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Stereochemistry of Chiral Ruthenium- and Iron-cyclopentadienyl Alkylidenecarbene-diphosphine Complexes

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Abstract

The non-rigid behaviour of complexes of the type $[(\eta\text{-}C_5H_5)M(Ph_2PCHRCHR'PPh_2)(C{=}CHR'')]PF_6$ (M = Ru or Fe; R,R' = H, CH_3 or $-(CH_2)_3-$; R'' = CH_3, C_6H_5 or t-C_4H_9; not all combinations) has been investigated through ^{31}P NMR spectroscopy at variable temperature. The preferred geometry of the complexes in solution is the one in which the plane of the alkylidenecarbene moiety is perpendicular to the plane containing the carbene carbon atom, the metal atom and the centroid of the cyclopentadienyl ligand, the barrier of rotation being 9–10 kcal/mol. When $R \neq R'$, at least in the case of the ruthenium complexes, the stereogenic metal atom is sterically stable. For the complexes containing chiral diphosphine ligands, the two rotamers are in a diastereomeric relationship. The differences in the population of the two diastereomers (asymmetric induction) seem to be mostly determined by steric reasons. They increase on going from ruthenium to iron, by increasing the size of the alkylidene group on the carbene atom and by using diphosphines which cause a larger crowding around the metal. Furthermore for the complexes having a stereogenic metal atom, the asymmetric induction also depends on the absolute configuration at the metal (the chiral ligand being the same).

Introduction

Transition metal alkylidenecarbene (vinylidene) complexes have recently attracted much interest [1]. Possible pathways for their formation have been proposed [1–3] and their reactivity has been analyzed both from a theoretical [4] and a practical point of view [1]. Nevertheless the problems connected with the geometry of such complexes have received much less attention [4–7]. We have recently reported on the first determination of the preferred geometry in solution for iron complexes of the type $[(\eta\text{-}C_5H_5)M(Ph_2PCHRCHR'PPh_2)(C{=}CHR'')]PF_6$ (M = Fe) [8]. Furthermore, we could prepare analogous ruthenium complexes (M = Ru; R = H; R' = CH_3; R'' = CH_3 or C_6H_5) having chiral centers both at the diphosphine ligand and at the metal atom in a diastereomerically pure form [9]. We report here (a) their non-rigid behaviour in solution, (b) the connected energy barrier, (c) the diastereomeric equilibria and (d) a comparison of the asymmetric induction for those and for the corresponding (previously reported [7]) iron complexes.

Results and Discussion

Following previous literature reports [10], the alkylidenecarbene complexes (represented in Fig. 1) were prepared through reaction of the corresponding halide complexes with acetylenes in methanolic solution in the presence of a halogen scavenger such as KPF_6 or NH_4PF_6. However, in contrast to previous reports, the preparation was carried out at room temperature [8] using finely milled starting material. The milling permits shortening of the reaction time and, as a consequence, recovery of the product without contamination from the carbene complexes $[(\eta\text{-}C_5H_5)Ru(Ph_2PCHRCHR'$-

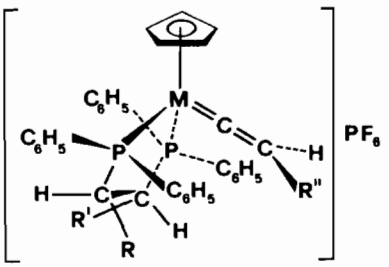

Fig. 1. General formula of the complexes investigated (M = Ru: R = R' = H, R'' = C_6H_5 **1**. R = R' = CH_3, R'' = C_6H_5 **2**; R'' = t-C_4H_9 **3**. R,R' = $-(CH_2)_3-$, R'' = C_6H_5 **4**; R'' = CH_3 **5**. R = CH_3, R' = H, R'' = CH_3 **6**; R'' = C_6H_5 **7**. R = H, R' = CH_3, R'' = CH_3 **6'**; R'' = C_6H_5 **7'**. M = Fe: R = R' = CH_3, R'' = C_6H_5 **8**; R'' = CH_3 **9**. R, R' = $-(CH_2)_3-$, R'' = C_6H_5 **10**; R'' = CH_3 **11**; R'' = t-C_4H_9 **12**).

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TABLE I. Some NMR Parameters of the Complex $[(\eta\text{-}C_5H_5)Ru(Ph_2PCHRCHR'PPh_2)(C{=}CHR'')]PF_6$ (Fig. 1)

Complex	R	R'	R''	T (°C)	δ(Cp)[a]	P_A[b]	P_B[b]	J_{PP}[b]	δ(=C=)[c]	J_{CP}[c]
1	H	H	C_6H_5	298	5.60	76.4			n.d.[e]	n.d.
				165	n.d.	77.7	75.7	21	n.d.	
2	CH_3	CH_3	C_6H_5	298	5.17	76.8	72.5	34	354	13;16
				168	n.d.	75.3	79.7	31	n.d.	n.d.
					n.d.	76.9	68.5	36	n.d.	n.d.
3	CH_3	CH_3	t-C_4H_9	300	4.88	77.9	72.0	37	349	13
				150	n.d.	77.0	68.0	n.d.	n.d.	n.d.
					n.d.	79.0	76.0	n.d.	n.d.	n.d.
4	$-(CH_2)_3-$		C_6H_5	298	5.34	57.1	51.4	34	355	13;17
				163	n.d.	56.7	55.9	34	n.d.	n.d.
5	$-(CH_2)_3-$		CH_3	298	5.12	60.0	54.0	35	347	12; 20
				153	n.d.	60.2	57.6	34	n.d.	n.d.
6	CH_3	H	CH_3	300	5.32	83.7	63.5	29	347	14;18
				163	n.d.	82.0	67.4	28	n.d.	n.d.
					n.d.	83.6[d]	65.3[d]	n.d.	n.d.	n.d.
7	CH_3	H	C_6H_5	298	5.16	80.0	61.0	28	355	13;18
				169	n.d.	78.6	64.5	28	n.d.	n.d.
6'	H	CH_3	CH_3	300	5.15	90.7	74.1	24	347	15
				153	n.d.	96.0[d]	70.1[d]	n.d.	n.d.	n.d.
					n.d.	90.5[d]	80.7[d]	n.d.	n.d.	n.d.
7'	H	CH_3	C_6H_5	298	5.42	83.1	67.9	26	354	15
				151	n.d.	86.0	63.7	25	n.d.	n.d.
					n.d.	68.4	78.1	28	n.d.	n.d.

[a] ^1H NMR. [b] ^{31}P NMR. [c] ^{13}C NMR. [d] Not resolved signals. [e] n.d. = not determined.

$PPh_2)C(OCH_3)CH_2R'']PF_6$, which arise from further reaction of the alkylidenecarbene complexes with methanol [11]. Furthermore, using this procedure, the stereochemistry at the ruthenium atom is maintained, thus allowing the preparation of complexes **6**, **7**, **6'**, and **7'**, in a stereochemically pure form. Some NMR parameters of the ruthenium complexes are reported in Table I. For complex **6** the crystal structure determination [9] showed that the plane containing the alkylidenecarbene ligand is orthogonal to the plane identified by the centroid of the cyclopentadienyl ligand, the ruthenium atom and the unsubstituted carbon atom of that ligand. A similar geometry had been found for the analogous complex containing the trimethylphosphine ligand [8]. Since this geometry cannot be confidently extrapolated for complexes in solution, we have synthesized the known triphenylphosphine complex $[(\eta\text{-}C_5H_5)Ru(PPh_3)_2(C{=}CHC_6H_5)]PF_6$ [10] and have studied by ^{31}P NMR its characteristics as a function of temperature. However, even though we could observe splitting of the single line (43.1 ppm at room temperature) at 153 K (121 MHz), we could not reach the limiting spectrum due to the low solubility. Therefore an unambiguous stereochemical assignment was not possible in this case. This has been possible, subject to a reasonable assumption (*vide infra*), in the case of the complex $[(\eta\text{-}C_5H_5)Ru(diphos)(C{=}CHC_6H_5)]PF_6$ (**1**). Fully analogous to the corresponding iron complex [7], the ^{31}P single resonance at 76.6 ppm observable at room temperature, splits at 194 K and eventually at 165 K is transformed into an A–B quartet (Table I). A rotational barrier of 9.1 kcal/mol can be extrapolated from the coalescence temperature. This barrier appears to be comparable to that for the analogous iron complex [7] (9.4 kcal/mol). The A–B quartet can be reconciled with the geometry found in the solid state, if we assume that the λ–δ interconversion of the two diastereomeric forms of the chelation ring is still rapid at the temperature of the slow exchange spectrum, which appears the most reasonable assumption [7, 12]. In fact complex **2**, in which the chelation ring exists only in the δ confirmation [13] (due to the (**S**) absolute configuration of the two asymmetric carbon atoms) exhibits the same non-rigid behaviour. The two doublets, due to the two diastereotopic phosphorus atoms, evolve in the low temperature spectrum in two sets of two doublets (having equal intensities) arising from the two diastereomeric rotamers. The barrier to rotation (~9.0 kcal/mol) appears to

TABLE II. Ratio Between the Populations for the Two Diastereomeric Conformations of the Complexes $[(\eta\text{-}C_5H_5)M(Ph_2PCHR\text{-}CHR'PPh_2)(C{=}CHR'')]PF_6$ (Fig. 1) at ~160 K.

R	R′	R″	Absolute configuration	Diastereomeric ratio	
				M = Fe	M = Ru
H	CH_3	C_6H_5	$(R)_{Ru}$, $(R)_C$		78/22
CH_3	H	C_6H_5	$(S)_{Ru}$, $(R)_C$		>90/10
H	CH_3	CH_3	$(R)_{Ru}$, $(R)_C$		50/50
CH_3	H	CH_3	$(S)_{Ru}$, $(R)_C$		90/10
CH_3	CH_3	C_6H_5	(*S*,*S*)	86/14	50/50
CH_3	CH_3	CH_3	(*S*,*S*)	55/45	
CH_3	CH_3	t-C_4H_9	(*S*,*S*)		~65/35
$-(CH_2)_3-$		C_6H_5	(*S*,*S*), (*R*,*R*)	>90/10	>90/10
$-(CH_2)_3-$		CH_3	(*S*,*S*), (*R*,*R*))	>90/10	90/10
$-(CH_2)_3-$		t-C_4H_9	(*S*,*S*), (*R*,*R*)	>90/10	

be almost independent of the diphosphine used. However, such a barrier is influenced by the alkylidene group bound to the carbene atom. In fact complex **3** has a lower coalescence temperature and the signals assignable to the two rotamers are still poorly resolved at 150 K and permit only a rough estimation of the relative population of the two diastereomers.

In complexes **7** and **7′** (as well as in complexes **6** and **6′**) the ruthenium atom is a chiral center with opposite absolute configuration for the two complexes. These compounds are stable in CD_2Cl_2 solution (at least for some days) with respect to possible epimerization, *i.e.*, they do not interconvert. Therefore any dissociative mechanism which would be responsible for the observed non-rigid behaviour appears unprobable. In the low temperature spectrum of complex **7′** the two diastereomeric rotamers are clearly separated. Again the rotational barrier does not appear to be influenced by the diphosphine ligand. However, the decrease of the temperature in the case of compound **7** affects the relative position of the two doublets (Table I). In fact only one species appears at ~170 K. Two species appear in the low temperature spectra of **6** and **6′**. Due to a somewhat lower rotational barrier, some doublets are not completely resolved (Table I). Both complexes containing the *trans*-1,2-cyclopentanediylbis(diphenylphosphine) ligand (**4** and **5**) show only one species in the low temperature spectra.

In Table II the relative populations at low temperature for the two diastereomeric conformations of the complexes investigated are reported. These results are compared with those obtained for the previously investigated similar iron compounds. Unfortunately a complete identification of the geometry of the complexes (*i.e.*, the determination of the configuration of the alkylidenecarbene ligand in the two diastereomeric rotamers) does not appear possible, at the moment. Furthermore, in some cases an accurate determination of the diastereomeric ratio is also impossible. In fact, when we do not see any sign of a second species in the low temperature spectrum, we assume its population to be less than 10% under those conditions. The rather high limit of detection [14] could obscure important differences in energy between the diastereomers of different complexes. Nevertheless some conclusions are possible. The asymmetric induction is ~0, 56 and >80% for complexes **2**, **7′** and **7** respectively. In complex **2** the ruthenium atom is chirotopic [15], whereas in **7′** and **7** it is stereogenic [15] and it has opposite absolute configuration for the two complexes. Analogously, asymmetric induction is ~0 and 80% for complexes **6′** and **6**. For the complexes containing the (R)-1,2-propanediylbis(diphenylphosphine) ligand (R = CH_3, R′ = H) and either the benzylidenecarbene or the ethylidenecarbene ligand, the asymmetric induction is higher when the ruthenium atom has the *S* absolute configuration. As already pointed out, we have no criterium to decide whether the configuration of the alkylidenecarbene ligand is influenced by the absolute configuration at the metal.

In fact, the CD-spectra of complexes **2**, **7** and **7′** (Fig. 2) in the visible region show two bands, one at about 510–520 nm and the second at about 390–400 nm. Both bands are negative for **2** and positive for **7** and **7′**; therefore they appear to be mostly influenced by the opposite configuration of the chiral diphosphine ligands [16]. Some differences in the intensities of these, and particularly of the second band might infer an influence of the benzylidenecarbene ligand; however, due to the limited number of complexes available, no definitive conclusion appears possible.

The difference in population between the two conformers appears to be mostly controlled by steric factors. It is larger for neopentylidene than for benzylidene and for benzylidene than for the ethyl-

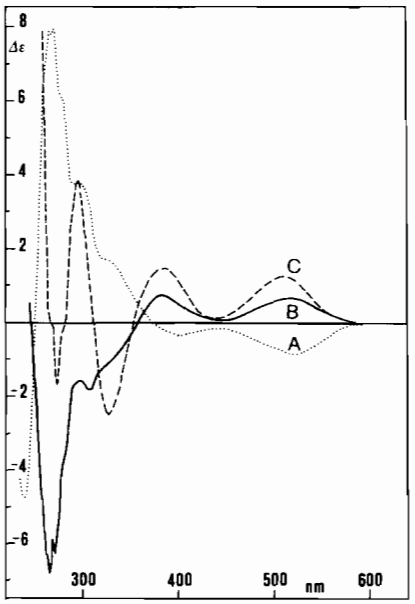

Fig. 2. CD-spectra of **2** (A), **7'** (B) and **7** (C).

idene substituent on the carbene atom. Clearly such substituents must be arranged in the chiral pocket formed by the phenyl substituent on the phosphorus atom. The same steric factors appear to operate also in the iron complexes; asymmetric induction is higher for **8** (containing the benzylidenecarbene ligand) than for **9** (ethylidenecarbene). Furthermore asymmetric induction is higher for the iron than for the corresponding ruthenium complexes, as expected on the basis of shorter bond distances. Space filling models show a more congested situation (*i.e.*, a smaller pocket) in the complexes containing the cypenphos ligand with respect to the other diphosphines examined. This situation appears, in fact, to be reflected in the higher asymmetric induction caused by this ligand. Unfortunately the differences in the diastereomeric population for complexes **10**, **11** and **12** cannot be determined.

The possible influence of a chiral center at the metal in transformations concerning prochiral ligands within transition metal complexes (having the same inducing chiral ligand) both for stoichiometric [17] and catalytic reactions has been stressed [18]. The reported results show for the first time (as far as we are aware) the influence of the chirality at the metal and of different metals on diastereomeric equilibria arising from the presence of prochiral ligands. Studies on similar olefin complexes show similar results.

Experimental

General Data

All synthetic manipulations were performed under nitrogen. Infrared spectra were taken in KBr-disk or in nujol on a Perkin-Elmer 397 spectrometer. Brucker models AM 300 WB and WH90 spectrometers supplied the NMR spectra, which were reported as δ values in ppm downfield from internal Me_4Si or from external H_3PO_4 (85%). Low temperature NMR spectra were recorded in $CDCl_3$–CD_2Cl_2 (30:70). Coupling constants are ±2 Hz. Rotational barriers have been evaluated from the coalescence temperature [19].

Starting Materials

Methylene chloride was distilled under nitrogen from P_2O_5, CH_3OH from Mg, toluene from Na and pentane and ether from $LiAlH_4$. Phenylacetylene and t-butylacetylene (Fluka products) were distilled under nitrogen before use. 1,2-Ethanediylbis(diphenylphosphine) (diphos), was obtained from Fluka and used without further purification. (*S,S*)-1,2-Dimethyl-1,2-ethanediylbis(diphenylphosphine)(chiraphos) [13], *rac*-1,2-cyclopentanediylbis(diphenylphosphine)(cypenphos) [20], (η-C_5H_5)Ru(PPh_3)$_2$Cl [10], (*S,S*)-(η-C_5H_5)RuCl(chiraphos) [16] (*S,S*)-[(η-C_5H_5)-Ru(chiraphos) (C=CHC_6H_5)]PF_6 [21], (η-C_5H_5)Fe-$(CO)_2Br$ [22] $(S)_{Ru}$, $(R)_C$- and $(R)_{Ru}$, $(R)_C$-[(η-C_5H_5)Ru(prophos)(C=CHC_6H_5)]PF_6 [9] $(S)_{Ru}$, $(R)_C$- and $(R)_{Ru}$, $(R)_C$-[(η-C_5H_5)Ru(prophos)(C=$CHCH_3$)]PF_6, [(η-C_5H_5)M(diphos)(C=CHPh)]PF_6 (M = Ru [10], Fe [7]) were prepared according to described procedures.

Preparation of rac-(η-C_5H_5)Ru(cypenphos)Cl

3.38 g (4.66 mmol) of (η-C_5H_5)Ru(PPh_3)$_2$Cl and 2.10 g (4.80 mmol) of cypenphos were dissolved in 100 ml of toluene and refluxed for 4 h. The solvent was removed under vacuum and the residue was extracted 3 times with 150 ml ethylether. The solid was dissolved in 50 ml hot toluene and filtered over celite. The solution was concentrated to 25 ml and slowly cooled down to room temperature. The resulting red–orange crystals were filtered and washed with ethylether. Yield 2.2 g (74%). ^1H NMR (δ, C_6D_6) 1.00 (m, 1H), 1.16 (m, 1H), 1.43 (m, 2H), 1.70 (m, 2H), 2.62 (m, 1H), 3.52 (m, 1H), 4.34 (s, 5H), 6.99–7.41 (m, 16H), 7.62–7.65 (m, 2H), 8.43–8.50 (m, 2H); ^{31}P NMR (ppm, C_6D_6) 42.1 and 63.6 (d, J(P–P) 48 Hz). *Anal.* Calc. for $C_{34}H_{33}ClP_2Ru$: C, 63.79; H, 5.20. Found: C, 63.48; H, 5.01%.

*Preparation of (S,S)-[(η-C_5H_5)Ru(chiraphos)(C=$CHC_4H_9^t$)]PF_6 (**3**)*

1.35 g (2.11 mmol) of (η-C_5H_5)Ru(chiraphos)Cl, 1.14 g of KPF_6 and 2 ml of t-butylacetylene in 20 ml methanol were stirred at room temperature for 3.5 h. The solvent was removed under vacuum, the residue was washed 3 times with 15 ml n-pentane and dissolved in 17 ml CH_2Cl_2. After filtration and removal of the solvent, the residue was washed with n-pentane and dried. 1.50 g (85% yield) of flesh-

colored microcrystalline material were recovered. ^{1}H NMR (δ, $CDCl_3$) 0.69 (s, t-C_4H_9), 0.91 (dd, J(H–H) 6.5 Hz, J(P–H) 13.6 Hz, CH_3), 1.10 (dd, J(H–H) 6.5 Hz, J(P–H) 13.7 Hz, CH_3), 2.60 (m, CH), 2.94 (m, CH), 3.59 (t, J(P–H) 2.3 Hz, =CH), 4.88 (s, C_5H_5), 7.08–7.14 (m, 2H) and 7.26–7.69 (m, 18H) (both C_6H_5); ^{31}P NMR (ppm, CD_2Cl_2/$CDCl_3$) 72.0 and 77.9 (d, J(P–P) 37 Hz); ^{13}C NMR (ppm, CD_2Cl_2/$CDCl_3$) 15.2 (dd, J(P–C) 4.1 and 18.2 Hz), 15.8 (dd, J(P–C) 4.3 and 17.3 Hz), 31.6 (s), 31.7 (s), 37.0 (dd, J(P–C) 14.8 and 33.2 Hz), 42.2 (dd, J(P–C) 16.2 and 33.2 Hz), 93.3 (s), 125.6 (s), 128.6–135.2 (m). *Anal.* Calc. for $C_{39}H_{43}F_6P_3Ru$: C, 57.14; H, 5.29. Found: C, 56.69; H, 5.21%.

Preparation of rac-[(η-C_5H_5)Ru(cypenphos)(C=CHC_6H_5)]PF_6 (4)

The procedure was identical to that used for the previous preparation. Starting with 0.48 g (0.74 mmol) of (η-C_5H_5)Ru(cypenphos)Cl, 0.52 g (83% yield) of salmon pink crystals of **4** were obtained. ^{1}H NMR (δ, CD_2Cl_2) 1.12–1.42 (m, 2H), 1.90–2.33 (m, 4H), 3.12 (m, 1H), 3.47 (m, 1H), 5.12 (t, J(P–H) 1.4 Hz, = CH), 5.33 (s, C_5H_5), 6.48–6.50 (m, 2H), 6.95–6.99 (m, 2H), 7.23–7.68 (m, 21H) (all C_6H_5); ^{31}P NMR (ppm, CD_2Cl_2) 50.9 and 56.6 (d, J(P–P) 34.8 Hz), –144 (h, J(F–P) 710 Hz); ^{13}C NMR (ppm, CD_2Cl_2/$CDCl_3$) 23.8 (dd, J(P–C) 4 and 17.4 Hz), 25.3 (dd, J(P–C) 4 and 18.8 Hz), 31.1 (t, J(P–C) 8.2 Hz), 48.1 (dd, J(P–C) 17.4 and 35 Hz), 50.2 (dd, J(P–C) 17.1 and 40 Hz), 92.7 (s), 119 (s), 122–136 (C_6H_5), 355 (dd, J(P–C) 13 and 17 Hz). *Anal.* Calc. for $C_{42}H_{39}F_6P_3Ru$: C, 59.23; H, 4.62. Found: C, 59.72; H, 4.78%.

Preparation of rac-[(η-C_5H_5)Ru(cypenphos)(C=CH-CH_3)]PF_6 (5)

0.20 g (0.31 mmol) of (η-C_5H_5)Ru(cypenphos)Cl was allowed to react with 0.15 g (0.92 mmol) of NH_4PF_6 under a propyne atmosphere in 10 ml CH_3-OH for 2 h, until yellow–orange solution was obtained. After removal of the solvent the crude product was recrystallized from CH_2Cl_2/n-hexane to give 0.20 g (80% yield) of chrome-yellow crystals. ^{1}H NMR (δ, CD_2Cl_2) 1.02 (d, J(H–H) 7.3 Hz, CH_3), 1.35 (m, 2H), 1.96 (m, 4H), 3.17 (m, 2H), 4.00 (qt, J(H–H) 7.3 Hz, J(P–H) 1.5 Hz, = CH), 5.12 (s, 5H), 7.14 (m, 20H); ^{31}P NMR (ppm, CD_2Cl_2) 53.6 and 59.6 (d, J(P–P) 36.6 Hz); ^{13}C NMR (ppm, CD_2Cl_2), 24.3 (m), 30.8 (t), 48.5 (m), 91.5 (s), 198.5 (s), 129–132 (C_6H_5), 347 (dd, J(P–C) 12 and 21 Hz). *Anal.* Calc. for $C_{37}H_{37}F_6P_3Ru$: C, 56.28; H, 4.72. Found: C, 55.43; H, 4.71%.

Preparation of (S,S)-(η-C_5H_5)Fe(chiraphos)Br

According to a literature procedure for the diphos complex, 2 g (4.69 mmol) of chiraphos and 4.69 (4.692 mmol) of (η-C_5H_5)Fe(CO)$_2$Br were dissolved in 500 ml of benzene and irradiated under reflux with a Hanovia lamp (450 W) for 1 h [21]. After filtration and removal of the solvent the residue was dissolved in 15 ml CH_2Cl_2. Then 200 ml of (n-pentane were allowed to slowly diffuse in the solution which causes crystals formation. Repetition of the crystallization process afforded 1.52 g (52% yield) of large black crystals (m.p. >190 °C (dec.)). Lines in the ^{1}H NMR spectra were rather broad due probably to some paramagnetic impurity. It was impossible to obtain a reasonable ^{31}P NMR spectrum. ^{1}H NMR (δ, C_6D_6) 0.93 (broad m, 6 H), 2.00 (broad m, 1 H), 2.88 (broad m, 1 H), 4.04 (broad s, 5 H), 7.15 (broad m, 16 H), 7.68 (broad m, 2 H), 8.50 (broad m, 2 H). *Anal.* Calc. for $C_{33}H_{33}P_2BrFe$: C, 63.18; H, 5.30; Br, 12.74. Found: C, 63.02; H, 5.30; Br, 12.49%.

Preparation of rac-(η-C_5H_5)Fe(cypenphos)Br

Analogous to the previous preparation 2.19 g (5 mmol) of cypenphos and 1.29 g (5 mmol) of (η-C_5H_5)Fe(CO)$_2$Br were irradiated in 500 ml benzene for 1 h. In spite of repeated crystallization from benzene/n-pentane, no sufficiently pure material was obtained. The product was nevertheless used with success for further transformation. *Anal.* Calc. for $C_{34}H_{33}P_2FeBr$: C, 63.07; H, 5.20; Br, 12.50. Found: C, 68.02; H, 5.64; Br, 10.49%.

Preparation of (S,S)-[(η-C_5H_5)Fe(chiraphos)(C=CHC_6H_5)]PF_6 (8)

The procedure was the same as that used for the preparation of (**5**). Starting with 0.785 g (1.25 mmol) of (*S,S*)-(η-C_5H_5)Fe(chiraphos)Br, 1.30 g of KPF_6, 5 ml of $C_6H_5C{\equiv}CH$ in 30 ml of methanol, 0.90 g of light-brown microcrystals of **8** were obtained. ^{1}H NMR (δ, CD_2Cl_2) 0.98–1.32 (m, 6 H), 2.84 (m, 1 H), 3.07 (m, 1 H), 5.01 (t, C_5H_5, J(P–H) 1.1 Hz), 5.76 (t, =CH, J(P–H) 3.5 Hz), 6.49–6.60 (m, 2 H) and 7.00–7.70 (m, 23 H); ^{31}P NMR (ppm, CD_2Cl_2/$CDCl_3$ 7:3), 94.7 and 93.0 (d, J(P–P) 52.7 Hz), –143.8 (h, J(P–F) 711 Hz); ^{13}C NMR (ppm, CD_2Cl_2/$CDCl_3$ 7:3), 15.8 (dd, J(P–C) 4.5 and 14.3), 16.9 (dd, J(P–C) 3.3 and 16.2 Hz), 39.1 (dd, J(P–C) 14.0 and 29.0 Hz), 40.1 (dd, J(P–C) 13.3 and 34.2 Hz), 90.6 (s), 122–135 (m), 365 (dd, J(P–P) 29.3 and 35.4. IR (Nujol): 1645 (m), 1624 (m), 840 (s) cm^{-1}. *Anal.* Calc. for $C_{41}H_{39}F_6P_3Fe$: C, 61.98; H, 4.95. Found: C, 61.50; H, 4.80%.

Preparation of (S,S)-[(η-C_5H_5)Fe(chiraphos)(C=CH-CH_3)]PF_6 (9)

The same procedure used in the preparation of **5** was followed. Starting with 0.200 g (0.32 mmol) of (*S,S*)-(η-C_5H_5)Fe(chiraphos)Br, 0.16 g of NH_4PF_6 in 20 ml of CH_3OH under propyne atmosphere for 2 h 0.190 g (82% yield) of **9** were obtained (yellow–orange crystals). ^{1}H NMR (δ, CD_2Cl_2) 1.11 (ddd, 3H,

J(H–H) 7.0 Hz, J(P–H) 0.6 and 13.4 Hz), 1.26 (ddd, 3 H, J(H–H) 6.7 Hz, J(P–H) 0.9 and 12.8 Hz), 1.35 (m, 3 H), 4.70 (m, 1 H), 4.86 (t, 5 H, J(P–H) 0.9 Hz), 7.04–7.64 (m, 20 H); ^{31}P NMR (ppm, $CD_2Cl_2/CDCl_3$ 7:3) 100.9 and 96.1 (d, J(P–P) 50.8 Hz, –143.8 (h, J(P–F) 711 Hz); ^{13}C NMR (ppm, $CD_2Cl_2/CDCl_3$ 7:3), 16.3 (d, J(P–C) 16 Hz), 17.6 (d, J(P–C) 16 Hz), 40.3 (m) 89 (s), 119 (s), 129–136 (m), 358.6 (d, J(P–C) 30.0 Hz). IR (Nujol) 1645 (m), 1624 (m), 840 (s) cm^{-1}. *Anal.* Calc. for $C_{36}H_{37}F_6P_3Fe$: C, 59.03; H, 5.09. Found: C, 58.82; H, 5.11%.

Preparation of rac-[(η-C_5H_5)Fe(cypenphos)(C=CHC$_6$H$_5$)]PF$_6$ (10)

This complex was prepared in the same manner as the corresponding ruthenium derivative. Starting with 1.052 g (1.646 mmol) of (η-C_5H_5)Fe(cypenphos)Br, 1.0 g of KPF_6 and 5 ml $C_6H_5C{\equiv}CH$ in 30 ml methanol, 1.16 g (87% yield) of brown microcrystalline **10** were obtained. ^{1}H NMR (δ, $CDCl_3$), 1.10 (m, 2 H), 1.52 (m, 2 H), 2.00 (m, 3 H), 2.20 (m, 1 H), 3.08 (m, 1 H), 3.46 (m, 1 H), 5.00 (s, 5 H), 5.79 (t, 1 H, J(P–H) 3.3 Hz), 6.46 (m, 2 H), 7.20–7.64 (m, 21 H); ^{31}P NMR (ppm, $CD_2Cl_2/CDCl_3$ 7/3), 71.6 and 70.0 (d, J(P–P) 61 Hz), –143.8 (h, J(F–P) 711 Hz); ^{13}C NMR (ppm, $CD_2Cl_2/CDCl_3$ 7/3) 24.2 (dd, J(P–C) 6 and 16 Hz), 26.3 (dd, J(P–C) 6 and 17 Hz), 30.1 (t, J(P–C) 8 Hz), 48.0 (dd, J(P–C) 16.4 and 30.9), 49.6 (q, J(P–C) 15.4 and 38.2), 89.7 (s), 122–136 (m), 368 (dd, J(P–C) 29.4 and 37.2 Hz) IR: (KBr pill) 1967 (m), 1644 (m), 1622 (m), 1595 (m), 1573 (m), 841 (s) cm^{-1}. *Anal.* Calc. for $C_{42}H_{39}F_6P_3Fe$: C, 62.54; H, 4.87. Found: C, 62.52; H, 4.66%.

Preparation of rac-[(η-C_5H_5)Fe(cypenphos)(C=CH-CH$_3$)]PF$_6$ (11)

Similar to the preparation of **5** 0.180 g (80% yield) of yellow **11** was obtained starting with 0.200 g (0.31 mmol) of (η-C_5H_5)Fe(cypenphos)Br. ^{1}H NMR (δ, CD_2Cl_2) 1.20 (dd, 3 H, J(H–H) 7.6 Hz, J(P–H) 1.2 Hz), 1.60 (m, 3H), 1.99–2.18 (m, 4 H), 3.04 (m, 1 H), 3.34 (m, 1 H), 4.86 (t, 5 H, J(P–H) 1 Hz), 7.25–7.72 (m, 20 H); ^{31}P NMR (ppm, CD_2Cl_2/$CDCl_3$: 7/3) 72.1 and 74.6 (d, J(P–P) 61.4 Hz), –143.8 (h, J(P–F) 711 Hz); ^{13}C NMR (ppm, $CD_2Cl_2/CDCl_3$: 7/3) 24.3 (m), 26.2 (m), 30.2 (m), 49.0 (m), 88.7 (s), 119 (s), 128–137 (m), 361.5 (dd, J(P–C) 28 and 37 Hz). IR (Nujol) 1690 (m), 1660 (m), 840 (s). *Anal.* Calc. for $C_{37}H_{37}F_6P_3Fe$: C, 59.69; H, 5.01. Found: C, 58.67; H, 5.11%.

Preparation of rac-[(η-C_5H_5)Fe(cypenphos)(C=CHC$_4$H$_9^t$)]PF$_6$ (12)

Analogous to the preparation of **5** 0.434 g (0.68 mmol) of (η-C_5H_5)Fe(cypenphos)Br, 0.44 g of KPF_6 and 2.5 ml of t-$C_4H_9C{\equiv}CH$ in 20 ml CH_3OH were reacted for 3.5 h. The recovered red material was recrystallized from CH_2Cl_2/n-pentane. Yield 0.42 g (49%). ^{1}H NMR (δ, $CDCl_3$) 0.76 (s, 9 H), 1.25 (m, 2 H), 1.58 (m, 1H), 2.10 (m, 3 H), 3.05 (m, 1 H), 3.22 (m, 1 H), 4.55 (t, 1 H, J(P–H) 1.1 Hz), 4.78 (s, 5 H), 7.20–7.55 (m, 20 H); ^{31}P NMR (ppm, $CD_2Cl_2/CDCl_3$ 7/3) 73.8 and 68.2 (d, J(P–P) 60.5 Hz) –143 (h, J(P–F) 711); ^{13}C NMR (ppm, $CD_2Cl_2/CDCl_3$: 7/3) 24.8 (m), 26.4 (m), 32.0 (s), 48.4 (dd, J(P–C) 17.0 and 31.4 Hz), 49.4 (dd, J(P–C) 16.4 and 36.8 Hz), 89.3 (s), 128–140 (m), 364.0 (dd, J(P–C) 28 and 36 Hz). IR (KBr pill) 1670 (m), 1642 (m), 835 (s). *Anal.* Calc. for $C_{40}H_{43}F_6P_3Fe$: C, 61.08; H, 5.51; Found: C, 60.58; H, 5.44%.

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