Thermodynamically Controlled Formation of Diastereopure Three-Legged Piano-Stool Complexes. The Substitution Chemistry of [RuCp(aminophosphinoferrocene)(CH_3CN)]PF_6

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Treatment of [RuCp(CH_3CN)$_3$]$^+$ with the chiral ligands PN* = (R_c,S_{pl})-2-(1-*N*,*N*-dimethylaminoethyl)-1-diphenylphosphinoferrocene, (S_{pl})-2-(*N*,*N*-dimethylaminomethyl)-1-diphenylphosphinoferrocene, and (R_c,S_{pl})-2-(1-*N*,*N*-diethylaminoethyl)-1-diphenylphosphinoferrocene affords diastereoselectively the labile cationic complexes [(S_{Ru})-RuCp(PN*)(CH_3CN)]$^+$. The exchange kinetics of CH_3CN has been studied as a function of temperature, revealing a dissociative mechanism, and therefore thermodynamic control is responsible for the diastereoselective formation of [(S_{Ru})-RuCp(PN*)(CH_3CN)]$^+$. These react with HC≡CPh to give the chiral vinylidene complexes [(R_{Ru})-RuCp(PN*)(=C=CHPh)]$^+$ in highly diastereoselective fashion. With CO complexes [RuCp(PN*)(CO)]$^+$ are obtained in high yields but with significantly decreased stereoselectivity due to kinetic control of the substitution reaction. Under photochemical conditions epimerization occurs to give [(R_{Ru})-RuCp(PN*)(CO)]$^+$ with a de of >98%. In the case of [RuCp((R_c,S_{pl})-2-(1-*N*,*N*-diethylaminoethyl)-1-diphenylphosphinoferrocene)(CO)]$^+$, the diastereomeric excess increases from 87 to >98% upon heating due to an intramolecular epimerization. The absolute configuration of representative complexes has been determined by X-ray crystallography.

Introduction

Enantio- and diastereopure organometallic complexes have become increasingly useful in mechanistic studies and in organic synthesis.[1] With respect to ruthenium, most work has been done on half-sandwich Ru(arene),[2] and RuCp and RuCp* complexes[3,4] containing C_2 symmetric bisphosphines or tethered functional groups as chiral auxiliaries. Configurationally stable chiral at ruthenium pseudo-tetrahedral three-legged piano-stool complexes are particularly interesting as chiral Lewis acids, e.g., in catalytic asymmetric Diels−Alder reactions.[2g,5] In this regard we are interested in the well-known chiral phosphinoamineferrocenes (PN*) as coligands. This class of chiral asymmetric bidentate ligands imposing not only a steric but also an electronic bias on an prochiral substrate[6] has received little attention in ruthenium chemistry,[2g,7] despite its extensive use in

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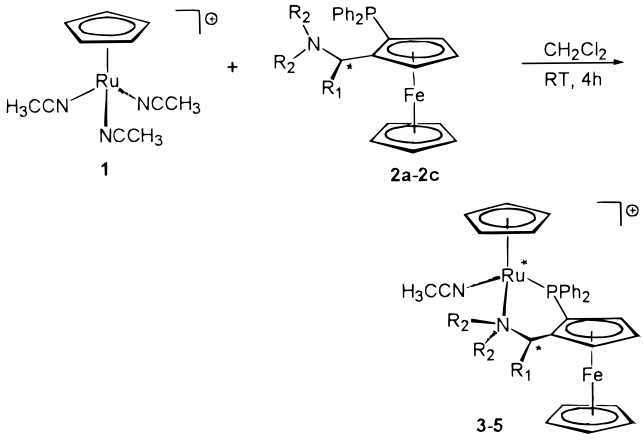
Table 1. Reaction of 1 with Chiral Aminophosphineferrocenes



ligand	product	R_1	R_2	product	yield	de[a]
2a	**3**	Me	Me	S_{Ru}, R_C, S_{pl}	96%	>98%
2b	**4**	H	Me	S_{Ru}, S_{pl}	98%	>98%
2c	**5**	Me	Et	S_{Ru}, R_C, S_{pl}	96%	>98%

[a] Determined by NMR spectroscopy.

palladium chemistry.[8] In the present paper we report first results of the synthesis, structure, and exchange kinetics of the diastereopure complexes $[RuCp(PN^*)(CH_3CN)]^+$ containing the ligands PN* = (R_c,S_{pl})-2-(1-*N*,*N*-dimethylaminoethyl)-1-diphenylphosphinoferrocene(**2a**),(S_{pl})-2-(*N*,*N*-dimethylaminomethyl)-1-diphenylphosphinoferrocene (**2b**), and (R_c,S_{pl})-2-(1-*N*,*N*-diethylaminoethyl)-1-diphenylphosphinoferrocene (**2c**). From those, other diastereopure Ru(II) complexes are accessible. X-ray structures of representative compounds are given.

Results and Discussion

Synthesis and Kinetics. Treatment of $[RuCp(CH_3CN)_3]^+$ (**1**) with 1 equiv of the chiral ligands PN* (**2a**, **2b**, or **2c**) in CH_2Cl_2 at room temperature provides the cationic complexes $[RuCp(PN^*)(CH_3CN)]^+$ (**3**−**5**) in high yields (Table 1). The formation of **3**−**5** is highly diastereoselective (de >98%) irrespective of the substituents on the $-NR_2$ group (R = Me, Et) and the substituent on the benzylic bridging carbon atom $-CHR-$ (R = H, Me) (as indicated by an asterisk in Table 1). All complexes have been characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopies and elemental analysis. The structural identity and the absolute configuration of **3** and **5** has been determined by single-crystal X-ray diffraction. ORTEP diagrams are depicted in Figures1 and 2 with selected bond distances given in Table 2.

The CH_3CN ligand in **3**−**5** is substitutionally labile and is replaced by CD_3CN (15 equiv) in a solution of **3**−**5** in $CDCl_3$ at room temperature. Interestingly, this exchange is completely stereospecific with retention of the configuration at the ruthenium center, as indicated by the absence of the second diastereomer. The kinetics of this process in **3** has been studied in detail by ^1H NMR spectroscopy as a function of temperature, with an Eyring plot shown in Figure 3.

The first-order rate constant obtained is 9.2×10^{-2} s^{-1} at room temperature (cf. 5.6 s^{-1} for **1**[9]). The large activation enthalpy (23.2 kcal mol^{-1}) and a positive entropy of activation (14.6 cal mol^{-1} K^{-1}) are characteristic of a unimolecular process (dissociative mechanism). Evidence is provided by the fact that the reaction rate is independent of the free CH_3CN concentration. It may thus be argued that the observed preference of

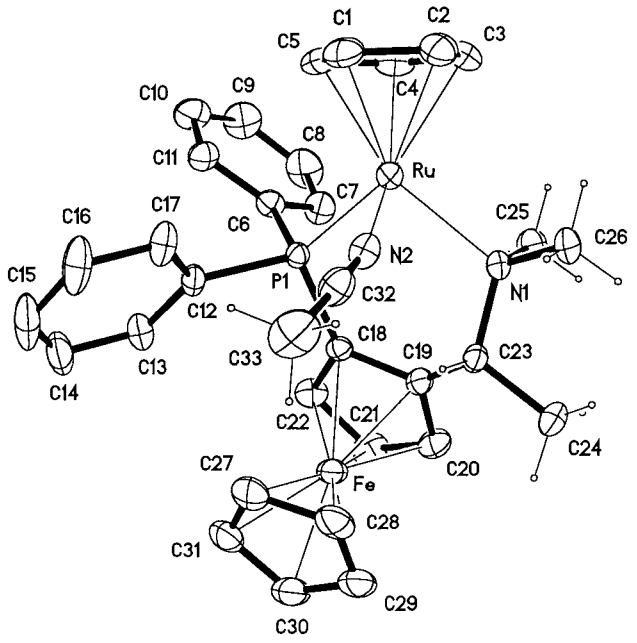


Figure 1. Structural view of **3** showing 20% thermal ellipsoids (PF_6^- and aromatic hydrogen atoms omitted for clarity). Priority for the assignment of the absolute configuration at Ru: Cp > PPh_2 > CH_3CN > NMe_2.

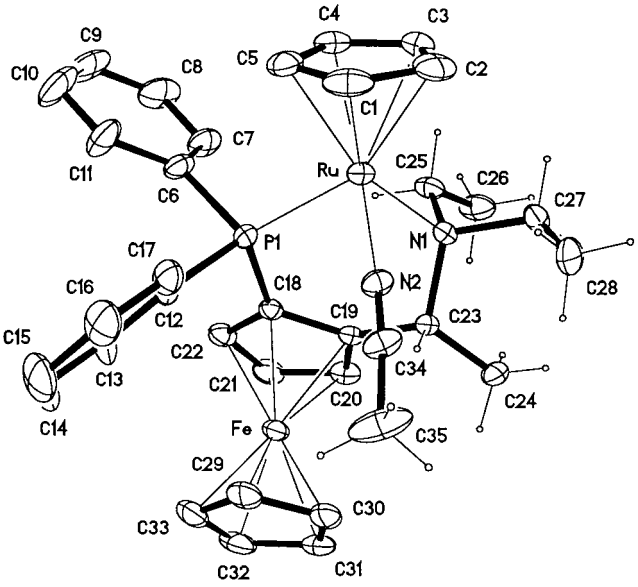


Figure 2. Structural view of **5**·CH_2Cl_2 showing 20% thermal ellipsoids (PF_6^-, CH_2Cl_2, and aromatic hydrogen atoms omitted for clarity). Priority for the assignment of the absolute configuration at Ru: Cp > PPh_2 > CH_3CN > NEt_2.

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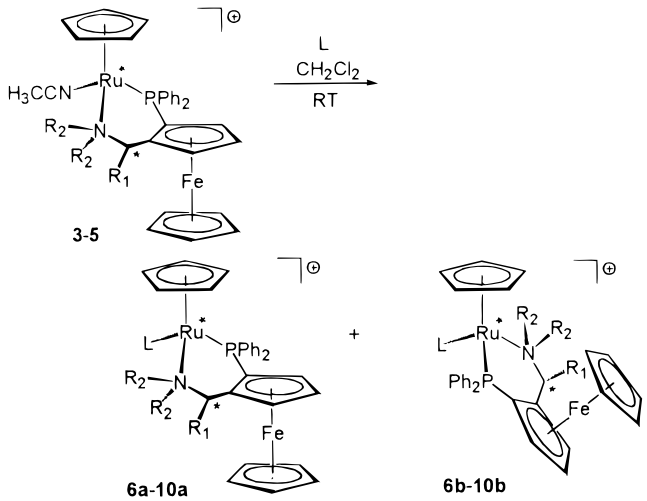
Table 2. Ligand Exchange Reactions of 3−5



educt	ligand	products	yield	R_{Ru}	S_{Ru}	ratio[a]	de[b]
3	=C=CHPh	**6a**/**6b**	96%	**6a**[b]	**6b**	21:1	91%
3	CO	**7a**/**7b**	90%	**7a**[b]	**7b**	2.4:1	42%[c]
4	=C=CHPh	**8a**/**8b**	92%	**8a**[b]	**8b**	28:1	96%
4	CO	**9a**/**b**	93%	**9a**	**9b**	1.8:1	28%
5	=C=CHPh		decomposition				
5	CO	**10a**/**b**	95%	**10a**[b]	**10b**	15:1	87%[d]

[a] Determined by NMR spectroscopies. [b] Isolated compound. [c] Under photochemical conditions **7a** is formed with a de of >98%. [d] Upon heating at 62 °C for 36 h a de of >98% is obtained.

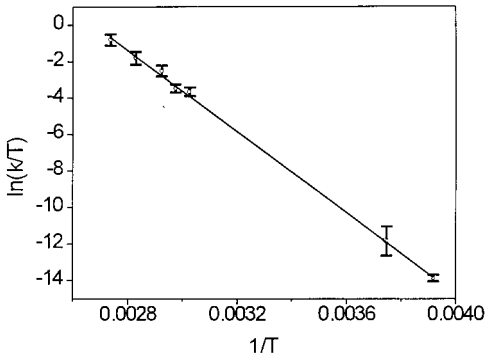


Figure 3. Temperature dependence of the acetonitrile exchange rate constants of **3**.

one diastereomer over the other is likely of thermodynamic rather than kinetic origin (Scheme 1).

The reactivity of **3**−**5** toward substitution has been further investigated as follows. Treatment of **3** and **4** with HC≡CPh yields the corresponding chiral vinylidene complexes **6** and **8** in high yields. These products are obtained as mixtures of the two diastereomeric complexes **6a**/**b** and **8a**/**8b** in 21:1 (de = 91%) and 28:1 (de = 96%) ratios, respectively (Table 3). With **5**, on the other hand, the reaction is not clean, with several as yet intractable materials formed. This may be explained by the hemilability of the sterically more demanding (R_c,S_{pl})-2-(1-*N*,*N*-diethylaminoethyl)-1-diphenylphosphinoferrocene (**2c**). We have previously shown[10] that aminophosphine ligands are hemilabile if the nitrogen site is sufficiently bulky (NMe_2 < NEt_2 < N-*i*-Pr_2), promoting the formation of vinylidene complexes as well as the deprotonation of the vinylidene ligand to afford reactive coordinatively unsaturated alkynyl species. These in turn, in the absence of potential 2e donor ligands, may undergo various (uncontrollable) reactions as in the present case. The structural identity and stereochemistry of **6a** has been established by X-ray crystallography (Figure 4). Selected bond distances and angles are reported in Table 2.

The formation of the vinylidene complexes is highly diastereoselective, again with retention of configuration at ruthenium. In view of the lability of the CH_3CN ligand in complexes **3**−**5** and the dissociative nature of substitution, the following reaction mechanism seems likely: HC≡CPh attacks the chiral 16e [RuCp(PN*)]$^+$ intermediate predominantly from one diastereoface to give an η^2-HC≡CPh complex, which subsequently tautomerizes irreversibly to the corresponding vinylidene complex (note that a reversible formation of vinylidene complexes has been reported[11]). Diastereoface selection may be based on steric arguments, since the intermediate side-on coordinated alkyne is sterically more demanding than the linear vinylidene ligand. Accordingly, the diastereoselectivity of the overall reaction appears to be kinetically controlled. In this context it has to be mentioned that at elevated temperatures no epimerization between **6a** and **6b** is observed and the diastereomeric ratio **6a**/**6b** remains unchanged.

Similar to HC≡CPh, also CO reacts with **3**−**5**, giving complexes **7a**/**b**, **9a**/**b**, and **10a**/**b** in high yields (Table 3). However, while with **5** the de is still 87%, in the case of **3** and **4** the de has significantly dropped to 42 and 28%, respectively. Characterization of **7a**, **9a**, and **10a** was again accomplished by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopies and elemental analysis. The isomers **7b**, **9b**, and **10b** could not be isolated in pure form, but their identity has been established by NMR spectroscopy. There was no evidence for the formation of any dicarbonyl species, as inferred from the resonances of the NMe_2 (two singlets rather than one singlet as observed for the free PN ligand) and NEt_2 (multiplet resonances rather than a quartet and a triplet as observed for the free PN ligand) groups. The identity and stereochemistry of the major isomers were again determined by X-ray crystallography (Figure 5). The formation of complexes **7** and **9** is kinetically controlled. The CO molecule is sterically undemanding, and the steric bias between the two diastereofaces is small. Furthermore, complexes **7** and **9** are inert at ambient temperatures and, thus, once formed do not epimerize anymore (cf. **3**−**5**). In the case of **5** the steric bias is enhanced due to the bulkier NEt_2 group of the PN* ligand **2c** accounting for the higher de. However, **2c** in contrast to **2a** and **2b** may become hemilabile, leading to Ru−N bond rupture. Accordingly, rotation of **2c** about the Ru−P bond can lead to the thermodynamically favorable isomer **10a**, as shown in Scheme 2. This has, indeed, been demonstrated by heating a mixture of **10a**/**b** in $CDCl_3$ for 36 h at 62 °C, leading to an increase of the de from 87 to >98%. Under the same conditions,

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Scheme 1

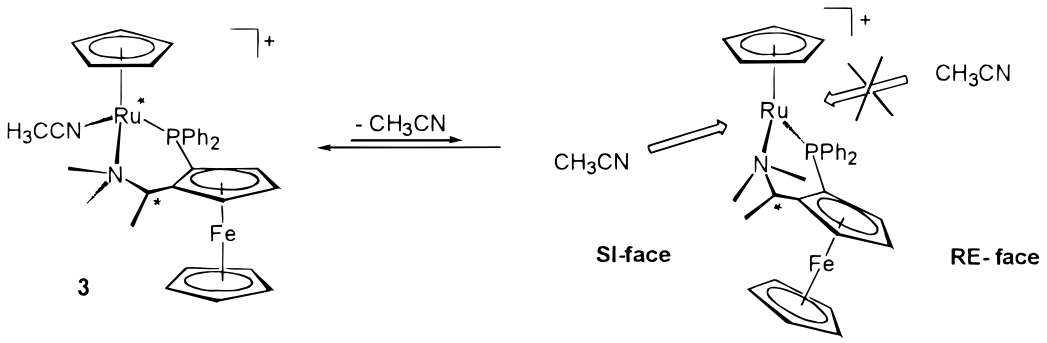

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 3, 5·CH_2Cl_2, 6a, and 7a

	3	5·CH_2Cl_2	6a[a]	7a
stereochemistry	S_{Ru}, R_C, S_{pl}	S_{Ru}, R_C, S_{pl}	R_{Ru}, R_C, S_{pl}	R_{Ru}, R_C, S_{pl}
L	CH_3CN	CH_3CN	=C=CHPh	CO
Ru−L	2.063(3)	2.051(3)	1.811(7)/1.823(8)	1.861(2)
Ru−P	2.287(1)	2.282(1)	2.305(2)/2.330(2)	2.300(1)
Ru−N	2.251(3)	2.288(3)	2.219(6)/2.211(6)	2.223(2)
⟨Ru−C_{cp}⟩	2.187(4)	2.178(4)	2.258(8)/2.247(11)	2.235(3)
Ru−rc_{cp}[b]	1.828(2)	1.827(2)	1.916(4)/1.911(5)	1.888(1)
∠rc_{cp}−Ru−L	123.8(1)	125.1(1)	126.2(2)/124.4(2)	123.5(1)
∠rc_{cp}−Ru−P	123.3(1)	123.6(1)	121.1(2)/119.7(2)	121.5(1)
∠rc_{cp}−Ru−N	127.0(1)	126.7(1)	127.3(2)/127.7(2)	125.6(1)
∠L−Ru−P	91.7(1)	88.9(1)	91.9(2)/97.0(2)	93.1(1)
∠L−Ru−N	87.2(1)	89.3(1)	88.1(3)/87.0(3)	90.9(1)
∠P−Ru−N	93.4(1)	92.3(1)	91.8(2)/91.9(2)	93.4(1)

[a] Two crystallographically independent Ru complexes present. [b] rc is the centroid of the Cp ring.

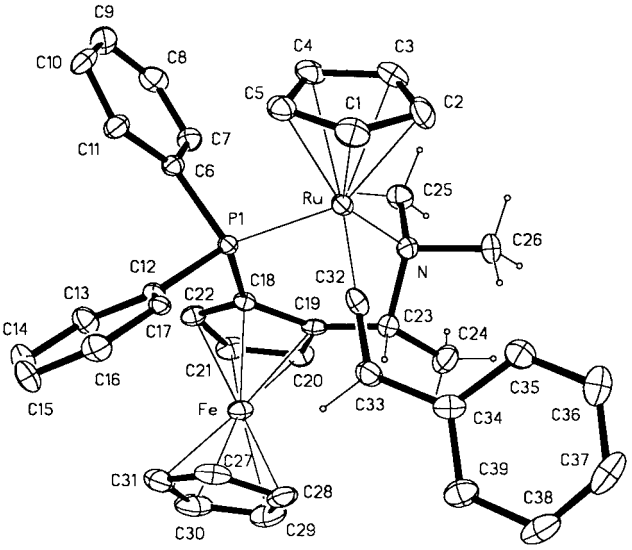

Figure 4. Structural view of **6a** showing 20% thermal ellipsoids (PF_6^- and aromatic hydrogen atoms omitted for clarity). Only one of the two crystallographically independent complexes is shown. Priority for the assignment of the absolute configuration at Ru: Cp > PPh_2 > NMe_2 > =C=HPh.

and even at higher temperatures (toluene, 110 °C) and prolonged heating of **7a**/**b** and **9a**/**b**, no epimerization is observed. However, UV irradiation of a solution of **7a**/**7b** in CD_3NO_2 under a CO atmosphere labilizes the CO ligand,[12] and epimerization takes place to give **7a** with a de of >98% together with small amounts of two unidentified byproducts (<5%), as indicated by $^{31}P\{^1H\}$ NMR spectroscopy.

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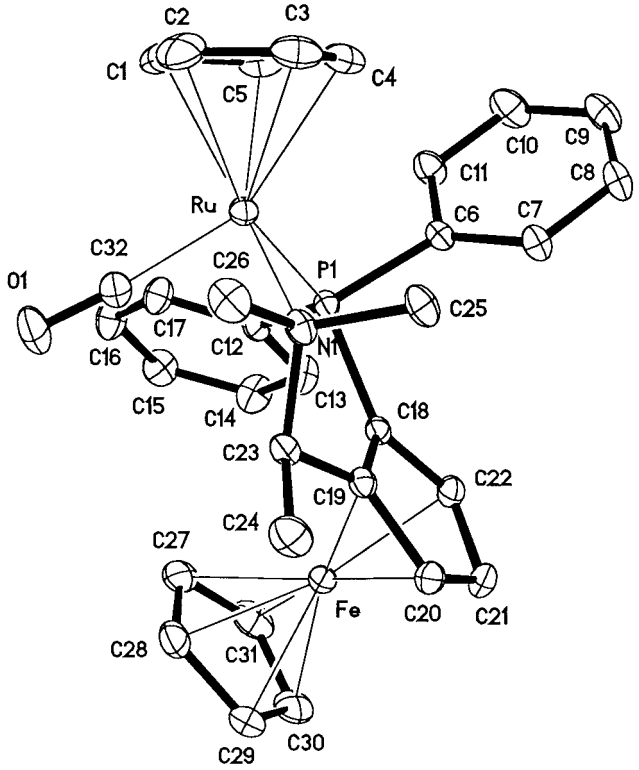

Figure 5. Structural view of **7a** showing 20% thermal ellipsoids (PF_6^- and aromatic hydrogen atoms omitted for clarity). Priority for the assignment of the absolute configuration at Ru: Cp > PPh_2 > NMe_2 > CO.

X-ray Structures of 3, 5·CH_2Cl_2, 6a, and 7a. All four investigated compounds (**3**, **5**·CH_2Cl_2, **6a**, **7a**) crystallize in chiral space groups (Table 4), and their absolute configurations were unequivocally determined via significant anomalous dispersion effects. Whereas

Scheme 2

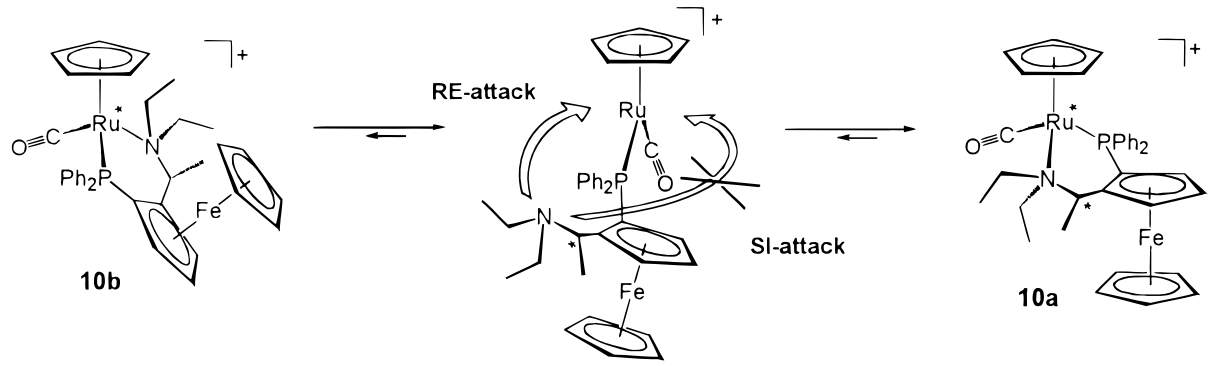

Table 4. Crystallographic Data for 3, 5·CH_2Cl_2, 6a, and 7a

	3	5·CH_2Cl_2	6a	7a
formula	$C_{33}H_{36}F_6FeN_2P_2Ru$	$C_{36}H_{42}Cl_2F_6FeN_2P_2Ru$	$C_{39}H_{39}F_6FeNP_2Ru$	$C_{32}H_{33}F_6FeNOP_2Ru$
fw	793.50	906.48	854.57	780.45
cryst size, mm	0.60 × 0.24 × 0.12	0.70 × 0.56 × 0.10	0.50 × 0.40 × 0.30	0.60 × 0.55 × 0.40
space group	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a, Å	10.730(3)	9.925(3)	11.363(5)	10.603(3)
b, Å	11.576(3)	13.515(3)	15.338(7)	14.106(3)
c, Å	27.868(5)	14.608(3)	42.054(15)	21.044(4)
β, deg	94.78(1)			
V, Å^3	3462.1(15)	1952.6(8)	7329(5)	3147.5(13)
Z	4	2	8	4
ρ_{calc}, g cm^{-3}	1.522	1.543	1.549	1.647
T, K	295(2)	295(2)	295(2)	295(2)
μ, mm^{-1} (Mo Kα)	1.005	1.034	0.955	1.106
abs corr	multiscan	multiscan	multiscan	multiscan
F(000)	1608	920	3472	1576
transmiss factor min/max	0.92−0.77	0.80−0.65	0.93−0.75	0.76−0.64
θ_{max}, deg	27	25	25	30
data completness (%)	99.7	99.8	98.7	99.6
index ranges	$-13 \le h \le 13$ $-14 \le k \le 14$ $-35 \le l \le 35$	$-11 \le h \le 11$ $-16 \le k \le 16$ $-17 \le l \le 17$	$-13 \le h \le 13$ $-18 \le k \le 18$ $-50 \le l \le 50$	$-14 \le h \le 14$ $-19 \le k \le 19$ $-29 \le l \le 29$
no. of rflns measd	41748	20281	63364	46381
no. of unique rflns	7541	6842	12729	9110
no. of rflns $I > 2\sigma(I)$	6824	6365	11216	8421
no. of params	407	468	901	398
R1 ($I > 2\sigma(I)$)[a]	0.036	0.030	0.060	0.026
R1 (all data)	0.042	0.080	0.070	0.032
wR2 (all data)[b]	0.140	0.084	0.118	0.063
diff Four peaks	−0.44/0.48	−0.25/0.51	−0.96/0.52	−0.42/0.37

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

3, **5**·CH_2Cl_2, and **7a** contain only one crystallographically independent Ru complex in the asymmetric unit, the structure of **6a** contains two independent Ru complexes in an orthorhombic unit cell with a longest dimension of $c = 42.05$ Å. All four compounds adopt a typical three-legged piano-stool coordination with a $S_{Ru}R_CS_{pl}$ configuration for **3** and **5**·CH_2Cl_2 and a R_{Ru}-R_CS_{pl} configuration for **6a** and **7a**. The acetonitrile complexes **3** and **5**·CH_2Cl_2 agree well in all major geometric features (Table 3), except for the Ru−N(1) bond distance, which is longer in **5**·CH_2Cl_2 by 0.037 Å, presumably due to the higher sterical demand of the NEt_2 moiety compared with NMe_2. In comparison to the acetonitrile complexes, the short Ru−C(vinylidene, CO) bonds of **6a** (Ru−C = 1.81−1.82 Å) and **7a** (Ru−C = 1.86 Å) are accompanied by a distinct lengthening of the Ru−C bonds to the Cp rings by 0.07 Å, a lengthening of the Ru−P bonds by 0.02−0.05 Å, as well as a shortening of the Ru−N(amine) bonds by 0.03−0.08 Å. These effects may be attributed to pronounced back-bonding effects of the vinylidene and CO ligands. In all four compounds the ferrocene moieties[13] as well as the conformation of the six-membered chelate ring show only insignificant variations.

Conclusion

We have shown that the pseudo-tetrahedral three-legged piano-stool complexes $[RuCp(PN^*)(CH_3CN)]^+$ are formed in >98% de for thermodynamic reasons. The diastereoselectivity is essentially controlled by the planar chirality of the ferrocene moiety. Despite their configurational stability, these complexes are substitutionally labile, providing readily a vacant coordination site, and may therefore be useful as Lewis acid catalysts in asymmetric C−C bond-forming reactions such as Diels−Alder and Mukaiyama reactions.[14]

(13) For a molecular structure of **2a** see: Einstein, F. W. B.; Willis, A. C. *Acta Crystallogr.* **1980**, *B36*, 39.

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Experimental Section

General Information. All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[15] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $[RuCp(CH_3CN)_3]PF_6$ (**1**),[16] (R_C,S_{pl})-2-(1-*N*,*N*-dimethylaminoethyl)-1-diphenylphosphinoferrocene (**2a**), (S_{pl})-2-(*N*,*N*-dimethylaminomethyl)-1-diphenyl-phosphinoferrocene (**2b**), and (R_C,S_{pl})-2-(1-*N*,*N*-diethylaminoethyl)-1-diphenylphosphinoferrocene (**2c**) were prepared according to the literature.[17] ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13, 62.86, and 101.26 MHz, respectively, or on a Bruker Avance DRX-400 spectrometer operating at 400.13, 100.62, and 161.97 MHz, and were referenced to $SiMe_4$ and H_3PO_4 (85%). The diastereomeric excess (de) was determined by ^{1}H NMR spectroscopy. The superscript in the assignment of Cp^s refers to the substituted FeCp ring. The assignment of the configuration has been made according to the literature.[18] Microanalyses were done by Microanalytical Laboratories, University of Vienna.

Synthesis. [(S_{Ru},R_C,S_{pl})-RuCp(2-(1-*N*,*N*-dimethylaminoethyl)-1-diphenylphosphino ferrocene)(CH_3CN)]PF_6 (3). A solution of **1** (100 mg, 0.230 mmol) and **2a** (101 mg, 0.230 mmol) in CH_2Cl_2 (4 mL) was stirred at room temperature for 4 h, whereupon the color changed from yellow to orange. The solvent was removed under reduced pressure and the residue redissolved in 1 mL of CH_2Cl_2. On addition of Et_2O (3 mL) a bright orange precipitate was formed, which was collected on a glass frit, washed with Et_2O (3 × 1 mL), and dried in vacuo. Yield: 176 mg (96%). Anal. Calcd for $C_{33}H_{36}F_6FeN_2P_2Ru$: C, 49.95; H, 4.57. Found: C, 50.16; H, 4.77. ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.23−8.14 (m, 2H, Ph), 7.76−7.66 (m, 3H, Ph), 7.34−7.29 (m, 3H, Ph), 7.07−6.98 (m, 2H, Ph), 4.72−4.70 (m, 1H, FeCp^s), 4.60−4.55 (m, 2H, FeCp^s), 4.46 (q, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*(Me)(NMe$_2$)), 4.26 (s, 5H, RuCp), 3.81 (s, 5H, FeCp), 3.39 (s, 3H, N*Me*$_2$), 2.64 (d, $^5J_{HP}$ = 1.4 Hz, 3H, N≡C−C*H*$_3$), 2.56 (s, 3H, N*Me*$_2$), 1.46 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH(*Me*)(NMe$_2$)). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 145.4 (d, $^1J_{CP}$ = 52.9 Hz, 1C, Ph^1), 136.7 (d, $^2J_{CP}$ = 12.5 Hz, 2C, Ph^{2,6}), 136.6 (d, $^1J_{CP}$ = 47.4 Hz, 1C, Ph$^{1'}$), 132.4 (d, $^3J_{CP}$ = 10.4 Hz, 1C, N≡*C*−CH$_3$), 131.9 (d, $^2J_{CP}$ = 9.8 Hz, 2C, Ph$^{2',6'}$), 131.6 (d, $^4J_{CP}$ = 2.7 Hz, 1C, Ph^4), 129.5 (d, $^4J_{CP}$ = 2.2 Hz, 1C, Ph$^{4'}$), 129.0 (d, $^3J_{CP}$ = 10.4 Hz, 2C, Ph^{3,5}), 128.5 (d, $^3J_{CP}$ = 9.3 Hz, 2C, Ph$^{3',5'}$), 94.1 (d, $^2J_{CP}$ = 22.3 Hz, 1C, FeCp^2), 78.1 (d, $^2J_{CP}$ = 2.2 Hz, CpRu), 76.5 (d, J_{CP} = 1.0 Hz, 1C, FeCp^s), 74.3 (d, $^1J_{CP}$ = 33.2 Hz, 1C, FeCp^1), 71.5 (d, J_{CP} = 4.9 Hz, 1C, FeCp^s), 71.4 (s, 5C, FeCp), 71.2 (d, J_{CP} = 8.7 Hz, 1C, FeCp^s), 62.5 (d, $^3J_{CP}$ = 1.8 Hz, 1C, *C*H(Me)(NMe$_2$)), 56.9 (d, $^3J_{CP}$ = 2.2 Hz, 1C, NMe$_2$), 48.9 (d, $^3J_{CP}$ = 1.1 Hz, 1C, NMe$_2$), 10.6 (s, 1C, CH(*Me*)(NMe$_2$)), 4.4 (s, 1C, N≡C-*C*H$_3$). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 41.7 (*P*Ph$_2$), −143.6 ($^1J_{PF}$ = 713.3 Hz, *P*F$_6$).

[(S_{Ru},R_C,S_{pl})-RuCp(2-(1-*N*,*N*-dimethylaminoethyl)-1-diphenylphosphino)ferrocene)(CD_3CN)]PF_6 (3^D). A sealed NMR tube charged with **3** (20 mg, 25 μmol) and CD_3CN (20 μL, 383 μmol) in acetone-d_6 was kept at room temperature for 15 min and was then transferred to the probe head. The ^{1}H NMR showed almost quantitative replacement of CH_3CN (<5% of **3** remained as determined by integration of the remaining CH_3CN resonance at 2.64 ppm). The NMR spectroscopic data for **3^D** are essentially the same as for **3**.

Epimerization of 3. A sealed NMR tube was charged with **3** in either $CDCl_3$ or CD_3NO_2 as the solvent was cooled to −10 °C and then gradually warmed in steps of 10 °C up to 100 °C and kept at this temperature for 2 h. The reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. Despite a broadening of the resonance for acetonitrile upon heating and some small shifts for the *N*-methyl resonances, no other changes are observed.

[(S_{Ru},S_{pl})-RuCp(2-(*N*,*N*-dimethylaminomethyl)-1-diphenylphosphinoferrocene)(CH_3CN)]PF_6 (4). This compound was prepared analogously to **3** with **1** (168 mg, 0.387 mmol) and **2b** (165 mg, 0.387 mmo) as the starting materials. Yield: 295 mg (98%). In the ^{31}P{^{1}H} NMR a small resonance (39.8 ppm intensity of <1/100 of the resonance of **4**) of a byproduct is observed, which may be due to the formation of another diasteromer. Anal. Calcd for $C_{32}H_{34}F_6FeN_2P_2Ru$: C, 49.31; H, 4.40. Found: C, 49.38; H, 4.66. ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.22−8.14 (m, 2H, Ph), 7.75−7.65 (m, 3H, Ph), 7.35−7.30 (m, 3H, Ph), 7.09−7.01 (m, 2H, Ph), 4.66−4.51 (m, 3H, FeCp^s), 4.39 (d, $^2J_{HH}$ = 13.7 Hz, 1H, C*H*$_2$NMe$_2$), 4.30 (s, 5H, RuCp), 3.78 (s, 5H, FeCp), 3.25 (s, 3H, N*Me*$_2$), 3.04 (d, $^2J_{HH}$ = 13.7 Hz, 1H, C*H*$_2$NMe$_2$), 2.65 (d, $^5J_{HP}$ = 1.1 Hz, 3H, N≡C−C*H*$_3$), 2.63 (s, 3H, N*Me*$_2$). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 145.6 (d, $^1J_{CP}$ = 51.8 Hz, 1C, Ph^1), 137.6 (d, $^1J_{CP}$ = 48.0 Hz, 1C, Ph$^{1'}$), 136.3 (d, $^2J_{CP}$ = 13.0 Hz, 2C, Ph^{2,6}), 131.9 (d, $^3J_{CP}$ = 10.2 Hz, 1C, N≡*C*−CH$_3$), 132.3 (d, $^2J_{CP}$ = 10.4 Hz, 2C, Ph$^{2',6'}$), 132.2 (d, $^4J_{CP}$ = 2.7 Hz, 1C, Ph^4), 130.2 (d, $^4J_{CP}$ = 1.6 Hz, 1C, Ph$^{4'}$), 129.7 (d, $^3J_{CP}$ = 10.4 Hz, 2C, Ph^{3,5}), 129.3 (d, $^3J_{CP}$ = 9.8 Hz, 2C, Ph$^{3',5'}$), 90.7 (d, $^2J_{CP}$ = 22.9 Hz, 1C, FeCp^2), 78.3 (d, $^2J_{CP}$ = 2.2 Hz, RuCp), 75.3 (d, J_{CP} = 1.0 Hz, 1C, FeCp^s), 74.1 (d, J_{CP} = 8.4 Hz, 1C, FeCp^s), 72.7 (d, $^1J_{CP}$ = 34.3 Hz, 1C, FeCp^1), 71.9 (s, 5C, FeCp), 71.4 (d, J_{CP} = 4.4 Hz, 1C, FeCp^s), 64.8 (d, $^3J_{CP}$ = 1.6 Hz, 1C, NMe$_2$), 61.4 (d, $^3J_{CP}$ = 2.2 Hz, 1C, *C*H$_2$NMe$_2$), 56.4 (d, $^3J_{CP}$ = 1.6 Hz, 1C, NMe$_2$), 5.2 (s, 1C, N≡C-*C*H$_3$). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 40.3 (*P*Ph$_2$), −142.7 ($^1J_{PF}$ = 709.7 Hz, *P*F$_6$).

[(S_{Ru},R_C,S_{pl})-RuCp(2-(1-*N*,*N*-diethylaminoethyl)-1-diphenylphosphinoferrocene)(CH_3CN)]PF_6 (5). This compound was prepared analogously to **3** with **1** (111 mg, 0.252 mmol) and **2c** (119 mg, 0.252 mmol) as the starting materials. Yield: 199 mg (96%). Anal. Calcd for $C_{35}H_{40}F_6FeN_2P_2Ru$: C, 51.17; H, 4.91. Found: C, 51.34; H, 5.08. ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.16−8.08 (m, 2H, Ph), 7.74−7.72 (m, 3H, Ph), 7.36−7.33 (m, 3H, Ph), 7.15−7.07 (m, 2H, Ph), 4.79−4.77 (m, 1H, FeCp^s), 4.71−4.66 (m, 2H, FeCp^s), 4.60 (q, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*(Me)NEt$_2$), 4.34 (s, 5H, RuCp), 3.80 (s, 5H, FeCp), 3.43−3.24 (m, 2H, N*CH*$_2$CH$_3$), 3.16 (m, 1H, N*CH*$_2$CH$_3$), 2.91 (m, 1H, N*CH*$_2$CH$_3$), 2.62 (d, $^5J_{HP}$ = 1.4 Hz, 3H, N≡C−C*H*$_3$), 1.84 (t, 3H, NCH$_2$*CH*$_3$), 1.55 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH(*Me*)-NEt$_2$), 0.93 (t, 3H, NCH$_2$*CH*$_3$). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 145.2 (d, $^1J_{CP}$ = 50.7 Hz, 1C, Ph^1), 137.8 (d, $^1J_{CP}$ = 49.6 Hz, 1C, Ph$^{1'}$), 137.2 (d, $^2J_{CP}$ = 12.0 Hz, 2C, Ph^{2,6}), 132.9 (d, $^3J_{CP}$ = 10.9 Hz, 1C, N≡*C*−CH$_3$), 132.4 (d, $^2J_{CP}$ = 9.8 Hz, 2C, Ph$^{2',6'}$), 132.3 (d, $^4J_{CP}$ = 2.2 Hz, 1C, Ph^4), 130.3 (d, $^4J_{CP}$ = 2.1 Hz, 1C, Ph$^{4'}$), 129.7 (d, $^3J_{CP}$ = 10.4 Hz, 2C, Ph^{3,5}), 129.4 (d, $^3J_{CP}$ = 9.3 Hz, 2C, Ph$^{3',5'}$), 95.3 (d, $^2J_{CP}$ = 22.9 Hz, 1C, CpFe^2), 78.6 (d, $^2J_{CP}$ = 2.1 Hz, CpRu), 77.1 (d, J_{CP} = 1.1 Hz, 1C, FeCp^s), 74.1 (d, $^2J_{CP}$ = 33.2 Hz, 1C, FeCp^1), 72.5 (d, J_{CP} = 4.9 Hz, 1C, FeCp^s), 72.1 (s, 5C, FeCp), 72.0 (d, J_{CP} = 9.3 Hz, 1C, FeCp^s), 59.8 (d, $^3J_{CP}$ = 1.7 Hz, 1C, *C*H(Me)NEt$_2$), 59.3 (d, $^3J_{CP}$ = 2.3 Hz, 1C, N*CH*$_2$CH$_3$), 57.3 (d, $^3J_{CP}$ = 2.1 Hz, 1C, N*CH*$_2$CH$_3$), 15.4 (1C, NCH$_2$*CH*$_3$), 15.2 (1C, NCH$_2$*CH*$_3$), 14.0 (s, 1C, CH(*Me*)-NEt$_2$), 5.4 (s, 1C, N≡C−*C*H$_3$). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 43.2 (*P*Ph$_2$), −142.7 ($^1J_{PF}$ = 709.5 Hz, *P*F$_6$).

[(R/S_{Ru},R_C,S_{pl})-RuCp(2-(1-*N*,*N*-dimethylaminoethyl)-1-diphenylphosphinoferrocene)(=C=CHPh)]PF_6 (6a/6b). To a solution of **3** (85 mg, 0.107 mmol) in CH_2Cl_2 (4 mL) was added HC≡CPh (35 μL, 0.321 mmol), and the mixture was stirred for 4 h at room temperature. The solvent was removed under reduced pressure, and the residue was dissolved in 3 mL of CH_2Cl_2. Additional HC≡CPh (12 μL, 0.107 mmol) was

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added, and the mixture was stirred for another 2 h. After that time, the solvent was removed in vacuo and the residue redissolved in 1 mL of CH_2Cl_2. On addition of Et_2O (3 mL) a brown precipitate formed, which was collected on a glass frit, washed with Et_2O (3 × 1 mL), and dried in vacuo. Yield: 85 mg (93%) of a mixture of two diasteromeres in a ratio of 21:1 (de = 91%). Anal. Calcd for $C_{39}H_{39}F_6FeNP_2Ru$: C, 54.81; H, 4.60. Found (from the mixture of both diastereomeres): C, 55.06; H, 4.88. Complex **6b** could not be isolated, and spectroscopic data are taken from the NMR spectra of the mixture. ^{1}H NMR (δ, acetone-d_6, 20 °C): 3.90 (s, 5H, FeCp), 1.82 (d, $^3J_{HH}$ = 7.0 Hz, CH(*Me*)NMe$_2$), all other resonances could not be observed. ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 72.8 (s, 5C, FeCp), all other resonances could not be observed. ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 40.0 (*P*Ph$_2$), −143.6 ($^1J_{PF}$ = 713.3 Hz, *P*F$_6$). Slow diffusion of Et_2O into a CH_2Cl_2 solution of the mixture yields red crystals of the major isomer **6a** in 60% yield (55 mg). ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.01−7.92 (m, 2H, Ph), 7.78−7.71 (m, 3H, Ph), 7.42−7.30 (m, 7H, Ph), 7.19−7.12 (m, 1H, Ph), 7.05−6.69 (m, 2H, Ph), 5.50 (d, $^4J_{PH}$ = 2.4 Hz, 1H, =C=C*H*Ph), 5.46−5.40 (q, $^3J_{HH}$ = 6.7 Hz, 1H, C*H*(Me)NMe$_2$), 5.42 (s, 5H, RuCp), 4.85 (m, 2H, FeCp^s), 4.78 (m, 1H, FeCp^s), 3.86 (s, 5H, FeCp), 3.13 (s, 3H, N*Me*$_2$), 2.47 (s, 3H, N*Me*$_2$), 1.35 (d, $^3J_{HH}$ = 6.7 Hz, CH(*Me*)NMe$_2$). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 350.0 (d, $^2J_{PC}$ = 15.3 Hz, =*C*=CHPh), 144.4 (d, $^1J_{CP}$ = 52.1 Hz, 1C, Ph^1), 136.6 (d, $^2J_{CP}$ = 12.7 Hz, 2C, Ph^{2,6}), 136.5 (d, $^1J_{CP}$ = 42.0 Hz, 1C, Ph$^{1'}$), 133.3 (d, $^4J_{CP}$ = 2.5 Hz, 1C, Ph^4), 132.4 (d, $^2J_{CP}$ = 8.9 Hz, 2C, Ph$^{2',6'}$), 131.5 (d, $^4J_{CP}$ = 2.5 Hz, 1C, Ph$^{4'}$), 130.7 (2C, Ph^{R3,5}), 130.0 (d, $^3J_{CP}$ = 10.2 Hz, 2C, Ph^{3,5}), 129.95 (d, $^3J_{CP}$ = 11.4 Hz, 2C, Ph$^{3',5'}$), 129.7 (1C, Ph^{R1}), 128.1 (1C, Ph^{R4}), 127.7 (2C, Ph^{R2,6}), 121.0 (d, $^3J_{CP}$ = 2.5 Hz, 1C, =C=*C*HPh), 95.3 (d, $^2J_{CP}$ = 20.4 Hz, 1C, FeCp^2), 94.6 (d, $^2J_{CP}$ = 2.2 Hz, RuCp), 77.6 (1C, FeCp^s), 73.4 (d, J_{CP} = 6.3 Hz, 1C, FeCp^s), 73.0 (d, J_{CP} = 8.3 Hz, 1C, FeCp^s), 72.7 (s, 5C, FeCp), 71.4 (d, $^1J_{CP}$ = 50.9 Hz, 1C, FeCp^1), 67.6 (1C, *C*H(Me)NMe$_2$), 63.5 (1C, NMe$_2$), 51.0 (1C, NMe$_2$), 11.9 (1C, CH(*Me*)NMe$_2$). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 41.7 (*P*Ph$_2$), −143.6 ($^1J_{PF}$ = 713.3 Hz, *P*F$_6$).

[(*R*/*S*$_{Ru}$,*R*$_C$,*S*$_{pl}$)-RuCp(2-(1-*N*,*N*-dimethylaminoethyl)-1-diphenylphosphinoferrocene)(CO)]PF$_6$ (7a/7b). A solution of **3** (100 mg, 0.126 mmol) in CH_2Cl_2 (4 mL) was purged with CO for 2 min and was stirred for 3 h at room temperature. After removal of the solvent, the residue was redissolved in 1 mL of CH_2Cl_2 and the product was precipitated upon addition of Et_2O (3 mL). Yield: 89 mg (90%) of a mixture of two diasteromeres in a ratio of 2.4:1 (de = 42%). Anal. Calcd for $C_{32}H_{33}F_6FeNOP_2Ru$: C, 49.25; H, 4.26. Found (from the mixture of both diastereomers): C, 49.43; H, 4.41. The minor diasteromer **7b** could not be isolated, and spectroscopic data are taken from the mixture. ^{1}H NMR (δ, acetone-d_6, 20 °C): 5.45 (s, 5H, RuCp), 3.89 (s, 5H, FeCp), 1.50 (d, $^3J_{HH}$ = 6.6 Hz, CH(*Me*)NMe$_2$), all other resonances could not be assigned unequivocally. ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 87.7 (d, $^2J_{CP}$ = 1.6 Hz, 5C, RuCp), all other resonances could not be assigned unambiguously. ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 39.8 (*P*Ph$_2$), −143.2 ($^1J_{PF}$ = 707.4 Hz, *P*F$_6$). The major isomer **7a** could be obtained in pure form by washing the mixture with small amounts (3 × 0.2 mL) of acetone. Yield: 25 mg (25%) of a bright yellow powder. ^{1}H NMR (δ, CD_3NO_2, 20 °C): 7.99−7.91 (m, 2H, Ph), 7.72 (m, 3H, Ph), 7.47−7.34 (m, 3H, Ph), 7.08−6.99 (m, 2H, Ph), 4.99 (s, 5H, RuCp), 4.84−4.74 (m, 4H, FeCp^s, C*H*(Me)NMe$_2$), 3.87 (s, 5H, FeCp), 3.29 (s, 3H, N*Me*$_2$), 2.45 (s, 3H, N*Me*$_2$), 1.53 (d, $^3J_{HH}$ = 6.7 Hz, 3H, CH(*Me*)NMe$_2$). ^{13}C{^{1}H} NMR (δ, CD_3NO_2, 20 °C): 204.8 (d, $^2J_{CP}$ = 18.0 Hz, 1C, CO), 142.6 (d, $^1J_{CP}$ = 52.9 Hz, 1C, Ph^1), 135.11 (d, $^2J_{CP}$ = 12.0 Hz, 2C, Ph^{2,6}), 135.08 (d, $^1J_{CP}$ = 62.7 Hz, 1C, Ph$^{1'}$), 132.0 (d, $^4J_{CP}$ = 2.7 Hz, 1C, Ph^4), 131.0 (d, $^2J_{CP}$ = 9.8 Hz, 2C, Ph$^{2',6'}$), 130.1 (d, $^4J_{CP}$ = 2.7 Hz, 1C, Ph$^{4'}$), 128.6 (d, $^3J_{CP}$ = 11.4 Hz, 2C, Ph^{3,5}), 128.5 (d, $^3J_{CP}$ = 10.4 Hz, 2C, Ph$^{3',5'}$), 92.8 (d, $^2J_{CP}$ = 20.7 Hz, 1C, FeCp^2), 88.1 (d, $^2J_{CP}$ = 1.6 Hz, RuCp), 75.7 (d, J_{CP} = 1.0 Hz, 1C, FeCp^s), 72.1 (d, J_{CP} = 6.5 Hz, 1C, FeCp^s), 71.9 (d, J_{CP} = 9.3 Hz, 1C, FeCp^s), 71.2 (s, 5C, FeCp), 70.9 (d, $^1J_{CP}$ = 34.9 Hz, 1C, FeCp^1), 70.6 (d, $^3J_{CP}$ = 1.3 Hz, 1C, *C*H(Me)NMe$_2$), 61.2 (d, $^3J_{CP}$ = 2.0 Hz, 1C, NMe$_2$), 48.9 (d, $^3J_{CP}$ = 1.0 Hz, 1C, NMe$_2$), 10.9 (s, 1C, CH(*Me*)NMe$_2$). ^{31}P{^{1}H} NMR (δ, CD_3NO_2, 20 °C): 40.1 (*P*Ph$_2$), −145.9 ($^1J_{PF}$ = 707.0 Hz, *P*F$_6$). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 42.8 (*P*Ph$_2$), −143.2 ($^1J_{PF}$ = 707.4 Hz, *P*F$_6$).

Epimerization of 7a/7b. In a sealed NMR tube, a solution of **7a**/**7b** in CD_3NO_2 at room temperature under a CO atmosphere was irradiated with UV light (75W) under a CO atmosphere for 2 h. The reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, indicating that epimerization took place to give **7a** with a de of >98%. In addition, small amounts (<5%) of two not identifiable byproducts were detected.

[(*R*/*S*$_{Ru}$,*S*$_{pl}$)-RuCp(2-(1-*N*,*N*-dimethylaminomethyl)-1-diphenylphosphinoferrocene)(=C=CHPh)]PF$_6$ (8a/8b). This compound was prepared analogously to **8a**/**8b** with **4** (119 mg, 0.153 mmol) and HC≡CPh (first 50 μL and then 17 μL) as the starting materials. Yield: 119 mg (92%) of a brown precipitate containing a mixture of diasteromeres in a ratio of 28:1 (de = 96%) as an estimation, taken from the integration of the ^{31}P{^{1}H} NMR resonances. Anal. Calcd for $C_{38}H_{37}F_6FeNP_2Ru$: C, 54.30; H, 4.44. Found (both diastereomers): C, 54.22; H, 4.57. Complex **8b** could not be isolated, and NMR data are taken from the isomeric mixture. ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 36.2 (*P*Ph$_2$), −143.6 ($^1J_{PF}$ = 713.3 Hz, *P*F$_6$). **8a** was purified by redissolving the isomeric mixture in CH_2Cl_2 and precipitation with Et_2O. Yield: 90 mg (70%): ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.00−7.92 (m, 2H, Ph), 7.77−7.68 (m, 3H, Ph), 7.46−7.32 (m, 7H, Ph), 7.20−7.15 (m, 1H, Ph), 7.10−7.03 (m, 2H, Ph), 5.50 (m, 6H, RuCp, =C=C*H*Ph), 5.03 (d, $^2J_{HH}$ = 13.9 Hz, 1H, C*H*$_2$NMe$_2$), 4.88 (m, 1H, FeCp^s), 4.77 (m, 2H, FeCp^s), 3.87 (s, 5H, FeCp), 3.03 (d, $^2J_{HH}$ = 13.9 Hz, 1H, C*H*$_2$NMe$_2$), 3.08 (s, 3H, N*Me*$_2$), 2.59 (s, 3H, N*Me*$_2$). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 349.9 (d, $^2J_{PC}$ = 16.2 Hz, =*C*=CHPh), 346.6 (d, $^2J_{PC}$ = 15.3 Hz, =*C*=CHPh), 143.8 (d, $^1J_{CP}$ = 51.2 Hz, 1C, Ph^1), 136.8 (d, $^1J_{CP}$ = 43.1 Hz, 1C, Ph$^{1'}$), 136.5 (d, $^2J_{CP}$ = 12.6 Hz, 2C, Ph^{2,6}), 133.3 (d, $^4J_{CP}$ = 2.7 Hz, 1C, Ph^4), 132.3 (d, $^2J_{CP}$ = 9.9 Hz, 2C, Ph$^{2',6'}$), 131.5 (d, $^4J_{CP}$ = 2.7 Hz, 1C, Ph$^{4'}$), 130.8 (bs, 2C, Ph^{R3,5}), 130.1 (d, $^3J_{CP}$ = 9.9 Hz, 2C, Ph^{3,5}), 130.0 (d, $^3J_{CP}$ = 11.7 Hz, 2C, Ph$^{3',5'}$), 129.7 (1C, Ph^{R1}), 128.1 (1C, Ph^{R4}), 127.6 (1C, Ph^{R2,6}), 127.5 (1C, Ph^{R2,6}), 120.8 (d, $^3J_{CP}$ = 2.8 Hz, 1C, =C=*C*HPh), 94.4 (d, $^2J_{CP}$ = 0.8 Hz, RuCp), 91.3 (d, $^2J_{CP}$ = 20.6 Hz, 1C, FeCp^2), 78.2 (d, J_{CP} = 1.0 Hz, 1C, FeCp^s), 74.7 (d, J_{CP} = 9.0 Hz, 1C, FeCp^s), 72.3 (d, J_{CP} = 6.3 Hz, 1C, FeCp^s), 72.6 (s, 5C, FeCp), 69.7 (d, $^1J_{CP}$ = 52.1 Hz, 1C, FeCp^1), 67.8 (1C, *C*H$_2$NMe$_2$), 67.2 (1C, NMe$_2$), 57.7 (1C, NMe$_2$). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20 °C): 45.5 (*P*Ph$_2$), −142.7 ($^1J_{PF}$ = 709.5 Hz, *P*F$_6$).

[(*R*/*S*$_{Ru}$,*S*$_{pl}$)-RuCp(2-(1-*N*,*N*-dimethylaminomethyl)-1-diphenylphosphinoferrocene)(CO)]PF$_6$ (9a/9b). This compound was prepared analogously to **7a** with **4** (100 mg, 0.128 mmol) as the starting material. Yield: 91 mg (93%) of a yellow precipitate containing a mixture of two diasteromeres in a ratio of 1.8:1 (de = 28%), taken from the integration of the ^{1}H and ^{31}P{^{1}H} NMR spectra. Anal. Calcd for $C_{31}H_{31}F_6FeNOP_2Ru$: C, 48.58; H, 4.08. Found (from the mixture of both diasteromers): C, 48.89; H, 4.33. Complexes **9a/b** could not be separated, and NMR data are taken from the mixture: **9a** (assignment was afforded by comparing the NMR spectra with those of **7a**/**b** and **10a**). ^{1}H NMR (δ, $CDCl_3$, 20 °C): 7.90−7.87 (m, 2H, Ph), 7.74 (m, 3H, Ph), 7.46−7.32 (m, 3H, Ph), 7.12−6.94 (m, 2H, Ph), 4.97 (s, 5H, RuCp), 5.00 (d, $^2J_{HH}$ = 13.5 Hz, 1H, C*H*$_2$NMe$_2$), 4.86−4.65 (m, 3H, FeCp^s), 3.80 (s, 5H, FeCp), 3.13 (d, $^2J_{HH}$ = 13.5 Hz, 1H, C*H*$_2$NMe$_2$), 3.17 (s, 3H, N*Me*$_2$), 2.66 (s, 3H, N*Me*$_2$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 206.6 (d, $^2J_{CP}$ = 19.3 Hz, 1C, CO), 142.4 (d, $^1J_{CP}$ = 49.5 Hz, 1C, Ph^1), 136.7 (d, $^1J_{CP}$ = 63.4 Hz, 1C, Ph$^{1'}$), 135.2 (d, $^2J_{CP}$ = 11.2 Hz, 2C, Ph^{2,6}), 133.2 (d, $^4J_{CP}$ = 2.3 Hz, 1C, Ph^4), 131.38 (d, $^2J_{CP}$ = 9.9 Hz, 2C, Ph$^{2',6'}$), 131.34 (d, $^4J_{CP}$ = 2.4 Hz, 1C, Ph$^{4'}$), 129.5 (d, $^3J_{CP}$ = 10.2 Hz, 2C, Ph^{3,5}), 129.4 (d, $^3J_{CP}$ = 10.1 Hz, 2C,

$Ph^{3',5'}$), 95.2 (d, $^2J_{CP}$ = 20.1 Hz, 1C, $FeCp^2$), 88.2 (d, $^2J_{CP}$ = 1.7 Hz, RuCp), 74.8 (d, J_{CP} = 1.1 Hz, 1C, $FeCp^s$), 73.6 (d, J_{CP} = 6.5 Hz, 1C, $FeCp^s$), 73.4 (d, J_{CP} = 10.2 Hz, 1C, $FeCp^s$), 71.7 (s, 5C, FeCp), 70.4 (d, $^1J_{CP}$ = 55.9 Hz, 1C, $FeCp^1$), 66.7 (1C, CH_2-NMe_2), 65.9 (1C, NMe_2), 55.8 (1C, NMe_2). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 41.5 (PPh_2), −143.4 ($^1J_{PF}$ = 712.1 Hz, PF_6). **9b** (minor diastereomer): ^1H NMR (δ, $CDCl_3$, 20 °C): 7.91−7.86 (m, 2H, Ph), 7.74 (m, 3H, Ph), 7.46−7.32 (m, 3H, Ph), 7.09−6.97 (m, 2H, Ph), 5.18 (s, 5H, RuCp), 5.04 (d, $^2J_{HH}$ = 13.7 Hz, 1H, CH_2NMe_2), 4.88−4.65 (m, 3H, $FeCp^s$), 3.70 (s, 5H, FeCp), 3.23 (d, $^2J_{HH}$ = 13.7 Hz, 1H, CH_2NMe_2), 3.18 (s, 3H, NMe_2), 2.51 (s, 3H, NMe_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 210.1 (d, $^2J_{CP}$ = 17.9 Hz, 1C, CO), 143.2 (d, $^1J_{CP}$ = 49.5 Hz, 1C, Ph^1), 135.2 (d, $^2J_{CP}$ = 10.7 Hz, 2C, $Ph^{2,6}$), 135.0 (d, $^1J_{CP}$ = 59.4 Hz, 1C, $Ph^{1'}$), 133.2 (d, $^4J_{CP}$ = 2.4 Hz, 1C, Ph^4), 131.6 (d, $^2J_{CP}$ = 10.1 Hz, 2C, $Ph^{2',6'}$), 131.3 (d, $^4J_{CP}$ = 2.4 Hz, 1C, $Ph^{4'}$), 129.4 (d, $^3J_{CP}$ = 10.0 Hz, 2C, $Ph^{3,5}$), 129.2 (d, $^3J_{CP}$ = 9.9 Hz, 2C, $Ph^{3',5'}$), 93.8 (d, $^2J_{CP}$ = 19.2 Hz, 1C, $FeCp^2$), 87.2 (d, $^2J_{CP}$ = 1.7 Hz, RuCp), 77.4 (d, J_{CP} = 7.1 Hz, 1C, $FeCp^s$), 75.8 (d, J_{CP} = 1.1 Hz, 1C, $FeCp^s$), 72.3 (d, J_{CP} = 9.9 Hz, 1C, $FeCp^s$), 72.1 (d, $^1J_{CP}$ = 55.9 Hz, 1C, $FeCp^1$), 71.8 (s, 5C, FeCp), 66.5 (1C, CH_2-NMe_2), 64.0 (1C, NMe_2), 53.2 (1C, NMe_2). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 41.4 (PPh_2), −143.4 ($^1J_{PF}$ = 712.1 Hz, PF_6).

[(*R*/S_{Ru},R_C,S_{pl})-RuCp(2-(1-*N*,*N*-diethylaminoethyl)-1-diphenylphosphinoferrocene)(CO)]PF_6 (10a/b). This compound was prepared analogously to **7a** with **5** (100 mg, 0.122 mmol) as the starting material. Yield: 94 mg (95%) of a yellow precipitate containing a mixture of two diasteromeres in a ratio of 15:1 (de = 87%). Anal. Calcd for $C_{34}H_{37}F_6FeNOP_2Ru$: C, 50.51; H, 4.61. Found (both diasteromeres): C, 50.88; H, 4.87. Complex **10b** could not be isolated, and NMR spectroscopic data are taken from the mixture. ^1H NMR (δ, $CDCl_3$, 20 °C): 5.31 (s, 5H, RuCp), 4.18 (s, 5H, FeCp), 1.35 (t, 3H, NCH_2CH_3), 1.10 (t, 3H, NCH_2CH_3). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 43.4 (PPh_2), −143.6 ($^1J_{PF}$ = 713.3 Hz, PF_6). **10a** could be obtained by heating of the mixture of diasteromeres at 62 °C in $CDCl_3$ for 36 h. ^1H NMR (δ, $CDCl_3$, 20 °C): 7.75−7.71 (m, 2H, Ph), 7.69−7.65 (m, 3H, Ph), 7.42−7.38 (m, 3H, Ph), 7.04−6.97 (m, 2H, Ph), 5.00 (s, 5H, RuCp), 4.85 (q, $^3J_{HH}$ = 6.4 Hz, 1H, $CH(Me)NEt_2$), 4.76 (m, 1H, $FeCp^s$), 4.72 (vt, $^3J_{HH}$ = 2.7 Hz, 1H, $FeCp^s$), 4.60 (m, 1H, $FeCp^s$), 3.78 (s, 5H, FeCp), 3.23−3.12 (bm, 1H, NCH_2CH_3), 2.98−2.73 (bm, 3H, NCH_2CH_3), 1.74 (t, 3H, NCH_2CH_3), 1.51 (d, $^3J_{HH}$ = 6.4 Hz, 3H, $CH(Me)NEt_2$), 0.84 (t, 3H, NCH_2CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 205.7 (d, $^2J_{CP}$ = 19.2 Hz, 1C, CO), 141.6 (d, $^1J_{CP}$ = 50.5 Hz, 1C, Ph^1), 136.0 (d, $^1J_{CP}$ = 63.4 Hz, 1C, $Ph^{1'}$), 135.0 (d, $^2J_{CP}$ = 11.7 Hz, 2C, $Ph^{2,6}$), 132.6 (d, $^4J_{CP}$ = 2.4 Hz, 1C, Ph^4), 131.3 (d, $^2J_{CP}$ = 10.0 Hz, 2C, $Ph^{2',6'}$), 131.0 (d, $^4J_{CP}$ = 2.4 Hz, 1C, $Ph^{4'}$), 129.40 (d, $^3J_{CP}$ = 10.0 Hz, 2C, $Ph^{3,5}$), 129.38 (d, $^3J_{CP}$ = 10.2 Hz, 2C, $Ph^{3',5'}$), 93.6 (d, $^2J_{CP}$ = 19.8 Hz, 1C, $FeCp^2$), 88.7 (d, $^2J_{CP}$ = 1.8 Hz, RuCp), 75.0 (d, J_{CP} = 1.0 Hz, 1C, $FeCp^s$), 72.6 (d, J_{CP} = 5.8 Hz, 1C, $FeCp^s$), 72.4 (d, J_{CP} = 10.0 Hz, 1C, $FeCp^s$), 71.4 (s, 5C, FeCp), 70.4 (d, $^1J_{CP}$ = 49.9 Hz, 1C, $FeCp^1$), 67.1 (1C, $CH(Me)NEt_2$), 59.0 (1C, NCH_2CH_3), 57.3 (1C, NCH_2CH_3), 15.3 (1C, NCH_2CH_3), 14.6 (1C, NCH_2CH_3), 14.1 (1C, $CH(Me)NEt_2$). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 42.6 (PPh_2), −143.5 ($^1J_{PF}$ = 712.1 Hz, PF_6).

Acetonitrile Exchange Kinetics on 3 in Acetone-d_6. The CH_3CN exchange in **3** (eq 1) was studied as a function of temperature (Table 2) by monitoring the increase in intensity of the proton NMR signal of free CH_3CN (at 1.97 ppm) and

$$[RuCp(PN^*)(CH_3CN)]PF_6 + CD_3CN \rightarrow [RuCp(PN^*)(CD_3CN)]PF_6 + CH_3CN \quad (1)$$

the decrease of the bound CH_3CN (at +2.63 ppm) after injection of CD_3CN (pn* = **2a**) in the temperature range below −2 °C. Typically 10 mg of **3** was dissolved in 0.5 mL of acetone-d_6. After adjusting to the temperature the deuterated acetonitrile was added by syringe and spectra were taken at regular intervals. The time dependence of the mole fraction $x = [CH_3CN]_c/([CH_3CN]_c + [CH_3CN]_f)$ of coordinated nondeuterated acetonitrile, obtained by integration of the signals, was fitted to eq 2, where x_0 and x_∞ are the values of x at $t = 0$ and ∞, and

$$x = x_\infty + (x_0 - x_\infty)\exp[-kt/(1 - x_\infty)] \quad (2)$$

k is the observed first-order rate constant for the exchange of a particular solvent molecule. The adjustable parameters were x_0, x_∞, and k. Above 55 °C the exchange reaction is fast enough to be followed by ^1H NMR line broadening. From the variable-temperature NMR studies, exchange rate constants were determined by visual comparison of the observed and computer-simulated spectra using the DNMR3 program.[19] Temperature readings were calibrated by using the method of Raiford et al.,[20] corrected to 250.13 MHz, by adding a capillary of methanol to the experimental sample. The temperature dependence of the rate constants is given by the Eyring equation (eq 3). The values of $\Delta H^‡$ and $\Delta S^‡$ were obtained from a plot

$$k = (k_B T/h)(\exp(-(\Delta H^‡ - T\Delta S^‡)/RT) \quad (3)$$

of $\ln(k/T)$ versus $1/T$ (Figure 3) by a weighted linear least-squares regression.[21]

X-ray Structure Determination for 3, 5·CH_2Cl_2, 6a, and 7a. Crystals of **3**, **5**·CH_2Cl_2, and **6a** were obtained by diffusion of Et_2O into CH_2Cl_2 solutions. **7a** was obtained by slow evaporation of an acetone solution. Crystal data and experimental details are given in Table 4. X-ray data were collected on a Siemens Smart CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å, nominal crystal-to-detector distance of 4.45 cm, 0.3° ω-scan frames). Corrections for Lorentz and polarization effects, for crystal decay, and for absorption (program SADABS[22]) were applied. The structures were solved by direct methods using the program SHELXS97.[23] Structure refinement on F^2 was carried out with program SHELXL97.[24] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded.

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Supporting Information Available: Listings of atomic coordinates, anisotropic temperature factors, bond lengths and angles, and least-squares planes for **3**, **5**·CH_2Cl_2, **6a**, **7a**, and superpositions of **6a** and **6a′**, **3** and **5**, and **7a** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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