*S*)-2,2″-bis[(*R*)-1-(dialkylphosphino)ethyl]-1,1″-biferrocenes ((*R*,*R*)-(*S*,*S*)-alkylTRAPs) were synthesized from (*R*)-*N*,*N*-dimethyl-1-ferrocenylethylamine in four steps in 38—68% overall yields (MeTRAP: 38%, EtTRAP: 68%, PrTRAP: 53%, BuTRAP: 56%, *i*-BuTRAP: 51%, *i*-PrTRAP: 42%). The reactions of alkylTRAP (Et-, Bu-, *i*-Bu, and *i*-PrTRAP) with 1 molar amount of $PdBr_2$ gave *trans*-[$PdBr_2$(alkylTRAP)] in good yields. The X-ray crystal structures of these palladium complexes revealed that alkylTRAPs coordinated to a palladium atom in a trans-chelating manner regardless of the *P*-alkyl substituents. The structures of palladium complexes of Et-, Bu-, and *i*-PrTRAP had nearly C_2-symmetry, but that of *i*-BuTRAP was deviated from C_2-symmetry significantly. AlkylTRAPs also reacted with [$PtCl_2$(MeCN)$_2$] and [RhCl(CO)$_2$]$_2$, giving the corresponding trans-chelate platinum and rhodium complexes. The crystal structure of *trans*-[RhCl(CO)(BuTRAP)] revealed that the conformation of the BuTRAP ligand in the complex was almost the same as that in the palladium complex *trans*-[$PdBr_2$(BuTRAP)].

Catalytic asymmetric synthesis has been one of the most attractive areas of modern organic synthetic chemistry.[1] Various chiral phosphines have so far been developed for ligands on chiral transition metal catalysts. Especially, diphosphine ligands, which have found wide applications for asymmetric synthesis, coordinate to metal atoms in a cis-chelating manner, and create a chiral environment around the metal center by sterically rigid and bulky substituents on each of the phosphorus atoms. Recently, we have developed a new type of chiral diphosphine ligands (TRAPs, (*R*,*R*)-(*S*,*S*)- and (*S*,*S*)-(*R*,*R*)-2,2″-bis[1-(diaryl- and dialkylphosphino)ethyl]-1,1″-biferrocenes), which were designed to coordinate to transition metals in a trans-chelating manner.[2—5] TRAPs have been demonstrated to be effective chiral ligands for some catalytic enantioselective reactions. TRAPs bearing *P*-aromatic substituents (arylTRAPs) were effective for the asymmetric



(*R*,*R*)-(*S*,*S*)-TRAP (1a–f)

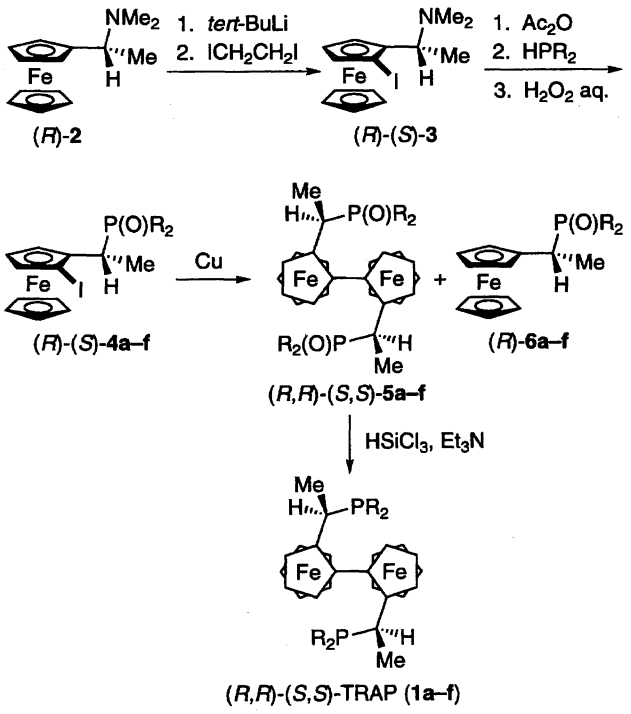
a: R = Me (MeTRAP)
b: R = Et (EtTRAP)
c: R = Pr (PrTRAP)
d: R = Bu (BuTRAP)
e: R = *i*-Bu (*i*-BuTRAP)
f: R = *i*-Pr (*i*-PrTRAP)

Chart 1. Figure of alkylTRAPs.

Michael addition[6] and allylation[7] of 2-cyanopropionates, and asymmetric cycloisomerization of 1,6-enynes.[8] The concave chiral environment provided by the four aromatic substituents on the trans-chelating phosphorus atoms is crucial for high enantioselectivity. On the other hand, TRAPs bearing flexible *P*-aliphatic substituents were more effective for the asymmetric hydrosilylation of ketones[9] as well as the asymmetric hydrogenation of itaconates[10] and α-acetamidoacrylates.[11] In the latter, congested and rigid *P*-substituents of TRAP prevent an effective enantiofaceselection of the substrates. This paper describes full details for the synthesis of alkylTRAPs (**1**) and the structures of their transition metal complexes (Chart 1).

Results and Discussion

Synthesis of AlkylTRAPs. Trans-chelating chiral peralkyldiphosphine ligands (*R*,*R*)-(*S*,*S*)-alkylTRAPs (**1**) were synthesized, starting from optically pure (*R*)-*N*,*N*-dimethyl-1-ferrocenylethylamine (**2**), which was obtained by the optical resolution of its racemate with tartaric acid (Scheme 1).[12] Ortho-lithiation of (*R*)-**2** with a 1.2 molar amount of *t*-butyllithium in diethyl ether at 0 °C followed by a treatment of the resulting *ortho*-lithioferrocene with 1.3 molar amount of 1,2-diiodoethane gave (*S*)-2-[(*R*)-1-(dimethylamino)ethyl]-1-iodoferrocene ((*R*)-(*S*)-**3**), in which a planar chirality (*S*) was newly induced, with 93—94% de in 90—100%



Scheme 1.

conversions.[13] For introducing a dialkylphosphinyl group on the ferrocene side chain, we first followed the procedure for the preparation of arylTRAPs. However, undesired 2-vinyliodoferrocene was obtained as a major product.[2] A successful introduction of the phosphinyl group was carried out by treatment of (*R*)-(*S*)-**3** with excess of acetic anhydride, followed by a substitution reaction with dialkylphosphines in acetic acid, giving (*S*)-2-[(*R*)-1-(dialkylphosphino)ethyl]-1-iodoferrocene.[14] The thus-obtained peralkylphosphines were not stable enough to be handled in the air. Therefore, they were converted to the corresponding phosphine oxide, (*R*)-(*S*)-**4** (83—96%), by oxidation with hydrogen peroxide in acetone. The substitution reaction proceeded with complete retention.[12] The homocoupling of (*R*)-(*S*)-**4** was performed with activated-copper powder (neat),[15] producing C_2-symmetric biferrocene (*R*,*R*)-(*S*,*S*)-**5** together with deiodination products (*R*)-**6**. The mixtures of **5** and **6** were subjected to separation and isolation with column chromatography on silica gel (**5a**, **5b**) or preparative gel permeation chromatography (**5c**—**f**) (58—79%). Finally, the reduction of the phosphine oxides (**5**) with trichlorosilane and triethylamine in benzene gave (*R*,*R*)-(*S*,*S*)-alkylTRAPs (78—99%).[16] The overall yields of alkylTRAPs from **2** were 38% (**1a**), 68% (**1b**), 53% (**1c**), 56% (**1d**), 51% (**1e**), and 42% (**1f**). MeTRAP and EtTRAP were isolated as orange powder, but other alkylTRAPs were an orange viscous oil.

Generally, peralkylphosphines must be treated with much care against air oxidation. However, alkylTRAPs, once isolated, were relatively stable against air oxidation. *AlkylTRAPs can be handled in the air* and stored for over a year under argon in a freezer. EtTRAP was converted to the EtTRAP monoxide in only 14% yield in not degassed C_6D_6 for 24 h at room temperature. Such unusual stability seems to be due to a steric factor rather than an electronic factor, since the monomeric phosphines ((*S*)-2-[(*R*)-1-(dialkylphosphino)ethyl]-1-iodoferrocene) formed by the substitution reaction with dialkylphosphines were very unstable to air oxidation.

Two ferrocene moieties of all alkylTRAPs were equivalent in solution, as demonstrated by their ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra. As in arylTRAPs reported previously, ^{13}C signals for *P*-substituents of alkylTRAPs split into multiplets, as shown in Fig. 1, indicating through-space P–P spin couplings, being suggestive of the close proximity of the two phosphorus atoms of the alkylTRAPs.[17,18]

The X-ray crystal structure of **5f**, the phosphine oxide of *i*-PrTRAP, is shown in Fig. 2. The torsion angle between the two linked cyclopentadienyl rings was 110°, and the two ferrocene moieties were located in gauche geometry with relation to each other. The dihedral angles P(1)–C(1)–C(3)–C(7) and P(2)–C(13)–C(15)–C(19) were −90.7° and −141.8°, respectively. The two phosphorus atoms on the asymmetric carbon centers were located on a sterically less crowded *exo* region of ferrocene. Such positions of the phosphorus atoms would be suitable for chelation to transition metal atoms. A similar conformation was also seen in the

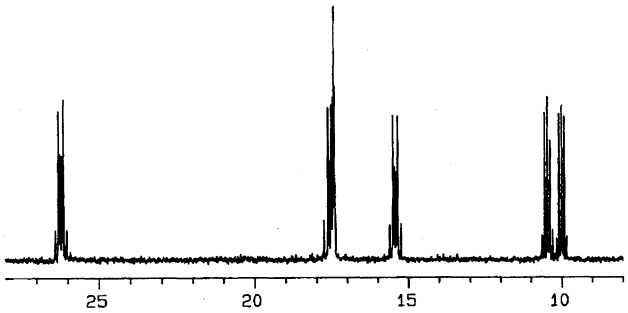


Fig. 1. $^{13}C\{^1H\}$ NMR (100 MHz) spectrum of **1b** in $CDCl_3$ (alkyl region).

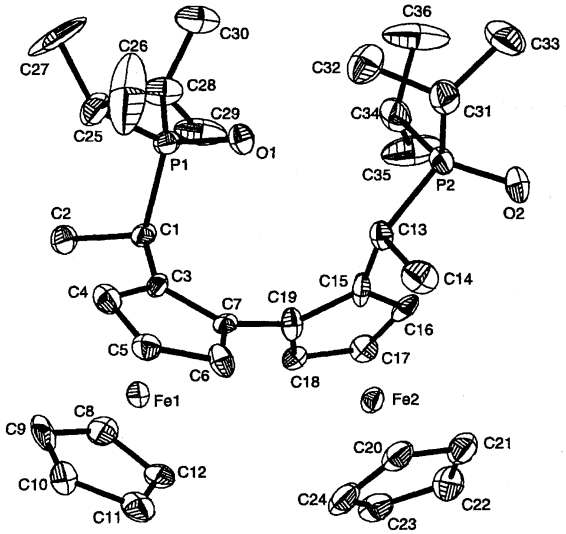


Fig. 2. ORTEP drawing (30% probability level) with atom-labeling scheme for **5f** (hydrogen atoms are omitted for clarity).

X-ray structure of 2,2″-bis[1-(dimethylamino)ethyl]-1,1″-biferrocene.[19] Reflecting the distance between the two phosphorus atoms in **5f** (5.099 Å), the $^{13}C\{^1H\}$ NMR spectrum of *P*-substituents in **5f** did not exhibit multiplet signals resulting from through-space P–P spin coupling, as shown in that of **1**, but simple doublet signals from P–C spin coupling.

Synthesis and NMR Spectra of Transition Metal Complexes of AlkylTRAPs. Palladium complexes, *trans*-$PdBr_2$[{(*R*,*R*)-(*S*,*S*)-alkylTRAP}] (**7**), were prepared by reactions of (*R*,*R*)-(*S*,*S*)-**1** with $PdBr_2$ in toluene under reflux. These compounds are orange-colored air-stable solids. Each $^{31}P\{^1H\}$ NMR spectrum of these TRAP-palladium complexes exhibited a characteristic singlet signal. Both the ^1H and $^{13}C\{^1H\}$ NMR spectra of **7** exhibited that the two 2-[1-(dialkylphosphino)ethyl]ferrocenyl moieties are equivalent, indicating a C_2-symmetric structure of **7** in solution. In the $^{13}C\{^1H\}$ NMR spectra, phosphorus-coupled resonances split into a 1 : 2 : 1 triplet. Such a triplet is observed in the case of the AXX′ spin system when $|J_{A-X} - J_{A-X'}|^2 < 8J_{X-X'}\Delta\nu_{1/2}$, where $\Delta\nu_{1/2}$ is the resolving power of the spectrometer.[20] The spectroscopic observation indicated a significantly large P–P spin coupling constant for the two phosphorus atoms of **7**, being suggestive of a trans-chelating structure.

The reaction of (*R*,*R*)- (*S*,*S*)- BuTRAP (**1d**) with $[PtCl_2(MeCN)_2]$ in $CDCl_3$ gave two platinum complexes in a ratio of ca. 10 : 1, as observed by the $^{31}P\{^1H\}$ NMR spectrum. The resonance ($\delta = 17.40$) for the major product was accompanied by its ^{195}Pt satellite with a J_{Pt-P} value of 2443 Hz, indicating the trans-geometry of the two phosphorus atoms, and suggesting C_2 symmetry of the complex.[21] On the other hand, the minor product showed a pair of doublet signals ($\delta = 9.86$ and 14.56, $J_{P-P} = 15$ Hz) in $^{31}P\{^1H\}$ NMR with their ^{195}Pt satellite ($J_{Pt-P} = 3699$ Hz and 3608 Hz respectively). The minor product is assigned to *cis*-$[PtCl_2$(BuTRAP)] with C_1 symmetry (note that two phosphorus atoms are not equivalent). *trans*-$[PtCl_2$\{(*R*,*R*)-(*S*,*S*)-BuTRAP\}] (**8d**) was isolated with 93% yield by column chromatography on silica gel. The reaction of (*R*,*R*)-(*S*,*S*)-*i*-PrTRAP (**1f**), which has larger *P*-substituents than **1d**, with $[PtCl_2(MeCN)_2]$ in C_6D_6 gave a single platinum complex, as revealed by the $^{31}P\{^1H\}$ NMR spectrum. The product showed a singlet ($\delta = 30.81$) with a ^{195}Pt satellite ($J_{Pt-P} = 2465$ Hz), indicating that the complex was *trans*-$[PtCl_2$\{(*R*,*R*)-(*S*,*S*)-*i*-PrTRAP]. The formation of a cis-chelating platinum complex would be prevented by the bulkiness of *P*-substituent of **1**.

A Vaska-type rhodium complex, *trans*-[RhCl(CO)\{(*R*,*R*)-(*S*,*S*)-BuTRAP\}] (**9d**), was obtained by the reaction of (*R*,*R*)-(*S*,*S*)-**1d** with $[RhCl(CO)_2]_2$ in CH_2Cl_2 at room temperature. The ^{31}P NMR spectrum of **9d** showed a pair of double doublets with a 341 Hz of P–P spin coupling constant and 119 and 119 Hz of Rh–P spin coupling constants. The large P–P spin coupling constant indicates that the BuTRAP coordinates to the rhodium atom in a trans-chelating manner.

X-Ray Crystal Structures of Transition Metal Complexes of AlkylTRAPs. X-Ray crystal structures were obtained for palladium complexes **7b** and **7d—f**. An X-ray analysis of *trans*-$[PdBr_2$\{(*R*,*R*)-(*S*,*S*)-EtTRAP\}] (**7b**) revealed that the unit cell contains a set of independent molecules. Their structures were essentially the same, except for the position of one of the terminal methyl groups on the *P*-substituents. An ORTEP drawing for one of the two molecules is shown in Fig. 3 (see Fig. 9 of the Experimental section for another molecule). Bond distances and angles are listed in Table 1. The coordination geometry on the palladium atom was slightly distorted from square planer. Two phosphorus atoms were located in the trans position of each other, with bond angles of P(1)–Pd(1)–P(2) and Br(1)–Pd(1)–Br(2) being 166.78° and 176.52°, respectively. The conformation of the chelating backbone in **7b** was simi-

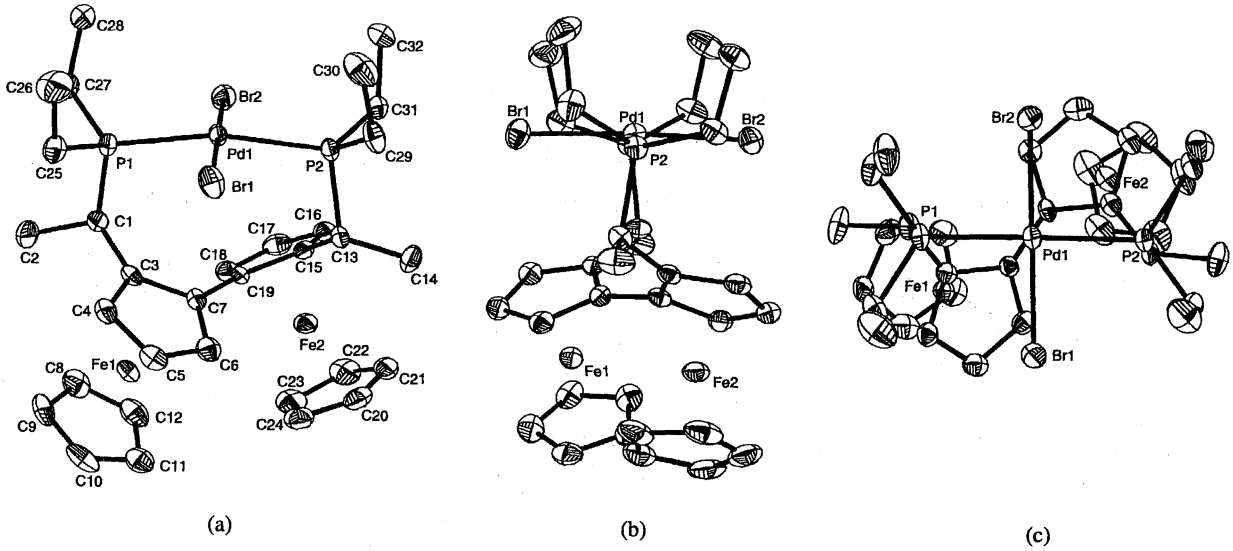


Fig. 3. ORTEP drawing (30% probability level) with atom-labeling scheme for **7b** (hydrogen atoms are omitted for clarity). Only one of the two molecules in a unit cell is shown. The second molecule is shown in Fig. 9 (a) Front view. (b) Side view. (c) Top view.

Table 1. Selected Bond Distances (Å) and Angles (deg) with esd's for **7b**

Bond distances	
Pd(1)–Br(1)	2.4307(9)
Pd(1)–P(1)	2.304(2)
Pd(1)–Br(2)	2.4320(9)
Pd(1)–P(2)	2.314(2)
Bond angles	
Br(1)–Pd(1)–Br(2)	176.52(2)
Br(1)–Pd(1)–P(2)	87.99(5)
Br(2)–Pd(1)–P(2)	91.66(5)
Pd(1)–P(1)–C(1)	105.1(2)
Br(1)–Pd(1)–P(1)	90.60(5)
Br(2)–Pd(1)–P(1)	88.94(5)
P(1)–Pd(1)–P(2)	166.78(7)
Pd(1)–P(2)–C(13)	103.6(2)

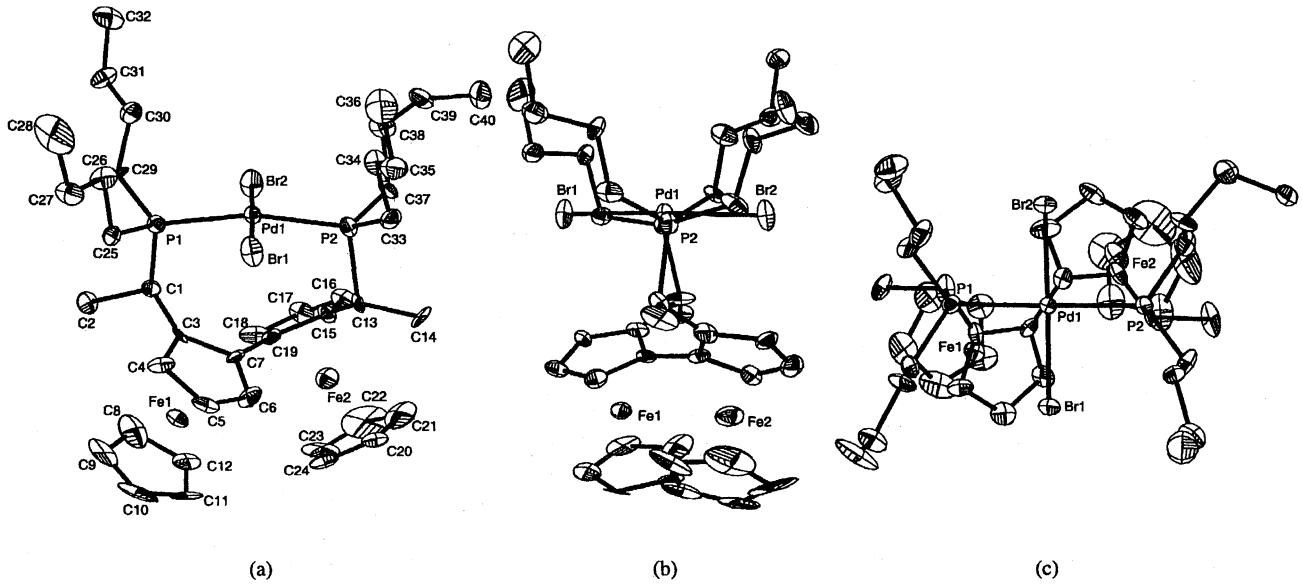
lar to that of phosphine oxide **5f** (Fig. 2). The torsional angle between two cyclopentadienyl rings linked with C(7)–C(19) was 123°. The two bromine atoms on palladium are positioned among a chiral cavity created by the biferrocene backbone and the ethyl groups on phosphorus atoms. The whole structure of the molecule is nearly C_2 symmetric, and the four ethyl groups on the phosphorus atoms are arranged in a C_{2v} symmetric fashion, as shown in Figs. 3(b) and 3(c).

The X-ray structures of *trans*-[$PdBr_2$\{(*R*,*R*)-(*S*,*S*)-BuTRAP\}] (**7d**) and *trans*-[$PdBr_2$\{(*R*,*R*)-(*S*,*S*)-*i*-PrTRAP\}] (**7f**) are shown in Figs. 4 and 5, and selected bond distances and angles are given in Tables 2 and 3, respectively. A schematic superposition of **7b**, **7d**, and **7f**, depicted in Fig. 6, shows that the conformations of the chelating backbones of these complexes, **7d** and **7f**, are quite similar to each other. Both of the torsional angles between the two connected cyclopentadienyl rings of **7d** and **7f** were 123°. The X-ray crystal structure of **7f** was solved as being a completely C_2-symmetric structure for the axis through the palladium atom and the median of the C(7)–C(7*) bond. The structure of **7d** was also essentially C_2-symmetrical, except for C(40), one of the terminal carbon atoms of the butyl groups.

The crystal structure of *trans*-[$PdBr_2$\{(*R*,*R*)-(*S*,*S*)-*i*-BuTRAP\}] (**7e**) was not C_2-symmetric (Fig. 7, Table 4). In the top view of **7e** (Fig. 7(c)), the biferrocene moiety of *i*-BuTRAP inclined to the upper side of the P(1)–Pd(1)–P(2) line. The torsional angle between the two linked cyclopentadienyl rings was 124°. The conformation of chelating backbone of **7e** resembled that of *trans*-[$PdBr_2$(PhTRAP)],[2b] rather than other *trans*-[$PdBr_2$(alkylTRAPs)]. Although the local symmetry of four *P*-substituents of **7b**,**7d**, and **7f** revealed pseudo C_{2v}, such a symmetry was lost in the structure of **7e**, releasing a steric repulsion between the terminal methyl groups on the *P*-isobutyl groups. The bond angles, P(1)–Pd(1)–P(2) and Br(1)–Pd(1)–Br(2), were 163.14 ° and 166.01°, respectively. The angle Br(1)–Pd(1)–Br(2) was narrower than those of **7b**,**7d**, and **7f**, so as to avoid steric repulsions between the isobutyl groups and the bromine atoms.

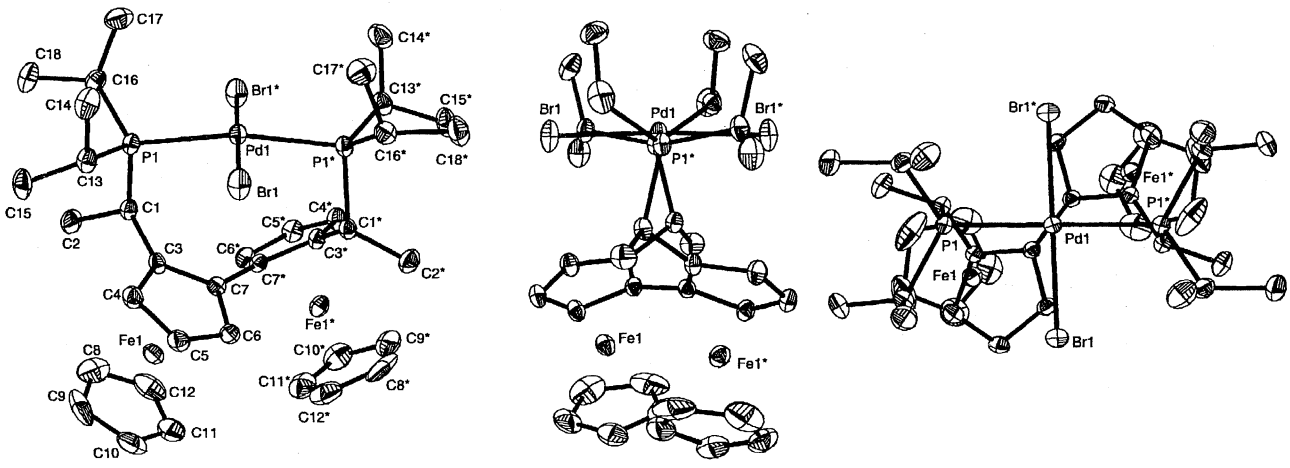
In the X-ray crystal structure of *trans*-[RhCl(CO)\{(*R*,*R*)-(*S*,*S*)-BuTRAP\}] (**9d**), the Cl–Rh–CO moiety, was disordered (55 : 45).[9a] The structure with 0.55 occupancy is shown in Fig. 8, and its selected bond distances and angles are given in Table 5. In the structure with 0.45 occupancy, the chloro and carbonyl ligands were interchanged (see Fig. 10 in Experimental section). The conformation of BuTRAP in **9d** was almost the same as that in **7d**.

As previously reported, the enantioselectivity in the asymmetric reactions using the TRAP ligands strongly depends on the ligand *P*-substituent. In the asymmetric hydrosilylation of ketones[9] and the hydrogenation of olefins,[10,11] (*R*,*R*)-(*S*,*S*)-*i*-PrTRAP (**1f**) gave much lower selectivities than did (*R*,*R*)-(*S*,*S*)-EtTRAP (**1b**) and BuTRAP (**1d**); the hydrosilylation of acetophenone (**1b**, 85% ee (*S*); **1d**, 92% ee (*S*); **1f**, 1% ee



(a) (b) (c)

Fig. 4. ORTEP drawing (30% probability level) with atom-labeling scheme for **7d** (hydrogen atoms are omitted for clarity). (a) Front view. (b) Side view. (c) Top view.



(a) (b) (c)

Fig. 5. ORTEP drawing (30% probability level) with atom-labeling scheme for **7f** (hydrogen atoms are omitted for clarity). (a) Front view. (b) Side view. (c) Top view.

Table 2. Selected Bond Distances (Å) and Angles (deg) with esd's for **7d**

Bond distances	
Pd(1)–Br(1)	2.431(4)
Pd(1)–P(1)	2.308(8)
Pd(1)–Br(2)	2.424(4)
Pd(1)–P(2)	2.320(8)
Bond angles	
Br(1)–Pd(1)–Br(2)	178.0(2)
Br(1)–Pd(1)–P(2)	89.7(3)
Br(2)–Pd(1)–P(2)	90.8(3)
Pd(1)–P(1)–C(1)	103.3(10)
Br(1)–Pd(1)–P(1)	91.2(3)
Br(2)–Pd(1)–P(1)	87.9(3)
P(1)–Pd(1)–P(2)	165.5(3)
Pd(1)–P(2)–C(13)	105.1(9)

Table 3. Selected Bond Distances (Å) and Angles (deg) with esd's for **7f**

Bond distances	
Pd(1)–Br(1)	2.4395(6)
Pd(1)–P(2)	2.3521(1)
Bond angles	
Br(1)–Pd(1)–Br(1*)	177.11(4)
Br(1)–Pd(1)–P(1*)	87.91(3)
Pd(1)–P(1)–C(1)	99.2(1)
Br(1)–Pd(1)–P(1)	91.78(3)
P(1)–Pd(1)–P(1*)	167.50(1)

(*R*)),[9a] the hydrogenation of dimethyl itaconate (**1b**, 96% ee (*S*); **1d**, 86% ee (*S*); **1f**, 30% ee (*S*)).[10] However, the X-ray crystal structure of the palladium complex of *i*-PrTRAP was unexpectedly similar to those of EtTRAP and BuTRAP concerning the chiral environment around the central metal atom (Fig. 6). Since the chiral environments created by **1b** and **1d** are expected to be fairly flexible, the ligand conformations in intermediates determining the enantioselectivity of the product would be considerably different from those in the crystal structures, and would be influenced by the flexibility and bulkiness of the *P*-substituents.

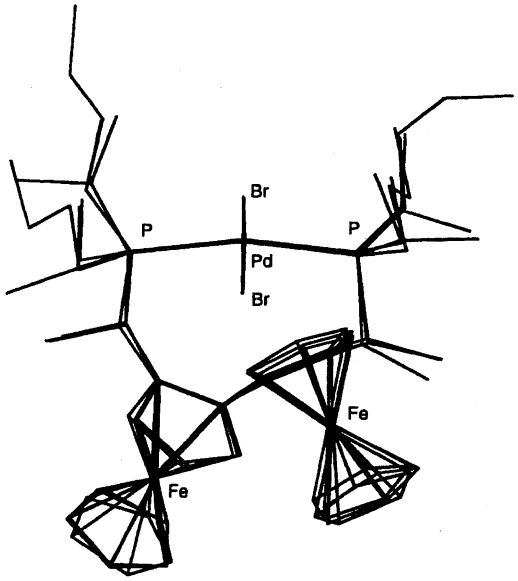


Fig. 6. Schematic superposition of the structures of the three complexes **7b**, **7d**, and **7f**.

Interestingly, *i*-BuTRAP (**1e**) also displayed quite different characteristics compared with other TRAP ligands with primary *P*-alkyl substituents. In the asymmetric hydrogenation of dimethyl itaconate, (*R*,*R*)-(*S*,*S*)-*i*-BuTRAP gave dimethyl 2-methylsuccinate with only 17% ee (*S*).[10] The ligand effect was more dramatic in the hydrogenation of methyl α-acetamidocinnamate, *i*-BuTRAP showing a higher enantioselectivity with the reverse sense of enantioselection (**1b**, 77% ee (*R*); **1e**, 92% ee (*S*)).[11] The X-ray crystal structure of palladium–*i*-BuTRAP complex **7e** was highly distorted from C_2-symmetry, and quite different from those of the palladium complexes of EtTRAP (**7b**) and BuTRAP (**7d**), which are es-

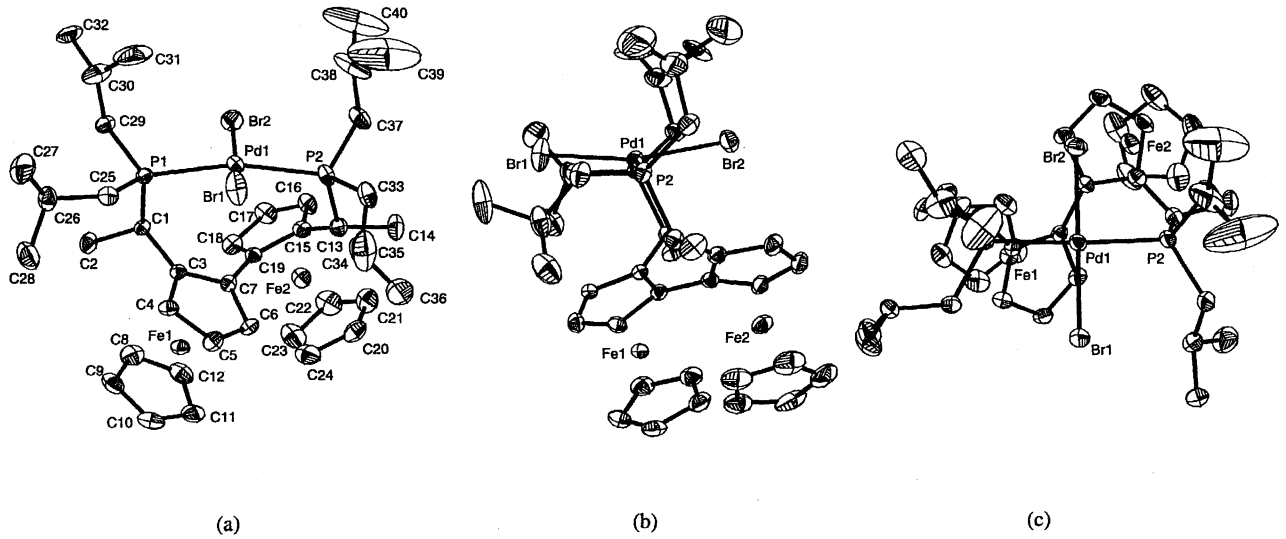


Fig. 7. ORTEP drawing (30% probability level) with atom-labeling scheme for **7e** (hydrogen atoms are omitted for clarity). (a) Front view. (b) Side view. (c) Top view.

Table 4. Selected Bond Distances (Å) and Angles (deg) with esd's for **7e**

Bond distances	
Pd(1)–Br(1)	2.4213(8)
Pd(1)–P(1)	2.330(2)
Pd(1)–Br(2)	2.4426(8)
Pd(1)–P(2)	2.332(2)
Bond angles	
Br(1)–Pd(1)–Br(2)	166.01(4)
Br(1)–Pd(1)–P(2)	93.40(4)
Br(2)–Pd(1)–P(2)	90.13(5)
Pd(1)–P(1)–C(1)	100.6(2)
Br(1)–Pd(1)–P(1)	92.17(4)
Br(2)–Pd(1)–P(1)	88.27(4)
P(1)–Pd(1)–P(2)	163.14(5)
Pd(1)–P(2)–C(13)	109.9(2)

sentially C_2-symmetric. The difference in the structures may be in accord with the results of the asymmetric reactions.

Conclusion

A variety of alkylTRAPs bearing *P*-aliphatic substituents, which are useful as chiral ligands for catalytic asymmetric synthesis, were synthesized from optically pure *N*,*N*-dimethyl-1-ferrocenylethylamine in good overall yield. Although alkylTRAPs were peralkylphosphine, these are relatively stable to air oxidation and easy to handle. Palladium, platinum, and rhodium complexes of alkylTRAPs were synthesized and characterized by NMR and X-ray crystal structure analyses; these results demonstrated the trans-chelation of alkylTRAPs to transition metal. We are trying to investigate the mechanisms of asymmetric reactions catalyzed by TRAP–metal complex and to develop new catalytic asymmetric reactions using TRAP.

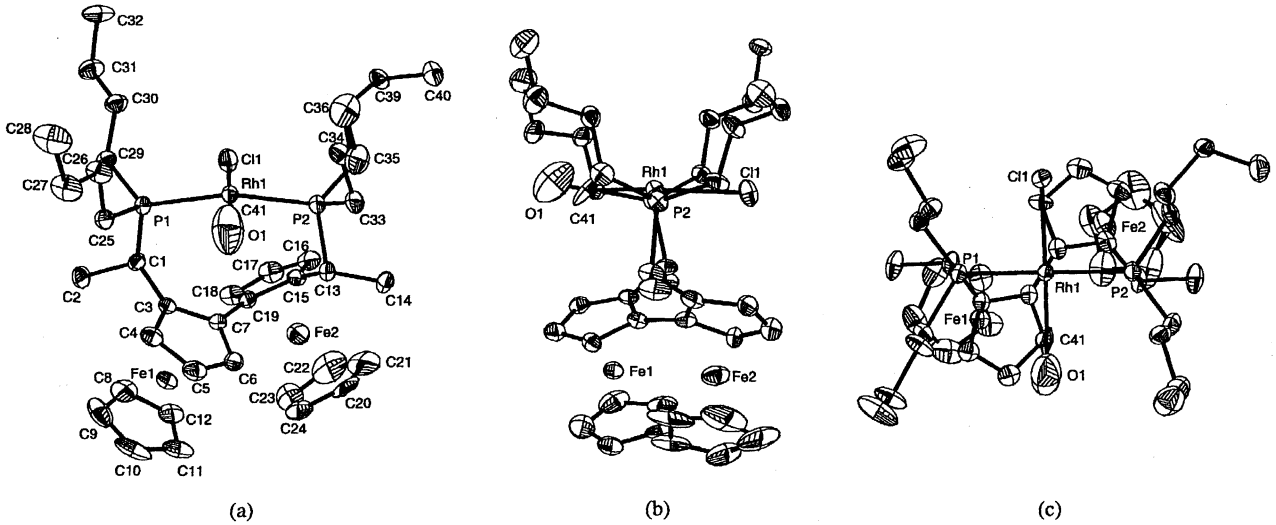


Fig. 8. ORTEP drawing (30% probability level) with atom-labeling scheme for **9d** (hydrogen atoms are omitted for clarity). The structure with 0.55 occupancy is shown. (a) Front view. (b) Side view. (c) Top view.

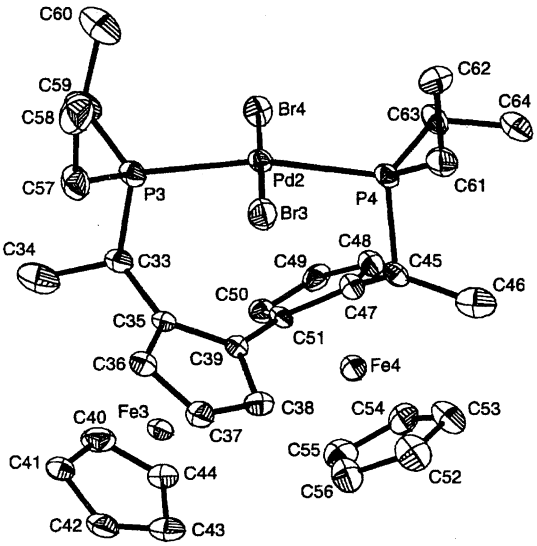


Fig. 9. ORTEP drawing (30% probability level) with atom-labeling scheme for **7b** which did not appear at Fig. 3 (hydrogen atoms are omitted for clarity).

Table 5. Selected Bond Distances (Å) and Angles (deg) with esd's for **9d**

Bond distances	
Rh(1)–Cl(1)	2.54(1)
Rh(1)–P(2)	2.305(2)
C(41)–O(1)	1.07(5)
Rh(1)–P(1)	2.307(2)
Rh(1)–C(41)	1.75(2)
Bond angles	
Cl(1)–Rh(1)–P(1)	90.9(2)
Cl(1)–Rh(1)–C(41)	177(1)
P(2)–Rh(1)–C(41)	91.6(8)
Rh(1)–P(1)–C(1)	103.9(3)
Rh(1)–C(41)–O(1)	172(4)
Cl(1)–Rh(1)–P(2)	88.7(2)
P(1)–Rh(1)–C(41)	88.0(8)
P(1)–Pd(1)–P(2)	164.42(8)
Rh(1)–P(2)–C(13)	106.0(3)

Experimental

General. The melting points were measured with a Yamato-MP apparatus and are uncorrected. The optical rotations were measured with a Perkin–Elmer 243 polarimeter. NMR spectra were obtained with a Varian VXR-200 (^{1}H 200 MHz, ^{13}C 50 MHz, ^{31}P 81 MHz), Varian Gemini-2000 (^{1}H 300 MHz, ^{13}C 75 MHz, ^{31}P 121 MHz), JEOL JNM-A400 (^{13}C 100 MHz), or JEOL JNM-A500 (^{13}C 125 MHz) spectrometer. Mass spectra were recorded with a JEOL JMS-SX102A spectrometer. Column chromatographies were performed with silica gel 60 (230—400 mesh, E. Merck) or alumina activated 200 (abt. 200 mesh, Nacalai tesque). Preparative gel permeation chromatographies on polystyrene were performed with JAI LC-908 equipped with JAIGEL-1H and -2H columns.

Materials. Diethyl ether, tetrahydrofuran (THF), and benzene were distilled from sodium-benzophenone ketyl under nitrogen. CH_2Cl_2 and triethylamine were distilled from CaH_2. AcOH was distilled from $Mg(ClO_4)_2$. (*R*)-*N*,*N*-Dimethyl-1-ferrocenylethylamine (**2**),[12] dimethylphosphine,[22] diethylphosphine,[23] dibutylphosphine,[24] diisopropylphosphine,[25] and $[PtCl_2(MeCN)_2]$[26] were prepared according to the literature procedures. Dipropylphosphine and diisobutylphosphine were prepared according to the procedures for preparing diethylphosphine[23] and dibutylphosphine,[24] respectively. Copper powder (300 mesh) was purchased from Lancaster, and shaken with iodine in acetone until the color of iodine disappeared, then successively washed with acetone, acetone/concd HCl = 1/1, and acetone, and dried under reduced pressure.[15] $PdBr_2$ and $[Rh(CO)_2Cl]_2$ were purchased and used without purification.

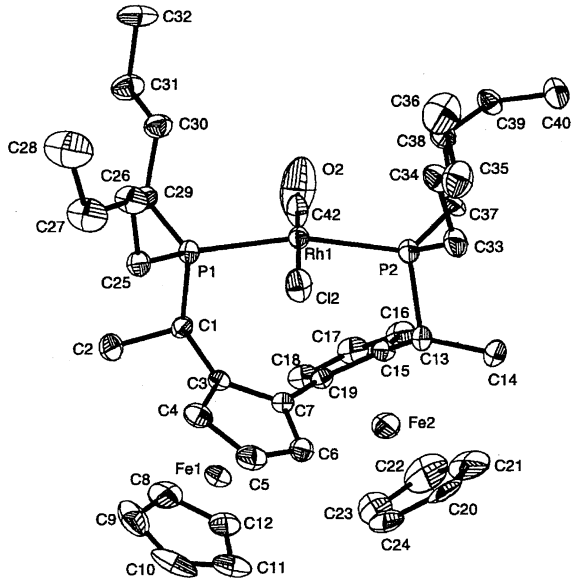


Fig. 10. ORTEP drawing (30% probability level) with atom-labeling scheme for **9d** (hydrogen atoms are omitted for clarity). The structure with 0.45 occupancy is shown.

(*S*)- 2- [(*R*)- 1- (Dimethylamino)ethyl]- 1- iodoferrocene (3). Prepared from (*R*)- **2** according to a modified Butsugan's procedure.[13] To a solution of 5.2 g (20 mmol) of (*R*)-**2** in 60 ml of diethyl ether was added 15 ml (24 mmol) of 1.62 M *t*-butyllithium (1 M = 1 mol dm^{-3}) in pentane for 20 min at −78 °C. The reaction mixture was stirred for 2 h at 0 °C. To the resulting solution of ferrocenyllithium was added 7.1 g (25 mmol) of 1,2-diiodoethane in 12 ml of THF for 30 min at −78 °C. After stirring for 15 min, the solution was warmed up to 0 °C and stirred for 20 min. The reaction was quenched by 20 ml of saturated $Na_2S_2O_3$ aq, extracted with diethyl ether, washed with brine, dried over Na_2SO_4, and evaporated. The residue (7.7 g) was a mixture of (*R*)-(*S*)-**3** and (*R*)-(*R*)-**3** (100% conversion, (*R*)-(*S*)-**3**/(*R*)-(*R*)-**3** = 97/3 in a molar ratio, 97% from (*R*)-**2** to (*R*)-(*S*)-**3**), and used without further purification: Brown solid; ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ = 1.50 (d, J = 6.8 Hz, 3H), 2.15 (s, 6H), 3.62 (d, J = 6.8 Hz, 1H), 4.12 (s, 5H), 4.12—4.17 (m, 1H), 4.24 (t, J = 2.6 Hz, 1H), 4.44—4.48 (m, 1H).

(*S*)- 2- [(*R*)- 1- (Dimethylphosphinyl)ethyl]- 1- iodoferrocene (4a). 1.83 g of (*R*)-(*S*)-**3** prepared above [(*R*)-(*S*)-**3**/(*R*)-(*R*)-**3** = 97/3 in a molar ratio, equivalent to 4.6 mmol of pure (*R*)-(*S*)-**3**] was stirred in 10 ml of acetic anhydride at room temperature for 18 h. The excess of acetic anhydride was removed in vacuo. The residue was transferred to a glass tube with 30 ml of degassed AcOH. 5.0 ml of dimethylphosphine was condensed into the tube cooled in a liquid nitrogen bath under an argon atmosphere. After the tube was sealed in vacuo, the mixture was heated at 80 °C for 30 min. After the excess of dimethylphosphine was removed by

bubbling with a flow of dry nitrogen gas for 10 h (the outlet for gas was connected to a sodium hypochlorite solution), the solvent was removed in vacuo. The residue was diluted with 20 ml of acetone, and 2.0 ml of 30% H_2O_2 aq was carefully added to the mixture at 0 °C. After 10 min, the excess H_2O_2 was carefully decomposed with 10 ml of saturated $Na_2S_2O_3$ aq. The mixture was diluted with water and then extracted four times with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4 and evaporated. The residue was chromatographed on silica gel (EtOAc/diethylamine = 5/1) to give 1.6 g of (*R*)-(*S*)-**4a** (84%): Orange powder; mp 152—153 °C; $[\alpha]_D^{20}$ −11.3 (*c* 0.477, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ = 1.21 (d, *J* = 12.0 Hz, 3H), 1.43 (d, *J* = 12.3 Hz, 3H), 1.75 (dd, *J* = 7.2, 14.7 Hz, 3H), 2.81 (dq, *J* = 7.2, 11.4 Hz, 3H), 4.21 (s, 6H), 4.31 (t, *J* = 2.6 Hz, 1H), 4.50 (dd, *J* = 1.4, 2.6 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ = 13.57 (d, *J* = 67 Hz), 14.82, 15.62 (d, *J* = 66 Hz), 34.94 (d, *J* = 64 Hz), 45.16, 65.06, 69.05, 71.62, 74.05, 90.20; ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 85% H_3PO_4) δ = 47.76. HRMS (FAB) Found: *m/z* 415.9495. Calcd for $C_{14}H_{18}OFeIP$: M, 415.9491.

(*S*)-2-[(*R*)-1-(Diethylphosphinyl)ethyl]-1-iodoferrocene (4b). (*R*)-1-[(*S*)-2-iodoferrocenyl]ethyl acetate was prepared from 2.11 g of crude (*R*)-(*S*)-**3** [(*R*)-(*S*)-**3**/(*R*)-(*R*)-**3**/(*R*)-**2** = 88/2/10 in a molar ratio, equivalent to 5.0 mmol of pure (*R*)-(*S*)-**3**] and 10 ml of acetic anhydride. To a degassed solution of (*R*)-1-[(*S*)-2-iodoferrocenyl]-ethyl acetate in 50 ml of AcOH was added 0.90 g (10 mmol) of diethylphosphine; the mixture was then stirred at 80 °C for 30 min. After the solvent and excess diethylphosphine were removed in vacuo, the residue was diluted with 20 ml of acetone, and 2.0 ml of 30% H_2O_2 aq was carefully added to the mixture at 0 °C. After 5 min, the excess H_2O_2 was carefully decomposed with 10 ml of saturated $Na_2S_2O_3$ aq. The mixture was diluted with water and then extracted twice with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by flash column chromatography on silica gel (EtOAc/diethylamine = 15/1) to give 2.29 g of a mixture of (*R*)-(*S*)-**4b** and (*R*)-**6b** (**4b**/**6b** = 90/10 in a molar ratio, 96% from **3** to **4b**). This crude product was used without further purification: Orange powder; ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.94 (dt, *J* = 15.7, 7.6 Hz, 3H), 1.14 (dt, *J* = 16.4, 7.7 Hz, 3H), 1.07—1.94 (m, 4H), 1.73 (dd, *J* = 7.4, 13.8 Hz, 3H), 2.77 (quintet, *J* = 7.4 Hz, 1H), 4.20 (s, 5H), 4.27—4.34 (m, 2H), 4.48 (t, *J* = 1.9 Hz, 1H); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 5.35 (d, *J* = 5 Hz), 6.68 (d, *J* = 4 Hz), 15.54, 18.17 (d, *J* = 65 Hz), 19.66 (d, *J* = 62 Hz), 31.81 (d, *J* = 59 Hz), 45.46 (d, *J* = 3 Hz), 65.82, 69.04, 71.54, 73.67, 90.51; ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = 54.31. HRMS (FAB) Found: *m/z* 443.9789. Calcd for $C_{16}H_{22}OFeIP$: M, 443.9804.

(*S*)-2-[(*R*)-1-(Dipropylphosphinyl)ethyl]-1-iodoferrocene (4c) was prepared in 94% yield based on (*R*)-(*S*)-**3** from 844 mg of crude (*R*)-(*S*)-**3** [(*R*)-(*S*)-**3**/(*R*)-(*R*)-**3**/(*R*)-**2** = 88/2/10 in a molar ratio, equivalent to 2.0 mmol of pure (*R*)-(*S*)-**3**] and 470 mg (4.0 mmol) of dipropylphosphine, as described for the preparation of **4b**. This crude product containing **6c** (**4c**/**6c** = 91/9) was used without further purification: Orange viscous oil; ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.83—0.93 (m, 3 H), 0.96—1.10 (m, 3H), 1.22—1.82 (m, 8H), 1.72 (dd, *J* = 7.3, 13.9 Hz, 3H), 2.75 (quintet, *J* = 7.4 Hz, 1H), 4.20 (s, 5H), 4.28—4.33 (m, 2H), 4.49 (t, *J* = 1.9 Hz, 1H); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 14.96 (d, *J* = 4 Hz), 15.46 (d, *J* = 2 Hz), 15.61, 15.91, 16.04 (d, *J* = 3 Hz), 27.91 (d, *J* = 63 Hz), 29.48 (d, *J* = 60 Hz), 32.41 (d, *J* = 59 Hz), 45.21 (d, *J* = 2 Hz), 65.63, 68.89, 71.41, 73.57, 90.43; ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = 50.86. HRMS (EI) Found: *m/z* 472.0121. Calcd for $C_{18}H_{26}OFeIP$: M, 472.0117.

(*S*)-2-[(*R*)-1-(Dibutylphosphinyl)ethyl]-1-iodoferrocene (4d) was prepared in 83% yield based on (*R*)-(*S*)-**3** from 2.11 g of crude (*R*)-(*S*)-**3** [(*R*)-(*S*)-**3**/(*R*)-(*R*)-**3**/(*R*)-**2** = 88/2/10 in a molar ratio, equivalent to 5.0 mmol of pure (*R*)-(*S*)-**3**] and 1.09 g (7.5 mmol) of dibutylphosphine, as described for the preparation of **4b**. This crude product containing **6d** (**4d**/**6d** = 92/8) was used without further purification: Orange viscous oil; ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.81 (brt, *J* = 6.9 Hz, 3H), 0.94 (brt, *J* = 6.9 Hz, 3H), 1.03—1.87 (m, 12H), 1.72 (dd, *J* = 7.3, 13.84 Hz, 3H), 2.75 (quintet, *J* = 7.5 Hz, 1H), 4.20 (s, 5H), 4.30 (d, *J* = 1.9 Hz, 2H), 4.48 (t, *J* = 1.9 Hz, 1H); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 13.53 (d, *J* = 4 Hz), 15.61 (d, *J* = 2 Hz), 23.35 (d, *J* = 4 Hz), 24.12, 24.41, 24.45 (d, *J* = 4 Hz), 25.68 (d, *J* = 64 Hz), 27.24 (d, *J* = 61 Hz), 32.58 (d, *J* = 59 Hz), 45.42 (d, *J* = 3 Hz), 65.85, 69.03, 71.55, 73.71, 90.66; ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = 51.99. HRMS (FAB) Found: *m/z* 500.0443. Calcd for $C_{20}H_{30}OFeIP$: M, 500.0430.

(*S*)-2-[(*R*)-1-(Diisobutylphosphinyl)ethyl]-1-iodoferrocene (4e) was prepared in 91% yield based on (*R*)-(*S*)-**3** from 844 mg of crude (*R*)-(*S*)-**3** [(*R*)-(*S*)-**3**/(*R*)-(*R*)-**3**/(*R*)-**2** = 88/2/10 in a molar ratio, equivalent to 2.0 mmol of pure (*R*)-(*S*)-**3**] and 440 mg (3.0 mmol) of diisobutylphosphine, as described for the preparation of **4b**. This crude product (**4e**/**6e** = 91/9) was used without further purification: Orange viscous oil; ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.88 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.97—1.88 (m, 5H), 1.09 (d, *J* = 6.6 Hz, 6H), 1.71 (dd, *J* = 7.4, 13.9 Hz, 3H), 1.93—2.21 (m, 1H), 2.68 (quintet, *J* = 7.5 Hz, 1H), 4.20 (s, 5H), 4.26—4.35 (m, 2H), 4.48 (t, *J* = 1.8 Hz, 1H); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 15.75 (d, *J* = 2 Hz), 23.57 (d, *J* = 5 Hz), 23.92 (d, *J* = 4 Hz), 24.50 (d, *J* = 6 Hz), 24.65 (d, *J* = 5 Hz), 25.01 (d, *J* = 9 Hz), 34.12 (d, *J* = 59 Hz), 35.72 (d, *J* = 62 Hz), 37.45 (d, *J* = 59 Hz), 45.72 (d, *J* = 3 Hz), 65.77 (d, *J* = 2 Hz), 68.90, 71.50, 73.61, 90.92; ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = 49.29. HRMS (EI) Found: *m/z* 500.0406. Calcd for $C_{20}H_{30}OFeIP$: M, 500.0430.

(*S*)-2-[(*R*)-1-(Diisopropylphosphinyl)ethyl]-1-iodoferrocene (4f) was prepared in 94% yield based on (*R*)-(*S*)-**3** from 844 mg of crude (*R*)-(*S*)-**3** [(*R*)-(*S*)-**3**/(*R*)-(*R*)-**3**/(*R*)-**2** = 88/2/10 in a molar ratio, equivalent to 2.0 mmol of pure (*R*)-(*S*)-**3**] and 350 mg (3.0 mmol) of diisopropylphosphine, as described for the preparation of **4b**. This crude product containing **6f** (**4f**/**6f** = 91/9) was used without further purification: Orange viscous oil; ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.81 (dd, *J* = 7.2, 14.0 Hz, 3H), 1.00 (dd, *J* = 7.3, 15.0 Hz, 3H), 1.27 (dd, *J* = 7.3, 14.3 Hz, 3H), 1.28 (dd, *J* = 7.3, 14.6, 3H), 1.55—2.32 (m, 2H), 1.77 (dd, *J* = 7.4, 12.9 Hz, 3H), 2.89 (quintet, *J* = 7.3 Hz, 1H), 4.19 (s, 5H), 4.28 (t, *J* = 2.5 Hz, 1H), 4.40—4.44 (m, 1H), 4.49 (dd, *J* = 1.4, 2.4 Hz, 1H); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 16.23 (d, *J* = 4 Hz), 16.74 (d, *J* = 2 Hz), 16.85 (d, *J* = 2 Hz), 17.15 (d, *J* = 2 Hz), 17.49 (d, *J* = 3 Hz), 25.36 (d, *J* = 55 Hz), 26.56 (d, *J* = 53 Hz), 30.12 (d, *J* = 54 Hz), 44.99, 66.72, 68.74, 71.51, 73.62, 92.07; ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = 57.92. HRMS (EI) Found: *m/z* 472.0110. Calcd for $C_{18}H_{26}OFeIP$: M, 472.0117.

(*S,S*)-2,2″-Bis[(*R*)-1-(dimethylphosphinyl)ethyl]-1,1′-biferrocene (5a). To a solution of 1.66 g of (*R*)-(*S*)-**4a** (4.0 mmol) in 10 ml of CH_2Cl_2 was added 12.71 g (200 mmol) of freshly activated-copper powder. Immediately, the mixture was evaporated in vacuo. The mixture was heated at 140 °C for 5 h under an argon atmosphere. The mixture was diluted with CH_2Cl_2, filtered through Celite, and evaporated. The residue was purified by flash column chromatography on silica gel (MeOH) to give an orange solid. The solid was dissolved in CH_2Cl_2, filtered through Celite, and evaporated to give 0.67g (58%) of (*R,R*)-(*S,S*)-**5a**: Orange

crystal; mp 180—185 °C (decomp); $[\alpha]_D^{20}$ −793 (*c* 0.440, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ = 1.25 (d, *J* = 12.3 Hz, 6H), 1.29 (d, *J* = 11.4 Hz, 6H), 1.65 (dd, *J* = 7.2, 16.2 Hz, 6H), 2.51 (dq, *J* = 12.6, 7.2 Hz, 2H), 4.34 (t, *J* = 2.7 Hz, 2H), 4.37 (s, 10H), 4.39—4.43 (m, 2H), 4.51 (dd, *J* = 3.9, 2.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ = 14.06 (d, *J* = 66 Hz), 14.96 (d, *J* = 66 Hz), 18.92, 31.98 (d, *J* = 66 Hz), 66.06 (d, *J* = 5 Hz), 66.35, 69.52, 71.31, 84.90 (d, *J* = 5 Hz), 91.22 ; $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 85% H_3PO_4) δ = 48.03. Anal. Found: C, 58.14; H, 6.42%. Calcd for: $C_{28}H_{36}O_2Fe_2P_2$: C, 58.16; H, 6.28%.

(*S*,*S*)-2,2″-Bis[(*R*)-1-(diethylphosphinyl)ethyl]-1,1′-biferrocene (5b) was prepared in 76% yield from 2.29 g of crude (*R*)-(*S*)-**4b** prepared above (equivalent to 4.8 mmol of pure (*R*)-(*S*)-**4b**) and 15.22 g (240 mmol) of activated-copper powder, as described for the preparation of **5a**, except for that the coupling reaction was performed at 80 °C for 24 h, and the crude product was purified by flash column chromatography on silica gel (EtOAc/diethylamine = 4/1) followed by recrystallization from CH_2Cl_2/EtOAc: Orange crystal; mp 215—220 °C (decomp); $[\alpha]_D^{20}$ −807 (*c* 0.475, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.98 (dt, *J* = 16.1, 7.3 Hz, 12H), 1.24—1.62 (m, 8H), 1.69 (dd, *J* = 7.5, 14.9 Hz, 6H), 2.65 (dq, *J* = 11.3, 7.5 Hz, 2H), 4.32 (t, *J* = 2.5 Hz, 2H), 4.36 (s, 10H), 4.41—4.47 (m, 2H), 4.48—4.55 (m, 2H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 5.70 (d, *J* = 5 Hz), 6.17 (d, *J* = 5 Hz), 18.70 (d, *J* = 62 Hz), 18.86 (d, *J* = 63 Hz), 18.99, 29.60 (d, *J* = 61 Hz), 66.25, 66.95(d, *J* = 3 Hz), 69.60, 70.39, 85.14 (d, *J* = 4 Hz), 90.77; $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = 53.89. Anal. Found: C, 60.56; H, 7.25%. Calcd for $C_{32}H_{44}O_2Fe_2P_2$: C, 60.59; H, 6.99%.

(*S*,*S*)-2,2″-Bis[(*R*)-1-(dipropylphosphinyl)ethyl]-1,1′-biferrocene (5c) was prepared in 74% yield from 936 mg of crude (*R*)-(*S*)-**4c** prepared above (equivalent to 1.9 mmol of pure (*R*)-(*S*)-**4c**) and 5.89 g (93 mmol) of activated-copper powder, as described for the preparation of **5b**, which was purified by flash column chromatography on silica gel (EtOAc/diethylamine = 15/1) followed by preparative gel permeation chromatography ($CHCl_3$): Orange powder; mp 162—163 C; $[\alpha]_D^{20}$ −614 (*c* 0.494, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.81—1.02 (m, 12H), 1.29—1.60 (m, 16H), 1.67 (dd, *J* = 7.6, 15.0 Hz, 6H), 2.66 (dq, *J* = 11.8, 7.6 Hz, 2H), 4.30 (t, *J* = 2.4 Hz, 2H), 4.35 (s, 10H), 4.41—4.49 (m, 2H), 4.48—4.56 (m, 2H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 15.31 (d, *J* = 4 Hz), 15.54 (d, *J* = 4 Hz), 15.71, 15.99, 18.90, 28.54 (d, *J* = 61 Hz), 28.81 (d, *J* = 62 Hz), 30.11 (d, *J* = 61 Hz), 66.01, 66.82 (d, *J* = 3 Hz), 69.48, 70.75, 85.06 (d, *J* = 4 Hz), 91.03; $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = 50.74. HRMS (FAB) Found: *m/z* 691.2230. Calcd for $C_{36}H_{53}O_2Fe_2P_2$: M+H, 691.2219.

(*S*,*S*)-2,2″-Bis[(*R*)-1-(dibutylphosphinyl)ethyl]-1,1′-biferrocene (5d) was prepared in 79% yield from 2.22 g of crude **4d** prepared above (equivalent to 4.2 mmol of pure (*R*)-(*S*)-**4d**) and 13.19 g (208 mmol) of activated-copper powder, as described for the preparation of **5b**, which was purified by flash column chromatography on silica gel (EtOAc) followed by preparative gel permeation chromatography ($CHCl_3$): Orange viscous oil; $[\alpha]_D^{20}$ −520 (*c* 0.508, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.77—0.98 (m, 12H), 1.12—1.62 (m, 24H), 1.68 (dd, *J* = 7.4, 15.0 Hz, 6H), 2.70 (dq, *J* = 11.7, 7.4 Hz, 2H), 4.30 (t, *J* = 2.5 Hz, 2H), 4.35 (s, 10H), 4.41—4.49 (m, 2H), 4.48—4.56 (m, 2H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 13.65, 13.74, 18.93, 23.83 (d, *J* = 4 Hz), 23.95 (d, *J* = 4 Hz), 24.23 (d, *J* = 3 Hz), 24.50 (d, *J* = 2 Hz), 26.24 (d, *J* = 62 Hz), 26.52 (d, *J* = 62 Hz), 30.21 (d, *J* = 61 Hz), 65.97, 66.92 (d, *J* = 3 Hz), 69.52, 70.78, 85.17, 91.11; $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = 51.10. HRMS (FAB) Found: *m/z* 746.2789. Calcd for $C_{40}H_{60}O_2Fe_2P_2$: M, 746.2767.

(*S*,*S*)-2,2″-Bis[(*R*)-1-(diisobutylphosphinyl)ethyl]-1,1′-biferrocene (5e) was prepared in 63% yield from 946 mg of crude **4e** prepared above (equivalent to 1.8 mmol of pure (*R*)-(*S*)-**4e**) and 5.62 g (88 mmol) of activated-copper powder, as described for the preparation of **5b**, which was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 1/3) followed by preparative gel permeation chromatography ($CHCl_3$): Orange powder; mp 37—38 °C; $[\alpha]_D^{20}$ −584 (*c* 0.515, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.83—1.06 (m, 24H), 1.24—2.13 (m, 12H), 1.66 (dd, *J* = 7.5, 14.9 Hz, 6H), 2.57 (dq, *J* = 11.4, 7.5 Hz, 2H), 4.27 (t, *J* = 2.5 Hz, 2H), 4.35 (s, 10H), 4.42—4.48 (m, 2H), 4.47—4.53 (m, 2H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 19.13, 23.57 (d, *J* = 4 Hz), 23.70 (d, *J* = 4 Hz), 24.52 (d, *J* = 7 Hz), 24.75 (d, *J* = 7 Hz), 24.98 (d, *J* = 6 Hz), 25.16 (d, *J* = 6 Hz), 31.50 (d, *J* = 61 Hz), 36.12 (d, *J* = 60 Hz), 65.72, 66.83 (d, *J* = 3 Hz), 69.47, 71.16, 85.20 (d, *J* = 5 Hz), 91.81; $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = 45.07. HRMS (FAB) Found: *m/z* 746.2748. Calcd for $C_{40}H_{60}O_2Fe_2P_2$: M, 746.2767.

(*S*,*S*)-2,2″-Bis[(*R*)-1-(diisopropylphosphinyl)ethyl]-1,1′-biferrocene (5f) was prepared in 47% yield from 935 mg of crude **4f** prepared above (equivalent to 1.9 mmol of pure (*R*)-(*S*)-**4f**) and 5.88 g (93 mmol) of activated-copper powder, as described for the preparation of **5b**, which was purified by a flash column chromatography on silica gel (EtOAc/Et_2NH = 50/1) followed by preparative gel permeation chromatography ($CHCl_3$): Orange powder; mp 190—195 °C (decomp); $[\alpha]_D^{20}$ −643 (*c* 0.525, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.96 (dd, *J* = 7.2, 13.5 Hz, 6H), 0.97 (dd, *J* = 7.1, 14.9 Hz, 6H), 1.14 (dd, *J* = 7.3, 14.0 Hz, 6H), 1.19 (dd, *J* = 7.2, 14.5 Hz, 6H), 1.75 (dd, *J* = 7.5, 14.4 Hz, 6H), 1.81—2.30 (m, 4H), 2.85 (dq, *J* = 12.9, 7.5 Hz, 2H), 4.29 (t, *J* = 2.6 Hz, 2H), 4.35 (s, 10H), 4.47—4.55 (m, 2H), 4.61 (dd, *J* = 1.4, 2.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 16.56 (d, *J* = 3 Hz), 16.82 (d, *J* = 3 Hz), 16.89 (d, *J* = 4 Hz), 17.38 (d, *J* = 2 Hz), 18.82, 24.62 (d, *J* = 61 Hz), 25.16 (d, *J* = 59 Hz), 28.67 (d, *J* = 57 Hz), 65.91, 69.04 (d, *J* = 3 Hz), 69.43, 71.63, 84.82 (d, *J* = 5 Hz), 91.43; $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = 57.33. Anal. Found: C, 62.53; H, 7.78%. Calcd for $C_{36}H_{52}O_2Fe_2P_2$: C, 62.63; H, 7.59%.

(*S*,*S*)-2,2″-Bis[(*R*)-1-(dimethylphosphino)ethyl]-1,1′-biferrocene ((*R*,*R*)-(*S*,*S*)-MeTRAP (1a)). To a mixture of 289 mg of **5a** (0.50 mmol), 410 mg (4.0 mmol) of triethylamine and 2.5 ml of dry benzene in a glass tube was added 400 mg (3.0 mmol) of trichlorosilane at 0 °C. The tube was cooled at −78 °C and sealed in vacuo. The mixture was heated at 100 °C for 10 h. After being cooled to −78 °C, the tube was opened. 15% NaOH aq was carefully added to the mixture. The mixture was filtered through Celite, extracted twice with benzene, dried with Na_2SO_4, and evaporated. Chromatography on alumina (benzene/Et_2O = 10/1) gave 221 mg (81%) of **1a**: Orange powder; mp 109—110 °C; $[\alpha]_D^{20}$ −930 (*c* 0.455, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ = 0.70—0.78 (m, 12H), 1.40—1.50 (m, 6H), 2.39 (q, *J* = 7.2 Hz, 2H), 4.11—4.15 (m, 2H), 4.22 (t, *J* = 2.4 Hz, 2H), 4.29 (s, 10H), 4.46 (dd, *J* = 1.5, 2.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ = 9.86 (dt, $|J_{P-C}+J_{P'-C}|$ = 16 Hz), 12.68 (dt, $|J_{P-C}+J_{P'-C}|$ = 12 Hz), 16.65 (t, $|J_{P-C}+J_{P'-C}|$ = 6 Hz), 29.53 (dt, $|J_{P-C}+J_{P'-C}|$ = 14 Hz), 65.55, 66.08 (t, $|J_{P-C}+J_{P'-C}|$ = 8 Hz), 69.40, 70.25, 84.68 (t, $|J_{P-C}+J_{P'-C}|$ = 3 Hz), 94.75 (t, $|J_{P-C}+J_{P'-C}|$ = 16 Hz); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 85% H_3PO_4) δ = −36.02. HRMS (FAB) Found: *m/z* M, 547.1060. Calcd for $C_{28}H_{27}Fe_2P_2$: M+H, 547.1069.

(*S*,*S*)-2,2″-Bis[(*R*)-1-(diethylphosphino)ethyl]-1,1′-biferrocene ((*R*,*R*)-(*S*,*S*)-EtTRAP (1b)) was prepared from 317 mg (0.50 mmol) of **5b** in 96% yield: Orange powder; mp 91—92 °C;

$[\alpha]_D^{20}$ −875 (*c* 0.460, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.74—0.98 (m, 12H), 1.06—1.29 (m, 8H), 1.46 (pseudo-t, 6H), 2.55 (q, J = 7.3 Hz, 2H), 4.10—4.16 (m, 2H), 4.19 (t, J = 2.5 Hz, 2H), 4.29 (s, 10H), 4.46 (dd, J = 1.5, 2.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 10.02 (quintet, $|J_{P-C}+J_{P'-C}|$ = 16 Hz), 10.48 (quintet, $|J_{P-C}+J_{P'-C}|$ = 16 Hz), 15.44 (dt, $|J_{P-C}+J_{P'-C}|$ = 16 Hz), 17.46 (t, $|J_{P-C}+J_{P'-C}|$ = 7 Hz), 17.58 (dt, $|J_{P-C}+J_{P'-C}|$ = 11 Hz), 26.23 (dt, $|J_{P-C}+J_{P'-C}|$ = 16 Hz), 65.28, 66.50 (t, $|J_{P-C}+J_{P'-C}|$ = 7 Hz), 69.35, 70.32, 84.68 (t, $|J_{P-C}+J_{P'-C}|$ = 3 Hz), 94.99 (t, $|J_{P-C}+J_{P'-C}|$ = 15 Hz); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = −5.13. HRMS (FAB) Found: *m/z* 603.1664. Calcd for $C_{32}H_{45}Fe_2P_2$: M+H, 603.1695.

(*S,S*)-2,2″-Bis[(*R*)-1-(dipropylphosphino)ethyl]-1,1′-biferrocene ((*R,R*)-(*S,S*)-PrTRAP (1c)) was prepared from 346 mg (0.50 mmol) of **5c** in 78% yield: Dark orange viscous oil; $[\alpha]_D^{20}$ −768 (*c* 0.490, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.80—0.92 (m, 12H), 0.98—1.38 (m, 16H), 1.46 (pseudo-t, 6H), 2.54 (q, J = 7.3 Hz, 2H), 4.11—4.15 (m, 2H), 4.18 (t, J = 2.5 Hz, 2H), 4.29 (s, 10H), 4.46 (dd, J = 1.5, 2.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 16.00 (t, $|J_{P-C}+J_{P'-C}|$ = 13 Hz), 16.30 (t, $|J_{P-C}+J_{P'-C}|$ = 12 Hz), 17.40 (t, $|J_{P-C}+J_{P'-C}|$ = 7 Hz), 19.77 (quintet, $|J_{P-C}+J_{P'-C}|$ = 18 Hz), 19.96 (quintet, $|J_{P-C}+J_{P'-C}|$ = 18 Hz), 25.84 (dt, $|J_{P-C}+J_{P'-C}|$ = 16 Hz), 26.78 (dt, $|J_{P-C}+J_{P'-C}|$ = 16 Hz), 28.28 (dt, $|J_{P-C}+J_{P'-C}|$ = 12 Hz), 65.19, 66.52 (t, $|J_{P-C}+J_{P'-C}|$ = 8 Hz), 69.33, 70.53, 84.59 (t, $|J_{P-C}+J_{P'-C}|$ = 3 Hz), 94.94 (t, $|J_{P-C}+J_{P'-C}|$ = 14 Hz); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = −15.23. HRMS (FAB) Found: *m/z* 658.2234. Calcd for $C_{36}H_{52}Fe_2P_2$: M, 658.2243.

(*S,S*)-2,2″-Bis[(*R*)-1-(dibutylphosphino)ethyl]-1,1′-biferrocene ((*R,R*)-(*S,S*)-BuTRAP (1d)) was prepared from 373 mg (0.50 mmol) of **5d** in 88% yield: Dark orange viscous oil; $[\alpha]_D^{20}$ −748 (*c* 0.516, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.74—0.89 (m, 12H), 1.00—1.36 (m, 24H), 1.39—1.51 (m, 6H), 2.56 (q, J = 7.3 Hz, 2H), 4.10—4.14 (m, 2H), 4.17 (t, J = 2.5 Hz, 2H), 4.28 (s, 10H), 4.43—4.49 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 13.88, 13.92, 17.14 (t, $|J_{P-C}+J_{P'-C}|$ = 6 Hz), 23.03 (dt, $|J_{P-C}+J_{P'-C}|$ = 16 Hz), 24.35 (t, $|J_{P-C}+J_{P'-C}|$ = 12 Hz), 24.73 (t, $|J_{P-C}+J_{P'-C}|$ = 12 Hz), 25.50 (dt, $|J_{P-C}+J_{P'-C}|$ = 13 Hz), 26.73 (dt, $|J_{P-C}+J_{P'-C}|$ = 16 Hz), 28.57 (quintet, $|J_{P-C}+J_{P'-C}|$ = 17 Hz), 28.79 (quintet, $|J_{P-C}+J_{P'-C}|$ = 17 Hz), 65.17, 66.53 (t, $|J_{P-C}+J_{P'-C}|$ = 7 Hz), 69.33, 70.50, 84.59, 94.86 (t, $|J_{P-C}+J_{P'-C}|$ = 15 Hz); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = −14.75. HRMS (FAB) Found: *m/z* 714.2873. Calcd for $C_{40}H_{60}Fe_2P_2$: M, 714.2869.

(*S,S*)-2,2″-Bis[(*R*)-1-(diisobutylphosphino)ethyl]-1,1′-biferrocene ((*R,R*)-(*S,S*)-*i*-BuTRAP (1e)) was prepared from 373 mg (0.5 mmol) of **5e** in 92% yield: Orange viscous oil; $[\alpha]_D^{20}$ −657 (*c* 0.491, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.80 (d, J = 6.4 Hz, 6H), 0.86 (d, J = 6.5 Hz, 18H), 0.90—1.30 (m, 8H), 1.39—1.63 (m, 10H), 2.43 (q, J = 7.3 Hz, 2H), 4.16 (d, J = 2.0 Hz, 4H), 4.29 (s, 10H), 4.46 (t, J = 2.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 18.02 (t, $|J_{P-C}+J_{P'-C}|$ = 8 Hz), 24.26 (t, $|J_{P-C}+J_{P'-C}|$ = 10 Hz), 24.29 (t, $|J_{P-C}+J_{P'-C}|$ = 10 Hz), 24.43 (t, $|J_{P-C}+J_{P'-C}|$ = 8 Hz), 24.58 (t, $|J_{P-C}+J_{P'-C}|$ = 8 Hz), 26.52 (quintet, $|J_{P-C}+J_{P'-C}|$ = 16 Hz), 26.81 (quintet, $|J_{P-C}+J_{P'-C}|$ = 18 Hz), 27.47 (dt, $|J_{P-C}+J_{P'-C}|$ = 15 Hz), 35.06 (dt, $|J_{P-C}+J_{P'-C}|$ = 19 Hz), 37.45 (dt, $|J_{P-C}+J_{P'-C}|$ = 15 Hz), 65.09, 66.64 (t, $|J_{P-C}+J_{P'-C}|$ = 10 Hz), 69.24, 70.95, 84.50, 95.44 (quintet, $|J_{P-C}+J_{P'-C}|$ = 15 Hz); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = −21.86. HRMS (FAB) Found: *m/z* 715.2977. Calcd for $C_{40}H_{61}Fe_2P_2$: M+H, 715.2947.

(*S,S*)-2,2″-Bis[(*R*)-1-(diisopropylphosphino)ethyl]-1,1′-biferrocene ((*R,R*)-(*S,S*)-*i*-PrTRAP (1f)) was prepared from 346 mg (0.5 mmol) of **5f** in 99% yield: Orange viscous oil; $[\alpha]_D^{20}$ −815 (*c* 0.518, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.77—1.12 (m, 24H), 1.41—1.93 (m, 4H), 1.51 (dd, J = 4.3, 7.3 Hz, 6H), 2.76 (q, J = 7.3 Hz, 2H), 4.10—4.20 (m, 4H), 4.27 (m, 10H), 4.22—4.47 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 17.22, 20.13 (t, $|J_{P-C}+J_{P'-C}|$ = 9 Hz), 20.33 (t, $|J_{P-C}+J_{P'-C}|$ = 13 Hz), 20.88 (dt, $|J_{P-C}+J_{P'-C}|$ = 22 Hz), 21.27 (t, $|J_{P-C}+J_{P'-C}|$ = 20 Hz), 22.73 (t, $|J_{P-C}+J_{P'-C}|$ = 24 Hz), 22.80 (dt, $|J_{P-C}+J_{P'-C}|$ = 18 Hz), 26.11 (dt, $|J_{P-C}+J_{P'-C}|$ = 22 Hz), 64.80, 67.50 (t, $|J_{P-C}+J_{P'-C}|$ = 8 Hz), 69.26, 71.56, 84.63 (t, $|J_{P-C}+J_{P'-C}|$ = 4 Hz), 96.25 (t, $|J_{P-C}+J_{P'-C}|$ = 20 Hz); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = 15.75. HRMS (FAB) Found: *m/z* 659.2341. Calcd for $C_{36}H_{53}Fe_2P_2$: M+H, 659.2321.

***trans*-[$PdBr_2${(*R,R*)-(*S,S*)-EtTRAP}] (7b).** To a solution of 30.1 mg (50 μmol) of **1b** in 1.0 ml of toluene was added 13.3 mg (50 μmol) of $PdBr_2$ at room temperature. The solution was stirred under reflux for 1.5 h, and the solvent was evaporated in vacuo. The residue was chromatographed on silica gel (benzene/CH_2Cl_2) to give 34.4 mg (79%) of **7b**: Orange powder; mp 239—241 °C (decomp); $[\alpha]_D^{20}$ −694 (*c* 0.503, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, TMS) δ = 1.08—1.21 (m, 12H), 1.61 (dt, J = 7.3 and 5.6 Hz, 6H), 1.74—1.93 (m, 4H), 2.20—2.34 (m, 2H), 2.34—2.47 (m, 2H), 3.21 (tq, J = 3.6 and 7.3 Hz, 2H), 4.06—4.10 (brs, 2H), 4.31 (s, 10H), 4.42 (t, J = 2.6 Hz, 2H), 4.50 (dd, J = 1.5 and 2.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, TMS) δ = 9.11, 10.19, 12.40 (t, $|J_{P-C}+J_{P'-C}|$ = 24 Hz), 16.70 (t, $|J_{P-C}+J_{P'-C}|$ = 25 Hz), 17.85, 32.31 (t, $|J_{P-C}+J_{P'-C}|$ = 20 Hz), 66.49, 67.14, 69.66, 72.64, 85.79, 92.54 (t, $|J_{P-C}+J_{P'-C}|$ = 7 Hz); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = 27.05. Anal. Found: C, 44.33; H, 5.19%. Calcd for $C_{32}H_{44}Br_2Fe_2P_2Pd$: C, 44.25; H, 5.11%.

***trans*-[$PdBr_2${(*R,R*)-(*S,S*)-BuTRAP}] (7d)** was prepared from 244 mg (0.34 mmol) of **1d** in 75% yield: Orange powder; mp 225—230 °C (decomp); $[\alpha]_D^{20}$ −703 (*c* 0.204, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.87 (t, J = 7.3 Hz, 6H), 0.91 (t, J = 7.1 Hz, 6H), 1.13—1.52 (m, 12H), 1.60 (dt, J = 7.3, 5.6 Hz, 6H), 1.53—1.93 (m, 8H), 2.02—2.40 (m, 4H), 3.09—3.27 (m, 2H), 4.04—4.12 (m, 2H), 4.30 (s, 10H), 4.41 (t, J = 2.5 Hz, 2H), 4.45—4.52 (m, 2H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, TMS) δ = 13.63, 13.85, 18.03, 19.20 (t, $|J_{P-C}+J_{P'-C}|$ = 22 Hz), 23.66 (t, $|J_{P-C}+J_{P'-C}|$ = 24 Hz), 24.63 (t, $|J_{P-C}+J_{P'-C}|$ = 14 Hz), 24.89 (t, $|J_{P-C}+J_{P'-C}|$ = 13 Hz), 26.78, 27.53, 32.25 (t, $|J_{P-C}+J_{P'-C}|$ = 20 Hz), 66.61, 67.11, 69.62, 72.50, 85.78, 92.67; $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = 20.81. Anal. Found: C, 48.82; H, 6.21%. Calcd for $C_{40}H_{60}Br_2Fe_2P_2Pd$: C, 48.99; H, 6.17%.

***trans*-[$PdBr_2${(*R,R*)-(*S,S*)-*i*-BuTRAP}] (7e)** was prepared from 35.3 mg (49 mmol) of **1e** in 100% yield: Orange powder; mp 212—217 °C (decomp); $[\alpha]_D^{20}$ −757 (*c* 0.243, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ = 0.99 (d, J = 6.3 Hz, 6H), 1.08 (d, J = 6.4 Hz, 12H), 1.10 (d, J = 6.1 Hz, 6H), 1.65 (dt, J = 7.2, 5.6 Hz, 6H), 1.80—2.35 (m, 12H), 3.22—3.44 (m, 2H), 4.08—4.19 (m, 2H), 4.31 (s, 10H), 4.37—4.45 (m, 2H), 4.45—4.54 (m, 2H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 18.60, 24.59 (t, $|J_{P-C}+J_{P'-C}|$ = 7 Hz), 24.66 (t, $|J_{P-C}+J_{P'-C}|$ = 6 Hz), 25.00 (t, $|J_{P-C}+J_{P'-C}|$ = 9 Hz), 25.38, 25.56, 25.84 (t, $|J_{P-C}+J_{P'-C}|$ = 8 Hz), 29.11 (t, $|J_{P-C}+J_{P'-C}|$ = 19 Hz), 31.39 (t, $|J_{P-C}+J_{P'-C}|$ = 21 Hz), 32.08 (t, $|J_{P-C}+J_{P'-C}|$ = 19 Hz), 67.07, 67.12, 69.65, 72.63, 86.02, 92.97 (t, $|J_{P-C}+J_{P'-C}|$ = 7 Hz); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ = 17.43. Anal. Found: C, 49.14; H, 6.05%. Calcd for $C_{40}H_{60}Br_2Fe_2P_2Pd$: C, 48.99; H, 6.17%.

***trans*-[$PdBr_2${(*R,R*)-(*S,S*)-*i*-PrTRAP}] (7f)** was prepared from 32.9 mg (50 μmol) of **1f** in 69% yield: Orange powder; mp 220—225 °C (decomp); $[\alpha]_D^{20}$ −798 (*c* 0.184, $CHCl_3$); ^1H NMR (200

Table 6. Summary of Crystal Data and Details of Data Collection and Refinement Parameters for **5f** and AlkylTRAP–Metal Complexes

Compound	**5f**	**7b**	**7d**	**7e**	**7f**	**9d**
Formula	$C_{36}H_{52}Fe_2O_2P_2$	$C_{32}H_{44}Br_2Fe_2P_2Pd$	$C_{40}H_{60}Br_2Fe_2P_2Pd$	$C_{40}H_{60}Br_2Fe_2P_2Pd$	$C_{36}H_{52}Br_2Fe_2P_2$	$C_{41}H_{60}OClFe_2P_2Rh$
MW	690.45	868.55	980.76	980.76	924.66	880.93
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (#19)	$P2_1$ (#4)	$P2_12_12_1$ (#19)	$P2_12_12_1$ (#19)	$P2_12_12$ (#18)	$P2_12_12_1$ (#19)
a/Å	13.499(5)	11.968(2)	13.763(5)	16.2271(8)	15.767(1)	13.74(1)
b/Å	23.381(6)	19.776(4)	23.29(1)	17.589(1)	9.7655(1)	23.34(1)
c/Å	10.778(3)	15.042(2)	12.996(6)	14.496(1)	11.714(3)	12.96(1)
α/deg	90.00	90.00	90.00	90.00	90.00	90.00
β/deg	90.00	112.656(10)	90.00	90.00	90.00	90.00
γ/deg	90.00	90.00	90.00	90.00	90.00	90.00
V/Å^3	3402(2)	3285.4(9)	4166(3)	4137.3(5)	1803.5(6)	4158(7)
Z	4	4	4	4	2	4
$D_{(calcd)}$/g cm^{-3}	1.37	1.756	1.56	1.574	1.703	1.41
Crystal size/mm	0.40 × 0.40 × 0.50	0.75 × 0.50 × 0.40	0.20 × 0.40 × 0.20	0.20 × 0.20 × 0.30	0.30 × 0.35 × 0.40	0.40 × 0.35 × 0.25
μ(Mo $K\alpha$)/cm^{-1}	9.745	39.71	31.113	31.63	36.22	11.64
Scan type	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ
Scan rate/deg min^{-1}	4.0	16.0	4.0	16.0	16.0	4.0
Scan width/deg	1.12+0.35 tan θ	1.57+0.30 tan θ	1.12+0.35 tan θ	1.57+0.30 tan θ	1.52+0.30 tan θ	1.04+0.35 tan θ
$2\theta_{max}$/deg	55.0	60.0	55.0	60.0	60.0	55.0
No. of measd reflns	4534	10269	5438	6646	2999	5424
Unique reflns		9851 (R_{int}=0.052)				
Obsd reflns	3579 ($I > 2.00\sigma(I)$)	6842 ($I > 3.00\sigma(I)$)	2894 ($I > 2.00\sigma(I)$)	4380 ($I > 3.00\sigma(I)$)	2413 ($I > 3.00\sigma(I)$)	3774 ($I > 3.00\sigma(I)$)
No. of variables	379	791	412	425	222	461
R	0.063	0.035	0.049	0.035	0.028	0.069
R_W	0.077	0.034	0.058	0.037	0.034	0.066
GOF	1.97	1.41	2.58	1.27	1.48	1.72
Max Shift/error in final cycle	0.02	0.12	0.01	0.01	0.16	0.08
Max peak in diff Fourier map/eÅ^{-3}	0.89	0.59	1.11	0.81	0.38	0.74
Min peak in diff Fourier map/eÅ^{-3}	−0.78	−0.88	−1.00	−0.69	−0.58	−0.90

MHz, $CDCl_3$, TMS) $\delta = 1.12$—1.57 (m, 24H), 1.83 (dt, $J = 7.5$ and 5.0 Hz, 6H), 2.36—2.65 (m, 2H), 3.22—3.71 (m, 2H), 4.08—4.19 (m, 2H), 4.34 (s, 10H), 4.44 (t, $J = 2.5$ Hz, 2H), 4.53 (dd, $J = 1.4$ and 2.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) $\delta = 19.52$, 21.48, 21.92, 22.25 (t, $|J_{P-C} + J_{P'-C}| = 28$ Hz), 22.77, 23.82 (t, $|J_{P-C} + J_{P'-C}| = 30$ Hz), 32.35 (t, $|J_{P-C} + J_{P'-C}| = 21$ Hz), 67.17, 67.46, 69.59, 72.25, 86.50, 93.28 (t, $|J_{P-C} + J_{P'-C}| = 10$ Hz); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) $\delta = 41.11$. Anal. Found: C, 46.66; H, 5.58%. Calcd for $C_{36}H_{52}Br_2Fe_2P_2Pd$: C, 46.76; H, 5.67%.

^{31}P NMR Study for the Reaction of 1d with [PtCl$_2$(MeCN)$_2$]. To a solution of 11.3 mg (16 μmol) of **1d** in 0.5 ml of $CDCl_3$ was added 5.6 mg (16 μmol) of $[PtCl_2(MeCN)_2]$. The solution was stand at room temperature for 16 h and heated at 40 °C for 2 h. The ^{31}P NMR spectrum of the solution indicated generation of two platinum species (ca. 10 : 1). The solvent was evaporated in vacuo. The residue was chromatographed on silica gel (CH_2Cl_2) to give 14.8 mg (93%) of *trans*-**8d**. An analytically pure sample was obtained by recrystallization from CH_2Cl_2/EtOH: ^{1}H NMR (200 MHz, $CDCl_3$, TMS) $\delta = 0.80$—0.97 (m, 12H), 1.17—2.20 (m, 30H), 2.96—3.16 (m, 2H), 4.02—4.10 (m, 2H), 4.31 (s, 10H), 4.40 (t, $J = 2.5$ Hz, 2H), 4.47 (dd, $J = 1.4$ and 2.4 Hz, 2H); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) $\delta = 17.40$ (s, and a ^{195}Pt satellite, $J^{195}Pt-^{31}P = 2443$ Hz). Anal. Found: C, 47.25; H, 5.99%. Calcd for $C_{40}H_{60}Cl_2Fe_2P_2Pt \cdot 1/2CH_2Cl_2$: C, 47.55; H, 6.01%.

^{31}P NMR Study for the Reaction of 1f with [PtCl$_2$(MeCN)$_2$]. To a solution of 6.6 mg (10 μmol) of **1f** in 0.5 ml of C_6D_6 was

Table 7. Fractional Atomic Coordinates and U_{iso} (Å^2) for **5f** without Hydrogen Atoms

Atom	x	y	z	U_{iso}
Fe(1)	0.47920(9)	0.19975(5)	1.08530(10)	0.0375(6)
Fe(2)	0.44533(9)	0.18031(5)	0.68413(10)	0.0382(6)
P(1)	0.43590(18)	0.39751(9)	0.99680(21)	0.042(1)
P(2)	0.53785(19)	0.36181(10)	0.54794(19)	0.045(1)
O(1)	0.4870(5)	0.3931(3)	0.8759(5)	0.049(3)
O(2)	0.5269(6)	0.3388(3)	0.4195(6)	0.066(4)
C(1)	0.3899(6)	0.3271(3)	1.0469(7)	0.039(4)
C(2)	0.3429(7)	0.3293(4)	1.1769(9)	0.052(5)
C(3)	0.4737(6)	0.2839(3)	1.0375(7)	0.035(4)
C(4)	0.5487(7)	0.2746(4)	1.1275(7)	0.045(5)
C(5)	0.6172(6)	0.2351(4)	1.0787(9)	0.043(4)
C(6)	0.5859(6)	0.2196(4)	0.9563(8)	0.042(4)
C(7)	0.4958(5)	0.2491(3)	0.9299(7)	0.030(3)
C(8)	0.3410(8)	0.1726(5)	1.1390(10)	0.059(6)
C(9)	0.4061(9)	0.1762(5)	1.2435(9)	0.065(7)
C(10)	0.4856(10)	0.1404(5)	1.2217(9)	0.062(6)
C(11)	0.4710(8)	0.1122(5)	1.1032(9)	0.058(6)
C(12)	0.3811(8)	0.1338(4)	1.0545(10)	0.056(5)
C(13)	0.5601(6)	0.3060(3)	0.6649(7)	0.039(4)
C(14)	0.6512(7)	0.2702(5)	0.6239(10)	0.057(5)
C(15)	0.4697(6)	0.2682(4)	0.6904(7)	0.041(4)
C(16)	0.3932(7)	0.2529(4)	0.6046(8)	0.043(4)
C(17)	0.3164(6)	0.2245(4)	0.6700(8)	0.047(5)
C(18)	0.3453(6)	0.2205(4)	0.7958(8)	0.040(4)
C(19)	0.4406(6)	0.2464(4)	0.8106(7)	0.041(4)
C(20)	0.5746(8)	0.1333(4)	0.6754(10)	0.060(6)
C(21)	0.5293(10)	0.1367(5)	0.5562(9)	0.065(6)
C(22)	0.4348(9)	0.1121(5)	0.5649(9)	0.065(7)
C(23)	0.4200(9)	0.0958(5)	0.6863(11)	0.067(6)
C(24)	0.5039(10)	0.1062(5)	0.7566(10)	0.064(6)
C(25)	0.5183(9)	0.4246(5)	1.1203(9)	0.065(6)
C(26)	0.6224(14)	0.4232(14)	1.0736(18)	0.21(2)
C(27)	0.492(2)	0.482(1)	1.170(2)	0.20(2)
C(28)	0.3260(7)	0.4436(4)	0.9844(11)	0.061(6)
C(29)	0.2429(9)	0.4141(5)	0.9162(18)	0.095(9)
C(30)	0.3524(9)	0.4985(5)	0.9145(16)	0.084(8)
C(31)	0.6517(8)	0.4051(5)	0.5598(11)	0.063(6)
C(32)	0.6704(10)	0.4343(6)	0.6837(13)	0.076(8)
C(33)	0.6656(12)	0.4444(7)	0.4479(15)	0.10(1)
C(34)	0.4323(9)	0.4056(5)	0.5962(10)	0.064(6)
C(35)	0.3341(11)	0.3807(7)	0.5629(24)	0.13(1)
C(36)	0.4365(13)	0.4654(7)	0.5528(24)	0.13(1)

Table 8. Fractional Atomic Coordinates and U_{iso} (Å^2) for **7d** without Hydrogen Atoms

Atom	x	y	z	U_{iso}
Pd(1)	0.95271(13)	0.24810(9)	0.26187(15)	0.029(1)
Br(1)	0.8299(2)	0.2351(2)	0.1296(2)	0.055(2)
Br(2)	1.0732(2)	0.2646(2)	0.3947(2)	0.061(2)
Fe(1)	0.7787(3)	0.4525(2)	0.2593(4)	0.043(3)
Fe(2)	1.0907(3)	0.4617(2)	0.1960(4)	0.060(3)
P(1)	0.8347(5)	0.2627(3)	0.3854(6)	0.033(4)
P(2)	1.0700(5)	0.2584(3)	0.1350(5)	0.037(5)
C(1)	0.832(2)	0.341(1)	0.399(2)	0.04(2)
C(2)	0.759(2)	0.362(1)	0.482(2)	0.05(2)
C(3)	0.816(2)	0.369(1)	0.296(2)	0.03(2)
C(4)	0.7262(19)	0.3709(10)	0.2407(24)	0.04(2)
C(5)	0.742(2)	0.397(1)	0.145(2)	0.05(2)
C(6)	0.841(2)	0.411(1)	0.138(2)	0.04(2)
C(7)	0.8880(18)	0.3944(10)	0.2289(20)	0.03(1)
C(8)	0.781(3)	0.503(2)	0.387(3)	0.08(3)
C(9)	0.687(3)	0.496(1)	0.355(4)	0.09(3)
C(10)	0.675(3)	0.516(1)	0.255(5)	0.09(3)
C(11)	0.767(3)	0.537(1)	0.225(3)	0.07(3)
C(12)	0.832(2)	0.530(1)	0.305(3)	0.06(2)
C(13)	1.0633(19)	0.3354(11)	0.0954(21)	0.04(2)
C(14)	1.135(2)	0.350(1)	0.009(2)	0.05(2)
C(15)	1.0730(19)	0.3742(10)	0.1890(22)	0.04(2)
C(16)	1.162(2)	0.390(1)	0.237(3)	0.05(2)
C(17)	1.140(2)	0.422(1)	0.325(3)	0.06(2)
C(18)	1.039(3)	0.429(1)	0.331(2)	0.06(2)
C(19)	0.9947(19)	0.4003(10)	0.2497(25)	0.03(2)
C(20)	1.077(4)	0.497(2)	0.052(3)	0.09(3)
C(21)	1.171(4)	0.499(2)	0.085(5)	0.12(5)
C(22)	1.178(5)	0.532(2)	0.171(7)	0.15(6)
C(23)	1.082(5)	0.550(2)	0.196(4)	0.10(4)
C(24)	1.022(3)	0.528(2)	0.123(5)	0.09(3)
C(25)	0.7096(17)	0.2405(11)	0.3578(17)	0.03(2)
C(26)	0.691(2)	0.176(1)	0.360(2)	0.05(2)
C(27)	0.589(2)	0.162(1)	0.327(2)	0.06(2)
C(28)	0.562(3)	0.099(1)	0.336(4)	0.14(3)
C(29)	0.8568(18)	0.2363(11)	0.5173(18)	0.04(2)
C(30)	0.892(2)	0.175(1)	0.527(2)	0.06(2)
C(31)	0.922(2)	0.160(1)	0.634(2)	0.06(2)
C(32)	0.948(3)	0.101(1)	0.650(2)	0.08(3)
C(33)	1.051(2)	0.219(1)	0.016(2)	0.05(2)
C(34)	1.028(2)	0.155(1)	0.032(2)	0.04(2)
C(35)	0.976(2)	0.129(1)	−0.058(2)	0.06(2)
C(36)	0.954(3)	0.065(2)	−0.043(3)	0.10(3)
C(37)	1.1984(18)	0.2458(11)	0.1659(20)	0.04(2)
C(38)	1.222(2)	0.188(1)	0.207(2)	0.05(2)
C(39)	1.330(2)	0.177(1)	0.220(2)	0.05(2)
C(40)	1.377(2)	0.161(2)	0.121(3)	0.08(3)

added 3.5 mg (10 μmol) of $[PtCl_2(MeCN)_2]$ at room temperature. The solution was stirred at 80 °C for 4 h. The ^{31}P NMR spectrum of the solution indicated the generation of one platinum species. The solution was filtered through Celite and evaporated in vacuo to give 9.2 mg (100%) of *trans*-**8f**: ^1H NMR (200 MHz, C_6D_6) $\delta = 1.11$ (pseudo-q, 6H), 1.30—1.69 (m, 24H), 2.34—2.70 (m, 2H), 3.18—3.44 (m, 2H), 3.51—3.71 (m, 2H), 4.03—4.10 (m, 2H), 4.25 (s, 10H), 4.40 (t, $J = 2.4$ Hz, 2H), 4.43—4.50 (m, 2H); $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, 85% H_3PO_4) $\delta = 30.81$ (s, and a ^{195}Pt satellite, $J_{^{195}Pt-^{31}P} = 2465$ Hz).

***cis*-8f:** $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, 85% H_3PO_4) $\delta = 9.86$ (d, $J_{P-P} = 15$, and a ^{195}Pt satellite, $J_{^{195}Pt-^{31}P} = 3699$ Hz), 14.56 (dt, $J_{P-P} = 15$, and a ^{195}Pt satellite, $J_{^{195}Pt-^{31}P} = 3608$ Hz).

***trans*-[RhCl(CO){(*R*,*R*)-(*S*,*S*)-BuTRAP}] (9d).** A solution of 79 mg (0.11 mmol) of (*R*,*R*)-(*S*,*S*)-**1d** and 22 mg (0.056 mmol) of $[RhCl(CO)_2]_2$ in 3 ml of CH_2Cl_2 was stirred at room temperature for 5 min. The solution was diluted with EtOH, and most of the CH_2Cl_2 was evaporated. Orange crystals were collected and dried in vacuo to give 79 mg (80%) of **9d**: mp 222—225 °C (decomp); $[\alpha]_D^{20}$ −760.1 (*c* 0.321, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS) $\delta = 0.81$—1.00 (m, 12H), 1.10—2.38 (m, 30H), 2.88 (quintet, $J = 6.6$ Hz, 1H), 3.08 (quintet, $J = 6.8$ Hz, 1H), 4.03—4.09 (m, 2H), 4.28 (s, 5H), 4.31 (s, 5H), 4.35—4.45 (m, 4H); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) $\delta = 27.27$ (dd, $J = 119$ and 341 Hz), 32.56 (dd, $J = 119$ and 341 Hz); IR (KBr) 1948 cm^{-1}. Anal. Found: C, 55.63; H, 7.03%. Calcd for $C_{41}H_{60}ClFe_2P_2ORh$: C, 55.90; H, 6.86%.

X-Ray Crystal Structure Analysis of 5f and 7d. Suitable crystals of **5f** for diffraction study were grown by gradually cooling a hot saturated solution in CH_2Cl_2/hexane. Crystals of **7d** were grown by slow diffusion of ethanol into a CH_2Cl_2 solution at 4 °C. The data were collected at 20 °C on a Mac Science MXC3 diffractometer with graphite monochromated Mo $K\alpha$ radiation. Cell constants and orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 22 carefully centered reflections (**5f**; $31.58 < 2\theta < 34.84°$, **7d**; $22.89 < 2\theta < 34.51°$). The intensities of three standard reflections monitored every 150 reflections showed no serious decay. All of the data were corrected for Lorentz and polarization effects. A summary of the

Table 9. Fractional Atomic Coordinates and B_{iso}/B_{eq} (Å) for **7b** without Hydrogen Atoms

Atom	*x*	*y*	*z*	B_{eq}	Atom	*x*	*y*	*z*	B_{eq}
Pd(1)	0.72728(4)	0.0660	0.16891(3)	2.560(9)	Pd(2)	0.39106(4)	0.33457(4)	0.56825(4)	2.89(1)
Br(1)	0.55277(7)	0.07128(5)	0.01721(6)	4.28(2)	Br(3)	0.38123(7)	0.29066(6)	0.41354(5)	4.54(2)
Br(2)	0.90626(6)	0.06715(5)	0.31794(5)	3.87(2)	Br(4)	0.40194(7)	0.37746(5)	0.72310(6)	4.14(2)
Fe(1)	0.70976(9)	0.32592(5)	0.06218(7)	2.99(2)	Fe(3)	0.4544(1)	0.07042(7)	0.63466(8)	4.11(2)
Fe(2)	1.04616(9)	0.22111(6)	0.09942(8)	3.41(2)	Fe(4)	0.14542(10)	0.15584(6)	0.68730(7)	3.26(2)
P(1)	0.6357(2)	0.14015(10)	0.2381(1)	3.00(4)	P(3)	0.5890(2)	0.2986(1)	0.6439(1)	3.55(4)
P(2)	0.8324(2)	0.01422(9)	0.0868(1)	2.70(4)	P(4)	0.1824(1)	0.34503(9)	0.5032(1)	2.80(3)
C(1)	0.6959(6)	0.2248(3)	0.2262(5)	3.1(2)	C(33)	0.5793(6)	0.2152(4)	0.6990(5)	3.4(2)
C(2)	0.642(1)	0.2810(5)	0.2692(7)	5.4(3)	C(34)	0.7041(8)	0.1833(6)	0.7471(7)	5.2(2)
C(3)	0.6817(6)	0.2379(3)	0.1242(5)	2.6(1)	C(35)	0.4874(6)	0.1709(4)	0.6248(5)	3.0(1)
C(4)	0.5733(6)	0.2606(4)	0.0509(5)	3.2(2)	C(36)	0.5098(7)	0.1329(4)	0.5530(5)	4.0(2)
C(5)	0.5902(6)	0.2635(4)	−0.0372(5)	3.6(2)	C(37)	0.4047(8)	0.1000(5)	0.4943(6)	4.6(2)
C(6)	0.7100(7)	0.2423(4)	−0.0184(5)	3.4(2)	C(38)	0.3104(7)	0.1166(4)	0.5280(5)	3.8(2)
C(7)	0.7678(5)	0.2254(3)	0.0783(4)	2.5(1)	C(39)	0.3606(6)	0.1608(4)	0.6077(4)	2.8(1)
C(8)	0.7796(8)	0.3993(4)	0.1647(6)	4.6(2)	C(40)	0.547(1)	0.0409(5)	0.7743(8)	6.4(3)
C(9)	0.6611(7)	0.4168(4)	0.1031(6)	4.3(2)	C(41)	0.602(1)	0.0123(5)	0.7138(8)	6.6(3)
C(10)	0.6591(8)	0.4217(4)	0.0092(7)	5.2(2)	C(42)	0.514(1)	−0.0280(5)	0.6443(9)	7.1(3)
C(11)	0.7779(8)	0.4073(4)	0.0132(6)	4.6(2)	C(43)	0.406(1)	−0.0238(5)	0.6619(9)	6.4(3)
C(12)	0.8513(8)	0.3925(4)	0.1107(7)	4.8(2)	C(44)	0.427(1)	0.0187(5)	0.7429(8)	6.8(3)
C(13)	0.8776(6)	0.0862(3)	0.0273(4)	2.8(1)	C(45)	0.1303(6)	0.2573(3)	0.5128(4)	2.8(1)
C(14)	0.9443(8)	0.0631(5)	−0.0356(6)	4.7(2)	C(46)	−0.0082(7)	0.2471(4)	0.4657(6)	4.2(2)
C(15)	0.9418(6)	0.1381(3)	0.1018(5)	2.7(1)	C(47)	0.1874(6)	0.2349(3)	0.6162(5)	2.7(1)
C(16)	1.0635(6)	0.1316(4)	0.1703(5)	3.4(2)	C(48)	0.1536(7)	0.2574(4)	0.6925(6)	3.6(2)
C(17)	1.0892(7)	0.1864(4)	0.2361(5)	3.8(2)	C(49)	0.2344(7)	0.2315(4)	0.7809(5)	3.5(2)
C(18)	0.9855(6)	0.2274(4)	0.2088(5)	3.2(2)	C(50)	0.3183(6)	0.1905(4)	0.7599(5)	3.2(2)
C(19)	0.8919(5)	0.1989(3)	0.1271(4)	2.5(1)	C(51)	0.2925(6)	0.1927(3)	0.6604(4)	2.7(1)
C(20)	1.0404(9)	0.2400(5)	−0.0365(7)	5.4(3)	C(52)	0.0225(8)	0.0911(4)	0.5914(6)	5.0(2)
C(21)	1.1596(8)	0.2181(5)	0.0274(7)	5.2(2)	C(53)	−0.0343(8)	0.1276(4)	0.6427(7)	5.1(2)
C(22)	1.2021(8)	0.2643(5)	0.1018(8)	5.5(2)	C(54)	0.030(1)	0.1125(5)	0.7414(8)	6.1(3)
C(23)	1.1147(8)	0.3150(5)	0.0889(9)	5.8(3)	C(55)	0.1267(10)	0.0671(5)	0.7502(6)	5.9(2)
C(24)	1.0135(8)	0.2983(5)	0.0015(7)	5.2(2)	C(56)	0.1198(9)	0.0547(4)	0.6582(7)	4.9(2)
C(25)	0.4720(7)	0.1485(5)	0.1848(6)	4.4(2)	C(57)	0.6782(8)	0.2824(5)	0.5712(7)	5.3(2)
C(26)	0.4039(9)	0.0837(6)	0.188(1)	7.0(3)	C(58)	0.699(1)	0.3425(8)	0.5202(10)	8.1(4)
C(27)	0.6704(9)	0.1320(4)	0.3679(6)	4.4(2)	C(59)	0.6906(6)	0.3483(5)	0.7458(6)	4.5(2)
C(28)	0.659(1)	0.0611(5)	0.4011(7)	6.2(3)	C(60)	0.6910(8)	0.4245(5)	0.7250(8)	5.7(2)
C(29)	0.7498(7)	−0.0441(4)	−0.0100(6)	4.2(2)	C(61)	0.1137(7)	0.3685(4)	0.3762(5)	3.7(2)
C(30)	0.6799(9)	−0.0992(5)	0.0167(9)	6.0(3)	C(62)	0.1552(8)	0.4377(5)	0.3561(7)	5.0(2)
C(31)	0.9729(7)	−0.0298(4)	0.1557(5)	3.5(2)	C(63)	0.1152(6)	0.4042(4)	0.5603(5)	3.5(2)
C(32)	0.9566(8)	−0.0944(4)	0.2044(7)	4.6(2)	C(64)	−0.0204(8)	0.4138(5)	0.5194(8)	5.2(2)

cell parameters, data collection conditions, and refinement results are given in Table 6.

The structures were solved by a direct method (SIR-92),[27] and expanded using a Fourier technique (DIRDIF-92).[28] All non-hydrogen atoms were refined anisotoropically by a full-matrix least-squares method on $|F|$. All hydrogen atoms were located at calculated positions (d(C–H) = 0.96 Å), and their isotropic temperature factors were set equal to U_{iso} of the carbon atoms to which they are attached. Though hydrogen atoms were included in the calculation, their parameters were not refined. All calculations were performed using the program package Crystan 6.3.[29] The fractional atomic coordinates and isotropic temperature factors of **5f** and **7d** are shown in Tables 7 and 8, respectively.[30]

Table 10. Fractional Atomic Coordinates and B_{iso}/B_{eq} (Å) for **7e** without Hydrogen Atoms

Atom	x	y	z	B_{eq}
Pd(1)	−0.79132(3)	−0.16808(2)	−0.71429(3)	2.527(8)
Br(1)	−0.66532(5)	−0.11679(4)	−0.65000(6)	5.55(2)
Br(2)	−0.93382(4)	−0.20336(4)	−0.74767(5)	4.06(1)
Fe(1)	−0.64361(5)	−0.38998(5)	−0.88846(5)	2.65(2)
Fe(2)	−0.83627(6)	−0.28112(6)	−1.06233(6)	3.48(2)
P(1)	−0.77963(9)	−0.27936(8)	−0.62811(9)	2.36(3)
P(2)	−0.7936(1)	−0.08111(8)	−0.8357(1)	2.88(3)
C(1)	−0.7729(3)	−0.3515(3)	−0.7223(4)	2.3(1)
C(2)	−0.7664(4)	−0.4331(3)	−0.6889(4)	3.6(1)
C(3)	−0.7064(3)	−0.3272(3)	−0.7906(3)	2.19(9)
C(4)	−0.6196(3)	−0.3277(3)	−0.7722(4)	2.7(1)
C(5)	−0.5798(4)	−0.2958(4)	−0.8494(4)	3.2(1)
C(6)	−0.6382(4)	−0.2759(4)	−0.9155(4)	2.9(1)
C(7)	−0.7192(3)	−0.2950(3)	−0.8808(4)	2.4(1)
C(8)	−0.6929(5)	−0.4966(4)	−0.9005(5)	4.5(2)
C(9)	−0.6137(5)	−0.5011(4)	−0.8626(5)	4.4(2)
C(10)	−0.5587(5)	−0.4702(4)	−0.9273(6)	4.9(2)
C(11)	−0.6033(5)	−0.4450(4)	−1.0038(5)	4.4(2)
C(12)	−0.6865(5)	−0.4613(4)	−0.9879(5)	4.4(2)
C(13)	−0.7846(4)	−0.1322(3)	−0.9475(4)	3.2(1)
C(14)	−0.8050(5)	−0.0795(4)	−1.0297(5)	4.7(2)
C(15)	−0.8289(4)	−0.2060(3)	−0.9530(4)	2.8(1)
C(16)	−0.9121(4)	−0.2171(4)	−0.9828(4)	3.5(1)
C(17)	−0.9338(4)	−0.2945(4)	−0.9748(5)	3.7(1)
C(18)	−0.8638(4)	−0.3341(4)	−0.9395(4)	3.2(1)
C(19)	−0.7995(4)	−0.2801(3)	−0.9254(3)	2.5(1)
C(20)	−0.7620(6)	−0.2454(5)	−1.1665(5)	5.6(2)
C(21)	−0.8431(7)	−0.2400(6)	−1.1944(5)	6.0(2)
C(22)	−0.8783(6)	−0.3134(6)	−1.1904(5)	6.0(2)
C(23)	−0.8158(7)	−0.3633(5)	−1.1610(5)	6.2(2)
C(24)	−0.7435(6)	−0.3230(6)	−1.1457(5)	5.7(2)
C(25)	−0.6902(4)	−0.2867(3)	−0.5517(4)	2.9(1)
C(26)	−0.6791(4)	−0.3523(4)	−0.4833(5)	4.0(2)
C(27)	−0.6616(6)	−0.3250(6)	−0.3874(5)	6.6(2)
C(28)	−0.6108(6)	−0.4054(5)	−0.5122(7)	6.3(2)
C(29)	−0.8675(4)	−0.3120(4)	−0.5606(4)	3.3(1)
C(30)	−0.8881(6)	−0.2661(6)	−0.4729(6)	6.2(2)
C(31)	−0.8750(8)	−0.1908(6)	−0.4684(9)	10.3(4)
C(32)	−0.9678(5)	−0.2956(6)	−0.4312(6)	6.5(2)
C(33)	−0.7103(5)	−0.0096(3)	−0.8425(5)	4.0(1)
C(34)	−0.6223(5)	−0.0367(4)	−0.8645(7)	5.3(2)
C(35)	−0.5609(5)	0.0080(6)	−0.8077(8)	8.1(3)
C(36)	−0.5989(6)	−0.0315(6)	−0.9645(8)	6.9(3)
C(37)	−0.8903(4)	−0.0265(4)	−0.8461(5)	4.0(2)
C(38)	−0.9165(6)	0.0171(6)	−0.7587(8)	7.9(3)
C(39)	−0.884(1)	0.084(1)	−0.744(2)	22.7(9)
C(40)	−1.0078(9)	0.025(1)	−0.754(2)	19.1(7)

X-Ray Crystal Structure Analysis of 7b, 7e, and 7f. Suitable crystals for a diffraction study were grown by the slow diffusion of ethanol into a CH_2Cl_2 solution of **7** at 4 °C. The data were collected at 20 °C on a Rigaku AFC7R diffractometer with graphite monochromated Mo $K\alpha$ radiation. The cell constants and orientation matrix for data collection were obtained from a least-square refinement using the setting angles of 25 carefully centered reflections (**7b**; $39.31 < 2\theta < 39.94°$, **7e**; $34.11 < 2\theta < 39.06°$, **7f**; $38.56 < 2\theta < 39.80°$). The intensities of three standard reflections monitored every 150 reflections showed no serious decay. An empirical absorption correction based on azimuthal scans of several reflections was applied to **7b** and **7f**. All of the data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 4.86092×10^{-7} (**7b**), 1.10157×10^{-7} (**7e**), 7.41658×10^{-7} (**7f**)). A summary of the cell parameters, data collection conditions, and refinement results are given in Table 6.

The initial positional parameters of palladium atoms were determined by a direct method (MITHRIL-90)[31] for **7b** and **7f**, or the heavy-atom Patterson method (SAPI-91)[32] for **7e**. A subsequent difference Fourier synthesis located all non-hydrogen atoms (DIRDIF-92),[28] which were refined anisotoropically by a full-matrix least-squares method on $|F|$. All hydrogen atoms were located at the calculated positions (d(C–H) = 0.95 Å), and their isotropic temperature factors were set equal to B_{eq} of the carbon atoms to which they were attached. Though all hydrogen atoms in **7b** and **7f** were included in the calculations, their positions were not refined; the isotropic B values were refined. On the other hand, though all hydrogen atoms in **7e** were included, their parameters were not refined. Two independent molecules were contained in each unit cell of **7b**. Another molecule, which did not appear at Fig. 3, is shown in Fig. 9. All of the calculations were performed using the teXsan crystallographic software package.[33] The fractional atomic

Table 11. Fractional Atomic Coordinates and B_{iso}/B_{eq} (Å) for **7f** without Hydrogen Atoms

Atom	x	y	z	B_{eq}
Pd(1)	−1.0000	0.0000	−0.21459(4)	2.274(8)
Br(1)	−0.90392(3)	−0.19571(5)	−0.21985(7)	4.16(1)
Fe(1)	−1.04824(4)	−0.21211(7)	−0.63058(6)	2.93(1)
P(1)	−1.11927(7)	−0.1423(1)	−0.2364(1)	2.36(2)
C(1)	−1.1405(3)	−0.1134(4)	−0.3921(4)	2.48(9)
C(2)	−1.2270(3)	−0.1580(7)	−0.4391(5)	3.7(1)
C(3)	−1.0647(2)	−0.1618(4)	−0.4600(4)	2.35(8)
C(4)	−1.0379(3)	−0.3017(5)	−0.4736(5)	3.11(10)
C(5)	−0.9582(3)	−0.3001(5)	−0.5306(4)	2.95(9)
C(6)	−0.9354(3)	−0.1630(5)	−0.5542(4)	2.63(9)
C(7)	−1.0013(3)	−0.0756(4)	−0.5105(3)	2.22(7)
C(8)	−1.1610(4)	−0.214(1)	−0.7177(6)	7.3(2)
C(9)	−1.1154(6)	−0.3453(8)	−0.7309(7)	6.8(2)
C(10)	−1.0383(5)	−0.3129(7)	−0.7838(6)	5.3(2)
C(11)	−1.0347(5)	−0.1780(8)	−0.8034(6)	5.3(2)
C(12)	−1.1049(5)	−0.1159(8)	−0.7644(6)	5.8(2)
C(13)	−1.1030(3)	−0.3279(4)	−0.2084(5)	3.14(9)
C(14)	−1.0866(4)	−0.3517(6)	−0.0809(6)	4.5(1)
C(15)	−1.1698(4)	−0.4268(5)	−0.2530(6)	4.4(1)
C(16)	−1.2137(3)	−0.0832(5)	−0.1564(4)	3.06(10)
C(17)	−1.1898(4)	−0.0427(7)	−0.0315(5)	4.7(1)
C(18)	−1.2920(3)	−0.1774(6)	−0.1520(6)	4.6(1)

coordinates and isotropic temperature factors of **7b**, **7e**, and **7f** are shown in Tables 9, 10, and 11, respectively.[30]

X-Ray Crystal Structure Analysis of 9d. Suitable crystals of **9d** were grown by slow diffusion of ethanol into a CH_2Cl_2 solution at 4 °C. The data were collected at 20 °C on a Mac Science MXC3 diffractometer with graphite monochromated Mo $K\alpha$ radiation. The cell constants and orientation matrix for data collection were obtained from a least-square refinement using the setting angles of 22 carefully centered reflections in the range of $6.18 < 2\theta < 9.91°$. The intensities of three standard reflections monitored every 150 reflections showed no serious decay. All data were corrected for Lorentz and polarization effects. A summary of the cell parameters, data collection conditions, and refinement results is given in Table 6.

The initial positional parameters of rhodium atom was determined by the direct method (SHELXS-86).[34] Subsequent difference Fourier syntheses located all non-hydrogen atoms, which were refined anisotoropically by full-matrix least-squares method on $|F|$. The atoms of disordered chloro and carbonyl ligands were located at positions defined by a difference Fourier synthesis for 0.55/0.45 occupancy. Hydrogen atoms were not included in the calculation. All calculations were performed using the program package CrystanGM ver 3.1.[35] The structure with 0.45 occupancy is shown in Fig. 10. The fractional atomic coordinates and isotropic temperature factors of **9d** are shown in Table 12.[30]

Table 12. Fractional Atomic Coordinates and B_{iso}/B_{eq} (Å) for **9d**

Atom	x	y	z	B_{eq}
Rh(1)	0.04523(4)	0.25092(3)	−0.23899(4)	2.81(1)
Fe(1)	0.22000(8)	0.04598(5)	−0.2427(1)	3.68(3)
Fe(2)	−0.0952(1)	0.03699(6)	−0.2946(1)	5.36(4)
Cl(1)	0.1730(8)	0.2594(7)	−0.3796(8)	4.5(2)
Cl(2)	−0.0785(7)	0.2334(4)	−0.1026(8)	4.7(2)
P(1)	0.1643(2)	0.23653(9)	−0.1162(2)	3.08(5)
P(2)	−0.0708(2)	0.2387(1)	−0.3655(2)	3.27(6)
O(1)	−0.096(3)	0.242(2)	−0.082(3)	13(2)
O(2)	0.184(3)	0.274(2)	−0.380(4)	14(2)
C(1)	0.1674(6)	0.1570(3)	−0.0994(6)	3.5(2)
C(2)	0.2491(8)	0.1377(4)	−0.0213(7)	5.4(3)
C(3)	0.1840(6)	0.1292(3)	−0.2065(6)	3.0(2)
C(4)	0.2734(6)	0.1261(3)	−0.2602(7)	3.9(2)
C(5)	0.2545(7)	0.1019(4)	−0.3615(7)	4.4(3)
C(6)	0.1535(6)	0.0867(3)	−0.3652(6)	3.5(2)
C(7)	0.1095(6)	0.1041(3)	−0.2721(6)	3.2(2)
C(8)	0.219(1)	−0.0057(4)	−0.1113(9)	6.4(4)
C(9)	0.3177(9)	0.0029(5)	−0.150(1)	7.0(4)
C(10)	0.321(1)	−0.0181(5)	−0.252(1)	8.2(5)
C(11)	0.2241(9)	−0.0397(4)	−0.278(1)	6.3(4)
C(12)	0.1645(8)	−0.0314(4)	−0.193(1)	5.3(3)
C(13)	−0.0643(6)	0.1604(4)	−0.4045(7)	4.0(2)
C(14)	−0.1437(8)	0.1458(4)	−0.4887(8)	5.5(3)
C(15)	−0.0745(6)	0.1243(4)	−0.3075(6)	3.9(2)
C(16)	−0.1655(6)	0.1104(4)	−0.2532(9)	4.6(2)
C(17)	−0.1421(8)	0.0783(4)	−0.1654(8)	5.2(3)
C(18)	−0.0385(7)	0.0714(4)	−0.1580(7)	4.2(2)
C(19)	0.0034(6)	0.0996(3)	−0.2477(7)	3.3(2)
C(20)	−0.092(2)	0.0003(5)	−0.437(1)	10.3(6)
C(21)	−0.189(1)	−0.0050(8)	−0.395(2)	12.5(9)
C(22)	−0.185(2)	−0.0357(6)	−0.299(2)	12.0(9)
C(23)	−0.081(1)	−0.0526(5)	−0.287(1)	8.1(5)
C(24)	−0.025(1)	−0.0315(5)	−0.371(1)	8.1(5)
C(25)	0.2904(5)	0.2572(4)	−0.1461(6)	3.6(2)
C(26)	0.3039(6)	0.3225(4)	−0.1491(9)	4.9(3)
C(27)	0.4115(6)	0.3359(4)	−0.179(1)	6.3(4)
C(28)	0.4333(8)	0.3996(5)	−0.168(1)	9.3(5)
C(29)	0.1407(6)	0.2597(4)	0.0174(6)	3.7(2)
C(30)	0.1048(7)	0.3238(4)	0.0252(6)	4.4(2)
C(31)	0.0753(8)	0.3374(4)	0.1344(8)	5.2(3)
C(32)	0.044(1)	0.4015(4)	0.1449(8)	6.2(3)
C(33)	−0.2009(5)	0.2522(4)	−0.3356(6)	3.8(2)
C(34)	−0.2190(6)	0.3104(4)	−0.2879(7)	4.5(2)
C(35)	−0.3321(6)	0.3218(4)	−0.2786(7)	3.9(2)
C(36)	−0.3759(7)	0.3409(5)	−0.3821(8)	5.7(3)
C(37)	−0.0501(7)	0.2768(4)	−0.4890(6)	4.4(2)
C(38)	−0.0242(6)	0.3411(4)	−0.4714(6)	4.1(2)
C(39)	0.0251(8)	0.3673(5)	−0.5645(8)	6.0(3)
C(40)	0.048(1)	0.4306(5)	−0.551(1)	7.8(4)
C(41)	−0.041(2)	0.241(2)	−0.141(2)	6(1)
C(42)	0.138(3)	0.260(2)	−0.337(2)	6.1(9)

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