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Novel chiral ferrocenyl-imino phosphine ligands and their use in palladium catalyzed allylic alkylations

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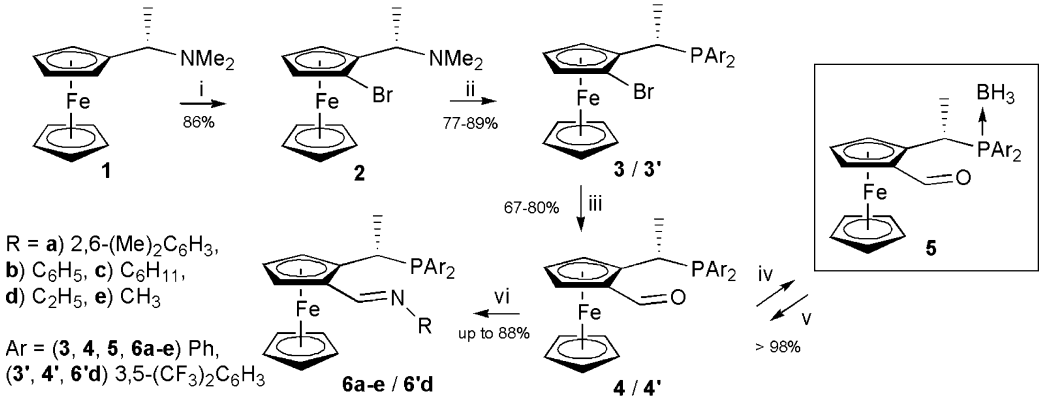
Abstract—New chiral *P*,*N*-ferrocenyl imino-phosphine ligands have been synthesized and the absolute configuration of the stereocenters in each molecule has been determined by a single-crystal X-ray analysis of a common intermediate. Pd^{II}-allyl complexes of the new ligands have been isolated and tested as catalyst precursors in the asymmetric allylic alkylation of 1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate in different solvents. Quantitative yields and enantiomeric excesses as high as 80% have been obtained.

The diastereoselective *ortho*-lithiation of *N*,*N*-dimethyl-(*R*)-1-ferrocenylethylamine, followed by complete stereo-conservative nucleophilic substitution at the ferrocenyl-methylene position, is being intensively investigated for the preparation of chiral ferrocenyl ligands with mixed donor atoms.[1] Among these, imino-phosphines have received increasing attention due to their flexible coordination behavior associated with tunable steric and electronic properties.[2,3] A common characteristic of most chiral ferrocenyl imino-phosphines reported so far is the presence of a phosphorus group directly linked to the ferrocenyl unit and a pendant 1-ethyl-imino substituent.



Scheme 1. Synthesis of the key ferrocenyl-formyl intermediate. *Regents and conditions*: i. *n*BnLi, Et_2O, −78°C, 1,2-$C_2Br_2Cl_4$, 1 h; ii. $HPAr_2$, AcOH, reflux, 4 h; iii. *n*BuLi, THF, −60°C, DMF, 35 min; iv: THF, BH_3Me_2S, 0°C, 20 min; v: TMEDA, 65°C, 4 h; vi: (**6a**) 2,6-$(Me)_2C_6H_3NH_2$, HCOOH cat., MeOH, reflux, 20 h; (**6b**) $C_6H_5NH_2$, HCOOH cat., MeOH, reflux, 20 h; (**6c**) $C_6H_{11}NH_2$, CH_3COOH cat., toluene, 60°C, 3 h; (**6d**/**6'd**) $C_2H_5NH_2$ reflux, 6 h; (**6e**) EtOH, CH_3NH_2 (35% soln. in H_2O), reflux, 30 min.

Keywords: chiral ligands; ferrocenes; imino-phosphines; asymmetric catalysis.

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In this communication we describe a new class of ferrocenyl imino-phosphine ligands bearing a phosphorus atom on the side-chain stereocenter. Some η^3-allyl palladium complexes of the new ligands have also been prepared and tested as catalyst precursors for asymmetric allylic alkylation reactions.

The synthetic procedure developed to synthesize the new ligands is illustrated in Scheme 1. The diastereoselective *ortho*-lithiation of amine **1**,[4] followed by treatment with 1,2-dibromotetrachloroethane, gave the bromo intermediate **2**,[5] which was converted to the bromo-diphenylphosphine compound **3** via a stereoconservative side-chain nucleophilic substitution with diphenylphosphine in acetic acid.[5a,6] Treatment of **3** with *n*-BuLi/DMF afforded (*R*)-1-[(*S*)-2-formylferrocenyl]ethyldiphenylphosphine **4** in 44–61% overall yield.[7]

Compound **4**[8] is the key precursor to the ultimate optically pure *P*,*N*-ligands **6a–e** and **6′d** which were obtained by treatment with an appropriate amine under reported reaction conditions.[9–11] Notably, the formylferrocenyl compound **4** can be converted to its borane adduct **5** by reaction with $BH_3{\cdot}Me_2S$. Compound **5** can be easily handled, stored in the air and purified by standard chromatographic techniques; moreover it regenerates **4** quantitatively by treatment with TMEDA.[12]

The absolute configurations of the *P*,*N*-ligands (**6a–e** and **6′d**) were assigned on the basis of a single-crystal X-ray diffraction analysis of the borane adduct **5** of their precursor (Fig. 1).[13]

The cationic Pd-π-allyl complexes $[(\mathbf{6a–e})Pd(C_3H_5)]PF_6$ (**7a–e**) and $[(\mathbf{6'd})Pd(C_3H_5)]PF_6$ (**7′d**) were prepared by conventional methods (Scheme 2).[4b,14] All the complexes were unambiguously characterized by multinuclear NMR spectroscopy.

The chiral transfer ability of the Pd-π-allyl complexes was preliminarily tested in the asymmetric allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate[4b,e,f,g,15] (Scheme 3). All reactions were carried out at room temperature in the presence of 1 mol% of the catalyst (**7a–e** and **7′d**), *N*,*O*-bis(trimethylsilyl)-acetamide (BSA) and a catalytic amount of potassium acetate.[16] Complete conversion of the starting allylic acetate to the allylated product with (*R*)-configuration[17] occurred for all precursors in 8–12 h (GC analysis). Unlike conversion and stereo-configuration, the enantioselectivity was affected by the nature of the

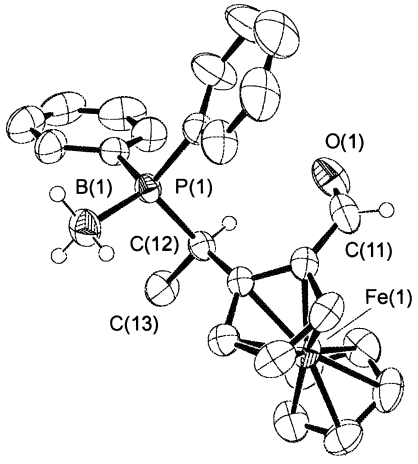
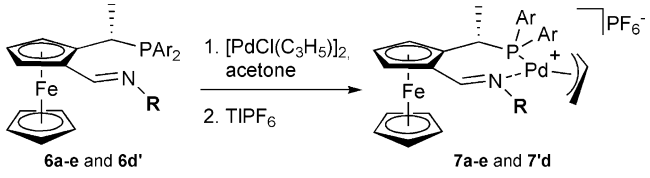


Figure 1. ORTEP drawing of (*R*)C-(*S*)Fe-**5**. Selected bond lengths (Å) and angles (°): P(1)-B(1) 1.918(4), C(11)-O(1) 1.201(5), P(1)-C(12) 1.850(3), C(13)-C(12)-P(1)-B(1).



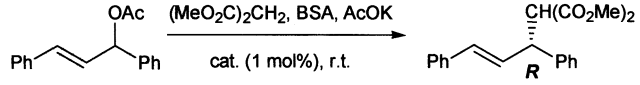
Scheme 2. Synthesis of Pd-π-allyl complexes **7a–e** and **7′d**.

Table 1. Asymmetric allylic alkylations catalyzed by *P*,*N*-Pd-allyl complexes **7a–e** and **7′d**[a]

Entry	Cat.	R	Ar	Solv.	e.e. (%)[b,c,d]
1	**7a**	2,6-$(Me)_2C_6H_3$	Ph	CH_2Cl_2	7.8 (*R*)
2	**7b**	C_6H_5	Ph	CH_2Cl_2	59.2 (*R*)
3	**7b**	C_6H_5	Ph	Toluene	58.2 (*R*)
4	**7c**	C_6H_{11}	Ph	CH_2Cl_2	56.5 (*R*)
5	**7d**	C_2H_5	Ph	CH_2Cl_2	70.1 (*R*)
6	**7d′**	C_2H_5	3,5-$(CF_3)_2C_6H_3$	CH_2Cl_2	70.3 (*R*)
7	**7d**	C_2H_5	Ph	Toluene	79.6 (*R*)
8	**7d**	C_2H_5	Ph	THF	67.4 (*R*)
9	**7d**	C_2H_5	Ph	DMF	75.3 (*R*)
10	**7d**	C_2H_5	Ph	DMSO	71.3 (*R*)
11	**7e**	CH_3	Ph	CH_2Cl_2	74.3 (*R*)
12	**7e**	CH_3	Ph	Toluene	75.5 (*R*)

[a] Molar ratio: acetate (1 equiv.), **7a–e**, **7′d** (0.01 equiv.), dimethyl malonate (2 equiv.), BSA (2 equiv.), KOAc (0.1 equiv.).
[b] Determined by GC analysis.
[c] Determined by HPLC analysis using a Daicel Chiralcel OD-H 0.46×25 cm column (eluent:hexanes/2-propanol = 98/2, 0.5 mL/min).
[d] Absolute configuration of the product was assigned through comparison of the sign of the specific rotations with literature data.[17]

substituent on the nitrogen atom. Selected results and experimental conditions are reported in Table 1. As a general trend, the enantiomeric excess (e.e.) increased upon decreasing the steric bulkiness of the substituent on the nitrogen atom when CH_2Cl_2 was used as the solvent (Table 1; entries 1, 2, 4, 5, 11). In the series of precursors with the PPh_2 group (**7a**–**e**), the methyl substituted complex **7e**[18] gave the best result in CH_2Cl_2 (74.3% e.e.) (entry 11).



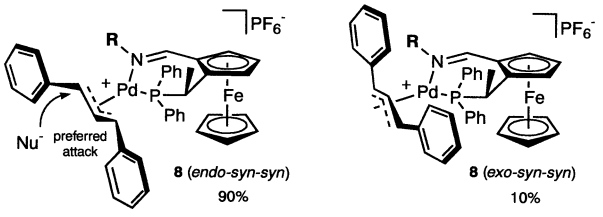
Scheme 3. Allylic alkylation of 1,3-diphenylprop-2-en-1-yl acetate with dimethyl malonate.

Changing the size and the chemical nature of the *P*-aryl substituents as in **6′d**, which bears 3,5-bis(trifluoromethyl)-groups, did not appreciably increase the e.e. (entry 6). In contrast, an interesting solvent effect was observed using **7d**[19] as catalyst precursor. With this catalyst, toluene proved to be the best solvent, yielding e.e.'s as high as 79.6% (entries 5 and 7). Dichloromethane, which is generally a good solvent for Pd-catalyzed allylic alkylation reactions (entry 5), as well as other polar solvents such as THF (entry 8), DMF (entry 9) and DMSO (entry 10) were even less efficient.

In order to rationalize the exclusive formation of the (*R*)-enantiomer, the model cationic Pd^{II}-η^3-1,3-diphenylallyl complex [(**6d**)Pd(1,3-Ph_2-C_3H_3)]PF_6 **8** was prepared[20] and its solution structure was studied by NMR techniques. The $^{31}P\{^1H\}$ NMR spectrum of **8** showed two singlets at 45.69 and 46.25 ppm in an 8:1 molar ratio, indicating the presence of two diastereomers. The two diastereomers were identified as the *endo*,*syn*,*syn* (major) and *exo*,*syn*,*syn* (minor) conformers, respectively, by 2D NMR and ^1H NOESY experiments (Scheme 4).[21]

On the basis of the NMR analysis of **8** and of previous studies by Brown, Pfaltz, Togni and Helmchen,[22–25] the observed formation of the (*R*)-enantiomer can be rationalized by a preferred nucleophilic addition of the malonate anion to the terminal allylic carbon atom *trans* to the phosphorus atom.

In conclusion, we have developed a high-yield, multigram-scale protocol for the synthesis of new ferrocenyl imino-phosphine ligands that combine planar and central chirality with a flexible and easy-to-tune molecular structure. η^3-Allyl-Pd^{II} complexes have provided interesting results in allylic alkylation reactions, which forecasts a wide and effective use of these *P*,*N*-ligands in metal-assisted asymmetric transformations.



Scheme 4. Isomer conformations of complexes **8**. The preferred nucleophilic attack on the allyl terminal carbon *trans* to the phosphorus donor atom gives the (*R*)-enantiomer.

Acknowledgements

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8. Compound **4**: $^{31}P\{^1H\}$ NMR (161.98 MHz, 294 K, $CDCl_3$): $\delta = 9.09$ (s, Ph_2P). ^1H NMR (400.13 MHz, 294

K, $CDCl_3$): $\delta = 9.46$ (s, 1H, HC=O), 7.61–7.63 (m, 2H, PhH), 7.45–7.49 (m, 3H, PhH), 7.20–7.22 (m, 1H, PhH), 7.09–7.13 (m, 2H, PhH), 6.97–7.03 (m, 2H, PhH), 4.59–4.61 (m, 1H, *H*Cp), 4.54–4.56 (m, 1H, *H*Cp), 4.52–4.55 (m, 1H, *H*Cp), 4.25 (s, 5H, *H*Cp′), 3.86 (qnt, 1H, C*H*Me, $J_{HH} = J_{HP} = 6.4$ Hz), 1.60 (dd, 3H, C*H*$_3$, $J_{HH} = 7.0$, $J_{HP} = 14.9$ Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz, 294 K, $CDCl_3$): $\delta = 168.23$ (s, C=O), 95.26 (d, Cp, $J = 15.4$ Hz), 71.67 (d, Cp, $J = 4.6$ Hz), 71.27 (s, HCp), 69.90 (s, C_5H_5), 68.74 (s, HCp), 68.17 (s, Cp), 29.57 (d, *C*HMe, $J = 14.8$ Hz), 18.59 (d, *C*H$_3$, $J = 20.0$ Hz). Anal. Calcd for $C_{25}H_{23}FeOP$: C, 70.44; H, 5.44. Found: C, 70.20; H, 5.13.

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10. Similar procedures were followed for the synthesis of compounds **3′**, **4′** and **6′d**.
11. The *P*,*N*-ligands **6a–d** and **6′d** were obtained as pure compounds in good to excellent yield after chromatographic purification over neutral aluminum oxide. In contrast, the ligand **6e** underwent partial hydrolysis on neutral alumina, therefore its purification was accomplished only for analytical and spectroscopic purposes.
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13. Crystal data for (*R*)-1-[(*S*)-2-formylferrocenyl]ethyldiphenylphosphine·BH_3 (*R*)-(*S*)-**5**: A suitable single crystal of **5** was obtained by recrystallization from AcOEt/heptane. $C_{25}H_{26}BFeOP$, $M = 440.09$, orthorhombic, $a = 7.229(4)$, $b = 13.631(2)$, $c = 22.707(3)$ Å, $V = 2237.5(13)$ Å^3, $T = 293(2)$ K, space group $P2_12_12_1$ (no. 19), $Z = 4$, μ (Mo Kα) = 0.758 mm^{-1}, 2239 measured reflections, 2239 independent reflections, *R* indices (all data) $R = 0.0319$ and $wR = 0.0812$. Flack parameter = 0.02(2). Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-204504. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +441223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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17. The absolute configurations of the products were assigned through comparison of the sign of the specific rotations with the literature data. See for example: von Matt, P.; Pfaltz, A. *Angew. Chem. Int. Ed.* **1993**, *32*, 566–568.
18. [(*R*)-(*S*)-**6e**-Pd(C_3H_5)]PF_6 (**7e**): (2 isomers in a 2.2: 1 molar ratio) $^{31}P\{^1H\}$ NMR (161.98 MHz, 294 K, $CDCl_3$): δ = isomer A 44.79 (s). ^1H NMR (400.13 MHz, 294 K, $CDCl_3$): selected data δ = isomer A 8.83 (t, 1H, *H*C=N, $J_{HH} = 1.5$ Hz), 5.51–5.55 (m, 1H, $C_3H_{5\ cent}$), 4.77 (ddd, 1H, $C_3H_{5\ anti}$, $J_{HH} = 2.5$, $J_{HP} = 6.2$, $J_{HH} = 8.1$ Hz), 4.73–4.77 (m, 1H, *H*Cp), 4.32 (s, 5H, *H*Cp′), 4.20 (t, 1H, *H*Cp, $J_{HH} = 2.6$ Hz), 4.03 (dq, 1H, *H*CMe, $J_{HH} = 5.4$, $J_{HP} = 6.9$ Hz), 3.85 (s, 3H, N*Me*), 3.56 (dd, 1H, $C_3H_{5\ syn}$, $J_{HH} = 13.9$, $J_{HP} = 9.7$ Hz), 3.46–3.49 (m, 1H, *H*Cp), 3.18 (bd, 1H, $C_3H_{5\ anti}$, $J_{HH} = 6.8$ Hz), 2.33 (d, 1H, $C_3H_{5\ syn}$, $J_{HH} = 12.6$ Hz), 1.44 (dd, 3H, HC*Me*, $J_{HH} = 6.8$, $J_{HP} = 12.2$ Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz, 294 K, $CDCl_3$): selected data δ = isomer A 172.96 (s, C=N), 120.85 (s, $C_3H_{5\ cent}$), 71.80 (s, HCp), 70.49 (s, Cp′), 69.44 (s, HCp), 30.19 (d, H*C*Me, $J_{CP} = 14.7$ Hz), 55.71 (s, N*Me*), 80.57 (s, C_3H_5), 56.65 (s, C_3H_5), 68.43 (s, HCp), 13.74 (s, HC*Me*). $^{31}P\{^1H\}$ NMR (161.98 MHz, 294 K, $CDCl_3$): δ = isomer B 45.65 (s). ^1H NMR (400.13 MHz, 294 K, $CDCl_3$): selected data δ = isomer B 8.92 (t, 1H, *H*C=N, $J_{HH} = 1.3$ Hz), 5.47–5.51 (m, 1H, $C_3H_{5\ cent}$), 4.84–4.86 (m, 1H, *H*Cp), 4.73 (ddd, 1H, $C_3H_{5\ anti}$, $J_{HH} = 2.0$, $J_{HP} = 5.9$, $J_{HH} = 8.1$ Hz), 4.34 (s, 5H, *H*Cp′), 4.31 (t, 1H, *H*Cp, $J_{HH} = 2.5$ Hz), 3.91–3.93 (m, 1H, *H*CMe), 3.75–3.79 (m, 3H, N*Me*), 3.73 (dd, 1H, $C_3H_{5\ syn}$, $J_{HH} = 14.1$, $J_{HP} = 9.5$ Hz), 3.64–3.66 (m, 1H, *H*Cp), 3.11 (bd, 1H, $C_3H_{5\ syn}$, $J_{HH} = 6.9$ Hz), 2.27 (bd, 1H, $C_3H_{5\ anti}$, $J_{HH} = 12.2$ Hz), 1.43 (dd, 3H, HC*Me*, $J_{HH} = 6.5$, $J_{HP} = 12.3$ Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz, 294 K, $CDCl_3$): selected data δ = isomer B 173.0 (s, C=N), 121.22 (s, $C_3H_{5\ cent}$), 71.86 (s, HCp), 70.67 (s, Cp′), 69.79 (s, HCp), 30.58 (d, H*C*Me, $J_{CP} = 13.9$ Hz), 56.54 (s, N*Me*), 82.32 (s, C_3H_5), 53.96 (s, C_3H_5), 68.64 (s, HCp), 13.78 (s, HC*Me*).
19. [(*R*)-(*S*)-**6d**-Pd(C_3H_5)]PF_6 (**7d**): (2 isomers in a 2:1 molar ratio) $^{31}P\{^1H\}$ NMR (161.98 MHz, 294 K, $CDCl_3$): δ = isomer A 44.63 (s), isomer B 45.71 (s). ^1H NMR (400.13 MHz, 294 K, $CDCl_3$): selected data δ = isomer A 8.93 (s, 1H, *H*C=N), 5.51–5.55 (m, 1H, $C_3H_{5\ cent}$), 4.82–4.84 (m, 1H, *H*Cp), 4.70–4.74 (m, 1H, $C_3H_{5\ anti}$), 4.32 (s, 5H, *H*Cp′), 4.24 (t, 1H, *H*Cp, $J_{HH} = 2.6$ Hz), 4.10–4.14 (m, 1H, CH_2CH$_3$), 3.89–3.91 (m, 1H, CH_2CH$_3$), 3.83–3.87 (m, 1H, *H*CMe), 3.51 (s, 1H, *H*Cp), 3.48 (dd, 1H, $C_3H_{5\ syn}$, $J_{HH} = 13.9$, $J_{HP} = 9.6$ Hz), 3.23–3.25 (m, 1H, $C_3H_{5\ anti}$), 2.40 (d, 1H, $C_3H_{5\ syn}$, $J_{HH} = 12.4$ Hz), 1.42 (dd, 3H, HC*Me*, $J_{HH} = 6.9$, $J_{HP} = 12.0$ Hz), 1.38 (t, 3H, CH$_2$C*H*$_3$, $J_{HH} = 7.3$ Hz). isomer B selected data $\delta = 9.00$ (s, 1H, *H*C=N), 5.48–5.52 (m, 1H, $C_3H_{5\ cent}$), 4.88–4.92 (m, 1H, *H*Cp), 4.67–4.71 (m, 1H, $C_3H_{5\ anti}$), 4.33–4.37 (m, 1H, *H*Cp), 4.34 (s, 5H, *H*Cp′), 4.02–4.06 (m, 1H, CH_2CH$_3$), 3.83–3.85 (m, 1H, *H*CMe), 3.78–3.82 (m, 1H, CH_2CH$_3$), 3.69 (dd, 1H, $C_3H_{5\ syn}$, $J_{HH} = 15.6$, $J_{HP} = 9.6$ Hz), 3.68 (s, 1H, *H*Cp), 3.19 (m, 1H, $C_3H_{5\ anti}$), 2.31 (d, 1H, $C_3H_{5\ syn}$, $J_{HH} = 12.4$ Hz), 1.41 (dd, 3H, HC*Me*, $J_{HH} = 7.2$, $J_{HP} = 12.0$ Hz), 1.20 (t, 3H, CH$_2$C*H*$_3$, $J_{HH} = 7.4$ Hz).$^{13}C\{^1H\}$ NMR (100.61 MHz, 294 K, $CDCl_3$): selected data δ = isomer A 171.24 (s, C=N), 120.93 (s, $C_3H_{5\ cent}$), 79.25 (d, C_3H_5, $J_{CP} = 23.1$ Hz), 72.15 (s, HCp), 70.57 (s, Cp′), 69.48 (s, HCp), 68.43 (s, HCp), 62.54 (s, *C*H$_2$CH$_3$), 57.34 (s, C_3H_5), 30.23 (d, H*C*Me, $J_{CP} = 16.6$ Hz), 17.09 (s, CH$_2$*C*H$_3$), 13.81 (s, HC*Me*). Isomer B selected data $\delta = 171.44$ (s, C=N), 120.99 (s, $C_3H_{5\ cent}$), 81.82 (d, C_3H_5, $J_{CP} = 22.9$ Hz), 72.11 (s, HCp), 70.66 (s, Cp′), 69.67 (s, HCp), 68.23 (s, HCp), 62.96 (s, *C*H$_2$CH$_3$), 54.11 (s, C_3H_5), 30.77 (d, H*C*Me, $J_{CP} = 15.1$ Hz), 16.23 (s, CH$_2$*C*H$_3$), 14.09 (s, HC*Me*). Anal. Calcd for $C_{30}H_{33}F_6FeNP_2Pd$: C, 48.31; H, 4.46; N, 1.88. Found: C, 48.09; H, 4.44; N, 1.77.
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