Electronic Effects in Asymmetric Catalysis. Synthesis and Structure of Model Rhodium Complexes Containing Ferrocenyl Ligands for Use in the Hydroboration Reaction

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A series of new rhodium complexes with chiral ferrocenyl chelating ligands containing a tertiary phosphine and a pyrazole moiety have been obtained in good yields from the reaction of the corresponding P,N ligand (**1a**−**p**) with $[Rh(1,5\text{-}COD)_2]BF_4$, $[Rh(CO)_2Cl]_2$, and $[Rh(COE)_2Cl]_2$. The electronic influence of the P,N ligands has been evaluated by the measurement of the carbonyl stretching vibration in the compounds **5a**−**p**. Qualitative trend correlations between ν(CO) values for such complexes and the enantioselectivities obtained in the Rh-catalyzed hydroboration of styrene utilizing the corresponding ligands have been found. Thus, both electron-donating groups on the pyrazole and electron-withdrawing substituents on the phosphine lead to both higher enantioselectivities and higher CO stretching frequencies. The compounds [{1-{(*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl}-3,5-dimethyl-1*H*-pyrazole}Rh(1,5-COD)]BF_4 (**3a**), [{1-{(*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl}-3,5-bis(trifluoromethyl)-1*H*-pyrazole}Rh(1,5-COD)]BF_4 (**3h**), [{1-{(*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl}-3,5-dimethyl-1*H*-pyrazole}Rh(CO)Cl] (**5k**), and [{1-{(*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl}-3,5-dimethyl-1*H*-pyrazole}Rh(CO)Cl] (**5n**) have been characterized by X-ray diffraction and were found to display very similar conformational features.

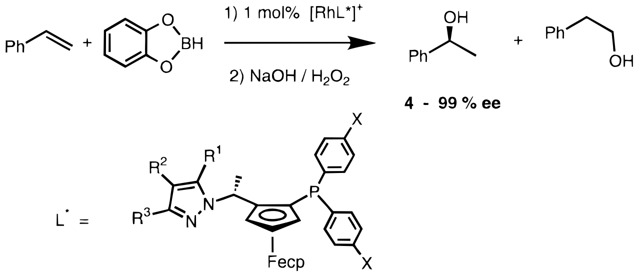
Introduction

We recently reported the synthesis of a series of new pyrazole-containing ferrocenyl phosphines of type **1**[1a] and their successful application in the asymmetric rhodium-catalyzed hydroboration of styrene with catecholborane (see Scheme 1),[1b] as well as in the palladium-catalyzed asymmetric allylic amination.[1c] The new P,N ligands have been shown to afford the highest known enantioselectivities for both catalytic reactions. Furthermore, they were found to exhibit pronounced electronic effects on the stereoselectivity of the former reaction, depending on the nature of the substituents on the pyrazole and the phosphine fragments.[1b]

We note that the mechanistic understanding of asymmetric catalytic hydroboration is rather vague.[2] Furthermore, only a few rhodium complexes related to this catalytic system have been prepared and characterized, and most of them contain monodentate phosphines.[3,4]

The observation of large electronic effects in our system prompted us to prepare two main types of model rhodium complexes of the general formula [Rh(COD)(P,N)]BF_4 (**3**) and [Rh(CO)Cl(P,N)] (**5**), respectively. The structural characterization of the catalyst precursors **3** allowed us to confirm the expected geometry at the rhodium center and define conformational aspects. On the other hand, the electronic properties of the ligands

Scheme 1



1a-r

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(1) (a) Burckhardt, U.; Hintermann, L.; Schnyder, A.; Togni, A.; *Organometallics*, **1995**, *14*, 5415. (b) Schnyder A., Hintermann, L.; Togni, A. *Angew. Chem.* **1995**, *107*, 996−998; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 931−933. (c) Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P. S. P.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031. (d) Burckhardt, U.; Gramlich, V.; Hofmann, P.; Nesper, R.; Pregosin, P. S.P.; Salzmann, R.; Togni, A. *Organometallics* **1996**, *15*, 3496.

(2) For mechanistic considerations, see, e.g.: (a) Burgess, K.; Ohlmeyer, M. J. *Adv. Chem. Ser.* **1992**, *No. 230*, 163. (b) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1191. For a recent theoretical study, see: (c) Musaev, D. G.; Mebel, A. M.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 10693.

(3) (a) Van Gaal, H. L. M.; Moers, F. G.; Steggerda, J. J. *J. Organomet. Chem.* **1974**, *65*, C43. (b) Kono, H.; Ito, K.; Nagai, Y. *Chem. Lett.* **1975**, 1095. (c) Busetto, C.; D'Alfonso, A.; Maspero, F.; Perego, G.; Zazetta, A. *J. Chem. Soc., Dalton Trans.* **1977**, 1828. (d) Fryzuk, M. D. *Inorg. Chem.* **1982**, *21*, 2134. (e) Baker, R. T.; Ovenall, D. W.; Calabrese, J. C.; Westcott, S. A.; Williams, L. D.; Taylor, N. J.; Marder, T. B. *J. Am. Chem. Soc.* **1990**, *112*, 9399. (f) Korr, J. R.; Merola, J. S. *Organometallics* **1990**, 9, 3008. (g) Westcott. S. A.; Taylor, N. J.; Marder, T. B.; Baker, R. T.; Jones, N. J.; Calabrese, J. C. *J. Chem. Soc., Chem. Commun.* **1991**, 304. (h) Burgess, K.; van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Calabrese, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 9350. (i) Baker, R. T.; Calabrese, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 4367. (j) Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Can. J. Chem.* **1993**, *71*, 930. (k) Nguyen, P.; Lesley, G.; Taylor, N. J.; Marder, T. B.; Pickett, N. L.; Clegg, W.; Elsegood, M. R. J.; Norman, N. C. *Inorg. Chem.* **1994**, *33*, 4623. (l) Cleary, B. P.; Eisenberg, R. *Organometallics* **1995**, *14*, 4525.

(4) For early work on Rh complexes containing P,N ligands, see, e.g.: (a) Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1974**, *96*, 3098. (b) Cullen, W. R.; Einstein, F. W. B.; Huang, C.-H.; Willis, A. C.; Yeh, E.-S. *J. Am. Chem. Soc.* **1980**, *102*, 988.

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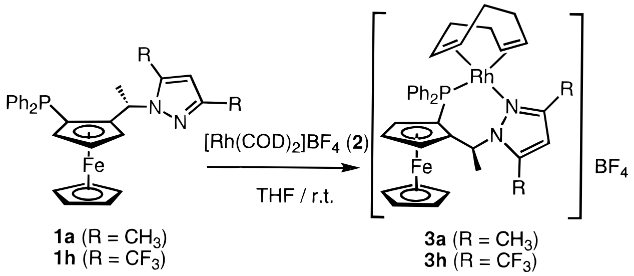
Scheme 2



are reflected by their influence on the carbonyl stretching vibration and the ^{31}P NMR parameters in complexes **5**.[5] We present herein full experimental details for the preparation, characterization, and structure of such rhodium complexes.

Results and Discussion

Synthesis and Structure of [Rh(1,5-COD)(P,N)]-BF$_4$ (3). As illustrated in Scheme 2, Rh complexes of type **3** are readily obtained from the reaction of the corresponding P,N ligand and [Rh(1,5-COD)$_2$]BF$_4$ (**2**).[6] This substitution reaction was carried out in THF at room temperature over 2 h, and the products were isolated in pure form after recrystallization in moderate yields (70%).

The two P,N ligands **1a** and **1h** have been chosen because they show very different behaviors in terms of electronic effects on the rhodium-catalyzed hydroboration of styrene (*vide infra*).

Single crystals of complexes **3a** and **3h** were obtained after recrystallization in layered mixtures of CH$_2$Cl$_2$/hexane and CH$_2$Cl$_2$/Et$_2$O, respectively. Table 1 collects crystal and data collection parameters. Views of the two molecules are shown in Figure 1. A selection of important bond distances, angles, and torsion angles for **3a** and **3h** are given in Table 2. The bonding parameters turn out to be rather routine and fall in the expected ranges.[7]

An inspection of the structural characteristics points out the following main features. (1) The pyrazole ring and one of the two phosphino phenyl groups lie in a pseudo-axial position pointing away from the ferrocene core with corresponding diagnostic torsion angles C(1)−C(2)−C(6)−N(1) and C(2)−C(1)−P(1)−C$_{ipso}$(Ph$_{ax}$) of 63° (**3a**) and 66° (**3h**) and 84° (**3a**) and 86° (**3h**), respectively, as has been shown earlier for the free ligands.[1a] The angles C(5)−C(1)−P(1)−C$_{ipso}$(Ph$_{eq}$) of −169 and 167° show that the second phenyl ring is in an *endo*-equatorial position. (2) The torsion angle C(1)−C(2)−C(6)−N(1) differs by almost 150° as compared to the same angle in the free ligands, due to the different orientations of the pyrazole fragment (in the free ligand the lone pair of the ligating nitrogen atom and the phosphorus atom are pointing in opposite directions).[1a] (3) The C═C double bond coordinated to Rh in a position trans to the pyrazole shows slightly shorter Rh−C distances in **3h**, as one would expect. Correspondingly, the Rh−N(2) distance is larger than in **3a**. However, the relatively large standard deviations observed only allow for trends to be recognized. (4) The bite angle of the chelating ligand is in both derivatives slightly below the expected 90° (87.3(3) and 87.4(4)°, respectively), a value much smaller than the one observed for cationic Pd−allyl complexes containing the same type of ligands.[1c,d]

Synthesis and Structure of [Rh(CO)Cl(P,N)] (5). A series of rhodium monocarbonyl complexes containing

Table 1. Experimental Data for the X-ray Diffraction Study of 3a and 3h

	3a	3h
formula	C$_{38}$H$_{43}$BCl$_2$F$_4$FeN$_2$PRh	C$_{38}$H$_{37}$BCl$_2$F$_{10}$FeN$_2$PRh
mol wt	875.2	983.1
cryst dimens (mm)	0.1 × 0.1 × 0.2	0.08 × 0.2 × 0.6
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
data collecn T (°C)	20	20
a (Å)	9.848(1)	9.960(2)
b (Å)	19.15(2)	13.37(2)
c (Å)	20.16(2)	29.24(4)
V (Å^3)	3801(7)	3893(10)
Z	4	4
ρ(calcd) (g cm^{-3})	1.530	1.678
F(000)	1784	1976
diffractometer	Syntex P2$_1$	Picker-STOE
radiation	Mo Kα, l = 0.710 73 Å	Mo Kα, l = 0.710 73 Å
measd rflns	$0 \leq h \leq 10, 0 \leq k \leq 20, 0 \leq l \leq 21$	$0 \leq h \leq 9, 0 \leq k \leq 12, 0 \leq l \leq 28$
2θ range (deg)	3.0−45.0	3.0−40.0
scan type	ω	ω
scan width (deg)	1.00	1.00
bkgd time (s)	0.3 × scan time	0.3 × scan time
scan speed (deg min^{-1})	2.0−15.65 in ω	2.0−4.0 in ω
no. of indep data collected	2864	2122
no. of obsd rflns (n_o)	2293, $\lvert F_o{}^2\rvert > 4.0\sigma(\lvert F\rvert^2)$	1564, $\lvert F_o{}^2\rvert > 4.0\sigma(\lvert F\rvert^2)$
abs cor	face-indexed numerical	N/A
transmissn coeff	0.7282−08178	
no. of params refined (n_v)	452	577
quantity minimized	$\Sigma w(F_o - F_c)^2$	$\Sigma w(F_o - F_c)^2$
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0010F^2$	$w^{-1} = \sigma^2(F) + 0.0010F^2$
R^a	0.0422	0.0552
$R_w{}^b$	0.0512	0.0652
GOF^c	1.24	1.80

[a] $R = \Sigma(\lvert\lvert F_o\rvert - (1/k)\lvert F_c\rvert\rvert)/\Sigma\lvert F_o\rvert$. [b] $R_w = \Sigma w(\lvert\lvert F_o\rvert - (1/k)\lvert F_c\rvert\rvert)^2/[\Sigma w\lvert F_o\rvert^2]^{1/2}$. [c] GOF $= [\Sigma w(\lvert F_o\rvert - (1/k)\lvert F_c\rvert)^2/(n_o - n_v)]^{1/2}$.

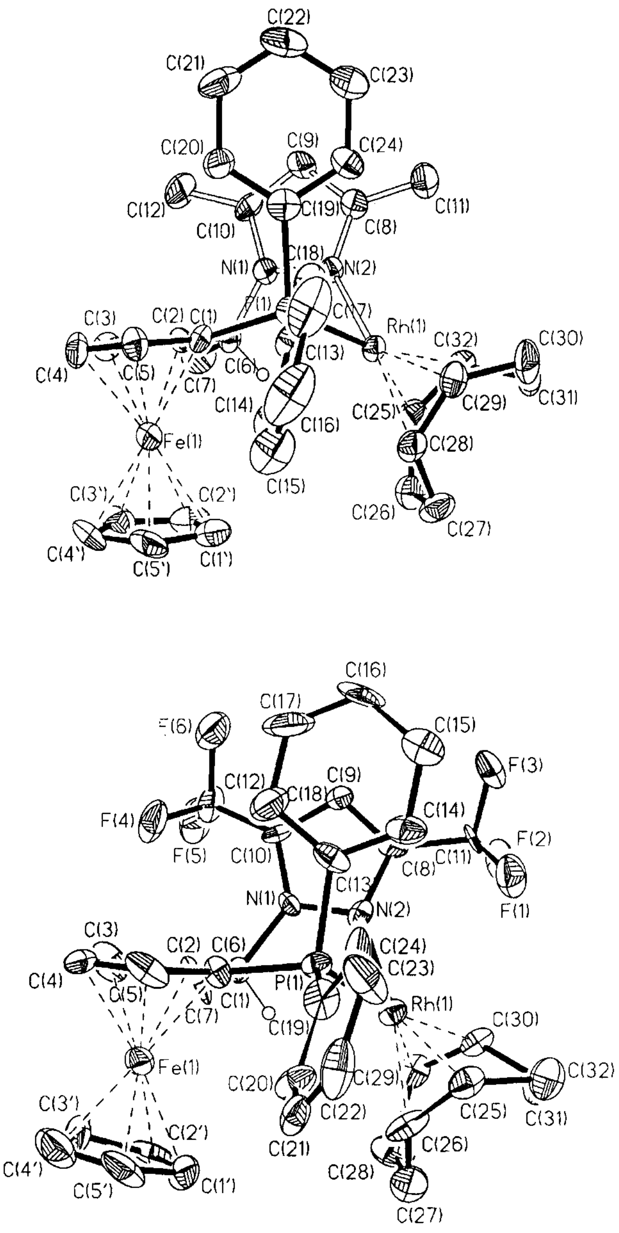


Figure 1. ORTEP views and atom-numbering schemes of the complex cations of **3a** (top) and **3h** (bottom).

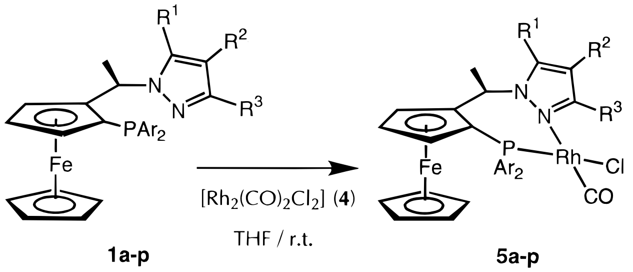
the P,N ligands **1a**−**p** have been prepared by the reaction of the latter with $[Rh(CO)_2Cl]_2$ as shown in Scheme 3, affording the corresponding [Rh(CO)Cl(P,N)] complexes **5a**−**p** in high yield.

Table 2. Selected Bond Distances (Å),[a] Angles (deg),[a] and Torsion Angles (deg) for 3a and 3h

	3a	3h
Bond Distances		
Rh−N(2)	2.130(8)	2.168(15)
Rh−P	2.311(4)	2.320(7)
Rh−C(28)	2.174(11)	2.105(22)
Rh−C(29)	2.115(11)	2.098(21)
Rh−C(25)	2.191(11)	2.210(21)
Rh−C(32)	2.222(9)	2.233(17)
N(1)−N(2)	1.387(11)	1.350(21)
Bond Angles		
P−Rh−N(2)	87.3(3)	87.4(4)
N(1)−N(2)−Rh	121.0(6)	118.2(10)
C(1)−P−Rh	112.1(4)	111.5(6)
P−Rh−C(28,29)[b]	94.35(4)	94.8(6)
N(2)−Rh−C(25,32)[b]	93.0(4)	91.7(7)
C(25,32)[b]−Rh−C(28,29)[b]	81.15(4)	81.95(8)
Torsion Angles		
C(1)−C(2)−C(6)−N(1)	−66	−63
C(3)−C(2)−C(6)−N(1)	118	118
C(2)−C(1)−P(1)−C(Ph_{ax})	84	86
C(5)−C(1)−P(1)−C(Ph_{eq})	28	25
C(2)−C(1)−P(1)−C(Ph_{eq})	−169	−167
C(3)−C(2)−C(6)−C(7)	−9	−13

[a] Numbers in parentheses are esd's in the least significant digits. [b] Midpoint of olefinic bond.

Scheme 3



For the complexes **5k** and **5n** suitable single crystals were obtained by recrystallization in CH_2Cl_2/hexane mixtures. For these two complexes crystallographic parameters are given in Table 3. ORTEP views of the molecules are shown in Figure 2, whereas important bond distances and angles are collected in Table 4. A schematic superposition of the structures of the four complexes **3a**, **3h**, **5k**, and **5n**, showing very similar conformational features, is depicted in Figure 3. Finally, important analytical data for the complexes **5a**−**p**, as well as the enantioselectivities obtained in the hydroboration of styrene using the P,N/$[Rh(COD)_2]BF_4$ system as catalyst precursor, are given in Table 5.[1b]

In **5k** and **5n** the configuration at the Rh center is the expected, thermodynamically most stable one, with the carbonyl group in a position trans to the pyrazole nitrogen, as one would anticipate from trans-influence considerations. The geometry is not perfectly square planar, and deviations from the expected 90° angles around rhodium have been found. Thus, the bite angle of the PN ligand is ca. 85° and the angle between the P atom and the neighboring carbonyl group is ca. 95°, since the phosphine fragment is the sterically most demanding ligand.

The observed Rh−CO bond lengths in the two complexes **5k** and **5n** (1.817(23) and 1.788(11) Å, respectively) are slightly shorter than the average value of 1.847 Å.[7] This reflects the relatively strong Rh-CO bond connected with a considerable π back-donation associated with the CO ligand. A discussion of the difference between bonding parameters of these two derivatives is hampered by the relatively large observed standard deviations.

As shown in Table 5, the different ligands **1a**−**p** afford different enantioselectivities in the Rh-catalyzed hydroboration of styrene.[1b] Thus, derivative **1h**, bearing

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(5) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. Recently, the IR properties of rhodium complexes containing carbonyl and tris(pyrazolyl)borate ligands were investigated. The observed influences on the CO IR stretching vibration (2080−2103 cm^{-1} for complexes with η^2 ligands and 2054−2091 cm^{-1} with η^3 ligands) were correlated to the steric and electronic properties of the tris(pyrazolyl)borate ligand. See: (b) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419 and references therein.

(6) Fryzuk, M. D.; Bosnich, B. *J. Am. Chem Soc.* **1977**, *99*, 6702.

(7) (a) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, Supplement S1−S83. (b) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans 2* **1987**, Supplement S1−S19. See also: (c) Bürgi, H.-B., Dunitz, J. D., Eds. *Structure Correlation*; VCH: Weinheim, Germany, 1994; Vol. 2, Appendix A.

Table 3. Experimental Data for the X-ray Diffraction Study of 5k and 5n

	5k	**5n**
formula	$C_{35}H_{39}Cl_3FeN_2OPRh$	$C_{33}H_{35}Cl_3FeN_2OPRh$
mol wt	799.8	771.7
crys dimens (mm)	0.1 × 0.1 × 0.6	0.2 × 0.3 × 0.4
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1$
data collecn T (°C)	20	20
a (Å)	8.721(8)	9.822(2)
b (Å)	18.632(1)	12.435(2)
c (Å)	22.82(3)	14.277(3)
β (deg)		97.28(3)
V (Å^3)	3708(6)	1723.6(6)
Z	4	4
ρ(calcd) (g cm^{-3})	1.433	1.487
F(000)	1632	784
diffractometer	Picker-STOE	Picker-STOE
radiation	Mo Kα, $\lambda = 0.710\,73$ Å	Mo Kα, $\lambda = 0.710\,73$ Å
measd reflcns	$0 \le h \le 8$, $0 \le k \le 17$, $0 \le l \le 22$	$-9 \le h \le 9$, $0 \le k \le 11$, $0 \le l \le 13$
2θ range (deg)	3.0–45.0	3.0–40.0
scan type	ω	ω
scan width	1.00	1.00
bkgd time (s)	0.3 × scan time	0.3 × scan time
scan speed (deg min^{-1})	1.0–4.0 in ω	1.0–4.0 in ω
no. of indep data collected	2002	1719
no. of obsd rflns (n_o)	1980	1677
	$\lvert F_o^2\rvert > 4.0\sigma(\lvert F\rvert^2)$	$\lvert F_o^2\rvert > 4.0\sigma(\lvert F\rvert^2)$
abs cor	N/A	N/A
no. of params refined (n_v)	213	374
quantity minimized	$\Sigma w(F_o - F_c)^2$	$\Sigma w(F_o - F_c)^2$
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0040F^2$	$w^{-1} = \sigma^2(F) + 0.0060F^2$
R^a	0.0699	0.0407
$R_w{}^b$	0.0945	0.0477
GOF^c	1.23	0.67

[a] $R = \Sigma(||F_o| - (1/k)|F_c||)/\Sigma|F_o|$. [b] $R_w = \Sigma w(||F_o| - (1/k)|F_c||)^2/[\Sigma w|F_o|^2]^{1/2}$. [c] $\mathrm{GOF} = [\Sigma w(|F_o| - (1/k)|F_c|)^2/(n_o - n_v)]^{1/2}$.

two electron-withdrawing CF_3 groups on the pyrazole, gave a very low stereoselectivity (33% ee). On the other hand, when trifluoromethyls are placed on the phenylphosphino fragment instead (**1p**), one obtains the best ee's so far observed for this particular reaction (98.5% ee). Furthermore, electron-donating substituents on the phosphorus lead to moderate selectivities (see **1i** and **1q**), whereas the combination of an electron-rich phosphine and an electron-poor pyrazole (**1r**) constitutes the worst case, affording essentially no enantioselectivity (5% ee). Considering that most of the ligands of this study do not differ significantly from a steric point of view, as e.g. **1o** (98% ee) and **1r** (5% ee), the effects observed on stereoselectivity are eminently electronic in nature.[8,9]

Complexes **5**, containing a single carbonyl fragment in a well-defined steric environment, are best suited for the purpose of defining the electronic effects of the chelating P,N ligand. We therefore examined the CO stretching frequencies for the series **5a**–**p**, containing the ferrocenyl ligands **1a**–**p**. The data are reported in Table 5. For the derivatives **5a**–**h** only the substituents on the pyrazole have been varied. A clear trend is recognizable, in terms of ascending electron-withdrawing capacity of the substituents, accompanied by an increasing ν(CO), (from 1989 cm^{-1} for **5a** to 1997 cm^{-1} for **5h**), thus reflecting the decreasing Rh–CO π back-bonding in the series. The enantioselectivity of the catalytic reaction utilizing these ligands follows the same trend, with two notable exceptions, however. Ligands **1d** and **1g**, containing Br and NO_2 substituents at position 4 of the heterocycle, respectively, give anomalously high ee's (95.5% and 84%, respectively). This indicates that the influence of substituents at this position cannot be understood only in terms of the resulting decreased donor ability of the pyrazole nitrogen. For the series **5i**–**p**, containing ligands in which only the substituents on the phosphorus atom have been varied, a similar qualitative trend may be identified. Thus, an enhanced selectivity is reflected by a more pronounced increase of the CO stretching frequency (from 1986 to 2008 cm^{-1}) of the corresponding complex **5**. The most prominent exception in this case is constituted by **1j** (in **5j**), containing the relatively weak electron-withdrawing 4-fluorophenyl substituent, for which one would expect both a higher ν(CO) value for **5** and a higher selectivity in the catalytic reaction.

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(8) Electronic effects in asymmetric catalysis with other types of ligands have been recently reported. Rh-catalyzed hydrogenation: (a) Inoguchi, K.; Sakuraba, S.; Achiwa, K. *Synlett* **1992**, 169 and references cited therein. (b) RajanBabu, T. V.; Ayers, T. A.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 4101. Ru-catalyzed hydrogenation with BINAP-type ligands: (c) Mashima, K.; Kusano, K.; Sato, N.; Matsumura, Y.; Nozaki, K.; Kumobayashi, H.; Sayo, N.; Hori, Y.; Ishizaki, T.; Akutagawa, S.; Takaya, H. *J. Org. Chem.* **1994**, *59*, 3064. Ni-catalyzed hydrocyanation of vinylarenes: (d) Casalnuovo, A. L.; RajanBabu, T. V.; Ayers, T. A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869. (e) RajanBabu, T. V.; Casalnuovo, A. L. *Pure Appl. Chem.* **1994**, *66*, 1535. (f) RajanBabu, T. V.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6265. Rh-catalyzed hydroformylation of olefins: (g) RajanBabu, T. V.; Ayers, T. A. *Tetrahedron Lett.* **1994**, *35*, 4295. Mn-catalyzed epoxidation of unfunctionalized olefins: (h) Jacobsen, E. N. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; pp 159–202, and references cited therein. Rh-catalyzed hydrosilylation of ketones: (i) Nishiyama, H.; Yamaguchi, S.; Kondo, M.; Itoh, K. *J. Org. Chem.* **1992**, *57*, 4306. For electronically controlled stoichiometric reactions of Mo–allyl complexes, see: (j) Faller, J. W.; Chao, K.-H. *J. Am. Chem. Soc.* **1983**, *105*, 3893. (k) Faller, J. W.; Nguyen, J. T.; Ellis, W.; Mazzieri, M. R. *Organometallics* **1993**, *12*, 1434.

(9) For a quantitative approach to ligand effects, see: (a) Bartholomew, J.; Fernandez, A.; Lorsbach, B. A.; Giering, W. P. *Organometallics* **1996**, *15*, 295 and references cited therein. For recent general references concerning steric effects, see: (b) Brown, T. L.; Lee, K. J. *Coord. Chem. Rev.* **1993**, *128*, 89. (c) Data, D.; Majumdar, D. *J. Phys. Org. Chem.* **1991**, 4, 611. (d) Seligson, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 2520.

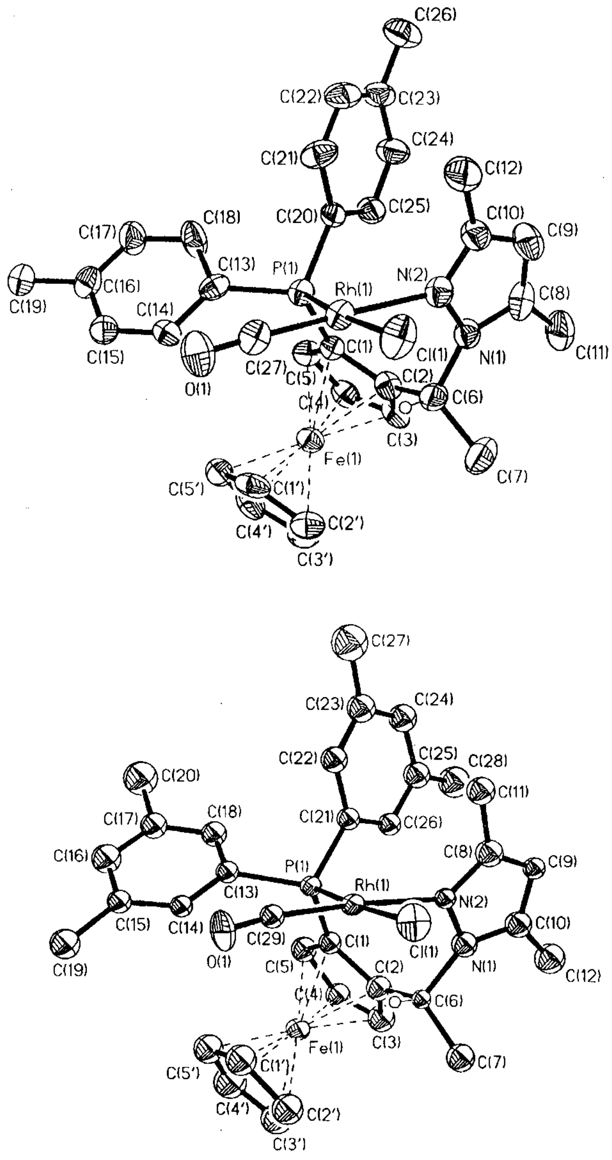


Figure 2. ORTEP views and atom-numbering schemes of complexes **5k** (top) and **5n** (bottom).

Table 4. Selected Bond Distances (Å)[a] and Angles (deg)[a] for 5k and 5n

	5k	5n
Bond Distances		
Rh−N(2)	2.141(17)	2.125(8)
Rh−P	2.246(7)	2.239(2)
Rh−C	1.817(23)	1.788(11)
Rh−Cl	2.371(7)	2.368(2)
C-O	1.125(29)	1.158(15)
N(1)−N(2)	1.348(29)	1.372(11)
Bond Angles		
Cl−Rh−C	89.0(7)	90.8(3)
C−Rh−P	96.6(7)	95.1(3)
P−Rh−N(2)	85.4(5)	85.9(2)
N(2)−Rh−Cl	89.1(5)	88.3(2)

[a] Numbers in parentheses are esd's in the least significant digits.

Conclusions

We have shown that rhodium complexes with ferrocenyl P,N ligands incorporating both a pyrazole and a phosphine moiety are easily obtained *via* a substitution reaction of $[Rh(1,5\text{-}COD)_2]BF_4$, $[Rh(CO)_2Cl]_2$, and $[Rh(COE)_2Cl]_2$ and the corresponding P,N ligand. These complexes are useful in terms of qualifying the electronic as well as steric influence of the ligands. The electronic influence of the two different fragments of the P,N ligands are reflected by the carbonyl stretching frequencies regardless of whether P or N is trans to the carbonyl group. A trans σ-donating pyrazole leads to a lower υ(CO), whereas a cis π-accepting phosphine causes an increase of υ(CO), and both effects are paralleled by higher enantioselectivity in the rhodium-catalyzed hydroboration of styrene. However, it must be added that, in the case of electron-poor pyrazole ligands, the event of achiral catalysis due to dissociation of the ligand cannot be excluded, although previously reported experimental evidence makes it unlikely.[1b]

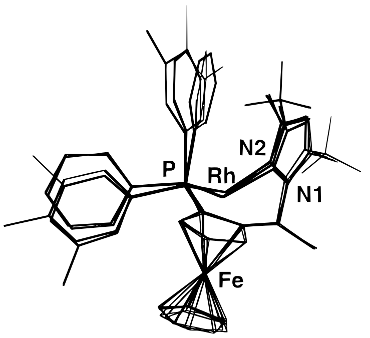


Figure 3. Schematic superposition of the structures of the four complexes **3a**, **3h**, **5k**, and **5n** (Cl, CO, and COD ligands are omitted for clarity).

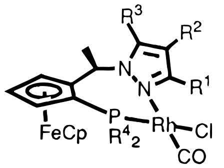
Our present study demonstrates the utility of simple model complexes containing the carbonyl ligand in helping to classify electronic effects in asymmetric catalysis, at least in a qualitative manner. In our specific case of the Rh-catalyzed hydroboration of styrene, from an electronic point of view optimum enantioselectivities are obtained when both the pyrazole moiety is a good σ-donor and the phosphine displays good π-accepting qualities, by virtue of their substituents. These features lead to the intuitive concept of an *electronically asymmetric ligand*, whose properties are reflected by the observed trends of the CO stretching frequencies. However, not knowing the mechanistic details of this Rh-catalyzed hydroboration reaction, it is not possible to understand the exact origin of the observed effects.

Experimental Section

General Considerations. All reactions with air- or moisture-sensitive materials were carried out under Ar using standard Schlenk techniques. Freshly distilled, dry, and oxygen-free solvents were used throughout. Routine ^1H (250.133 MHz), ^{13}C (62.90 MHz), ^{19}F (188.31 MHz), and ^{31}P NMR (101.26 MHz) spectra were recorded with a Bruker AM 250 spectrometer. Chemical shifts are given in ppm, and coupling constants (*J*) are given in Hz. The IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer, using CH_2Cl_2 solutions of the complexes. Melting points were obtained from samples in open capillary tubes with a Büchi SMP-20 and are uncorrected. Elemental analyses and EI/MS spectra were performed by the "Mikroelementaranalytisches Laboratorium der ETH". The preparation of the ligands **1a**−**r**[1a] and the conditions for the catalytic hydroboration reactions[1b] were reported previously.

General Method for the Synthesis of [Rh(1,5-COD)(P,N)]BF₄. A solution of the ligands **1a** and **1h** (1.1 equiv) and $[Rh(COD)_2]BF_4$ (1 equiv) in 1−2 mL of THF was stirred at room temperature for 2 h. The solvent was removed by rotary evaporation, and the crude product thus obtained was

Table 5. Summary of Important Spectroscopic Data for the Complexes [Rh(CO)Cl(P,N)] (5a–p)



complex/ligand	R^1	R^2	R^3	R^4	IR ν(CO) (cm^{-1})	^{31}P NMR (ppm)	J^1(P, Rh) (Hz)	ee[a] (%)
5a	Me	H	Me	Ph	1989	31.4	168	95 (*R*)
5b	^{i}Pr	H	^{i}Pr	Ph	1990	31.4	171	92 (*R*)
5c	Ph	H	Me	Ph	1990	31.8	168	80 (*R*)
5d	Me	Br	Me	Ph	1992	31.0	166	95.5 (*R*)
5e	a-Np	H	Me	Ph	1992	31.5	173	46 (*R*)
5f	CF_3	H	Me	Ph	1994	29.1	164	44 (*R*)
5g	Me	NO_2	Me	Ph	1997	30.2	165	84 (*R*)
5h	CF_3	H	CF_3	Ph	1997	29.4	161	33 (*R*)
5i	Ph	H	Me	Cy	1980	30.6	168	76 (*S*)
5j	Me	H	Me	4-F-Ph	1986	30.1	169	87 (*S*)
5k	Me	H	Me	3,5-Me_2-Ph	1987	30.6	168	76 (*S*)
5l	Me	H	Me	4-OMe-Ph	1987	28.4	168	90 (*S*)
5m	Me	H	Me	4-Ph-Ph	1989	35.6	176	76 (*S*)
5n	Me	H	Me	4-Me-Ph	1991	29.2	169	94.5 (*S*)
5o	Me	H	Me	4-CF_3-Ph	2006	33.0	133	98 (*S*)
5p	Me	H	Me	3,5-$(CF_3)_2$-Ph	2008	30.3	168	98.5 (*S*)
1q	Me	H	Me	4-NMe_2-Ph	*b*	*b*	*b*	72 (*S*)
1r	CF_3	H	CF_3	4-OMe-Ph	*b*	*b*	*b*	5 (*S*)

[a] Enantioselectivity afforded by the corresponding ligand in the Rh-catalyzed hydroboration of styrene, as reported previously.[1b]
[b] Complex **5** not prepared.

purified by suspending in hexane, recrystallizing as detailed below, and drying *in vacuo*.

[{1-{(*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl}-3,5-dimethyl-1*H*-pyrazole}Rh(1,5-COD)]BF$_4$ (3a) was obtained from 20 mg of **1a** (40 μmol, 1.1 equiv) and 15 mg of $[Rh(COD)_2]BF_4$ (37 μmol, 1 equiv), according to the general method. Recrystallization in CH_2Cl_2/hexane yielded suitable single crystals for an X-ray structural determination; yield 20 mg (69%). ^1H NMR ($CDCl_3$): δ 7.57–6.77 (m, 10 ar-*H*), 5.41 (dq, $J = 2$, C*H*MeN), 5.29 (m, COD C*H*), 5.25 (m, COD C*H*), 5.12 (m, COD C*H*), 4.95 (s, pz C*H*), 4.69 (m, COD C*H*), 4.55 (m, cp *H*), 4.46 (s, 5 cp *H*), 4.36 (m, cp *H*), 3.82 (m, cp *H*), 2.20 (d, $J = 7$, CH*Me*N), 2.12 (s, pz*Me*), 1.93 (s, pz*Me*), 2.9–1.6 (m, 4 COD CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 10.8 (d, $J = 144$). Anal. Calcd for $C_{37}H_{41}BF_4FeN_2PRh$ ($+1H_2O$): C, 55.01; H, 5.37; N, 3.45. Found: C, 55.27; H, 5.55; N, 3.29.

[{1-{(*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl}-3,5-bis(trifluoromethyl)-1*H*-pyrazole}Rh(1,5-COD)]BF$_4$ (3h) was obtained from 40 mg of **1h** (66 μmol, 1.1 equiv) and 28 mg of $[Rh(COD)_2]BF_4$ (60 μmol, 1 equiv), according to the general method. Recrystallization in CH_2Cl_2/Et_2O yielded single crystals for an X-ray structural determination; yield 42 mg (72%). ^1H NMR ($CDCl_3$): δ 7.90–7.15 (m, 10 ar-*H*), 6.85 (m, 2 COD C*H*), 6.36 (s, pz C*H*), 6.01 (m, COD C*H*), 5.21 (m, COD C*H*), 5.15 (dq, $J = 2$, C*H*MeN), 4.81 (m, cp *H*), 4.71 (s, 5 cp *H*), 3.98 (m, cp *H*), 3.79 (m, cp *H*), 2.38 (d, $J = 7$, CH*Me*N), 3.3–1.6 (m, 4 COD CH_2). ^{19}F NMR ($CDCl_3$): δ −56.7 (s, CF_3), −57.0 (s, CF_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 13.9 (d, $J = 141$). Anal. Calcd for $C_{37}H_{35}BF_{10}FeN_2PRh$ ($+1H_2O$): C, 48.50; H, 4.07; N, 3.05. Found: C, 48.50; H, 4.10; N, 2.72.

General Method for the Synthesis of [Rh(CO)Cl(P,N)]. A solution of **1a**–**p** (1 equiv) and of $[Rh(CO)_2Cl]_2$ (0.5 equiv) in 1–2 mL of THF was stirred between room temperature and 50 °C for 1–5 h. The solvent was removed by rotary evaporation, and the crude product thus obtained was purified by recrystallization and dried *in vacuo*. The associated solvent of crystallization was determined by ^1H NMR. A representative procedure is exemplified by the preparation of **5a**. Details for all other compounds are given as Supporting Information.

[{1-{(*S*)-1-[(*R*)-2-(Diphenylphosphino)ferrocenyl]ethyl}-3,5-dimethyl-1*H*-pyrazole}Rh(CO)Cl] (5a) was obtained from 30 mg of **1a** (61 μmol, 1 equiv) and 12 mg of $[Rh(CO)_2Cl]_2$ (30.5 μmol, 0.5 equiv), according to the general method. Recrystallization was carried out in CH_2Cl_2/hexane; yield 34 mg (85%). ^1H NMR ($CDCl_3$): δ 7.61–6.68 (m, 10 ar-*H*), 6.74 (dq, $J = 2$, C*H*MeN), 5.22 (s, pz-C*H*), 4.34 (m, cp *H*), 4.20 (m, cp *H*), 4.10 (s, 5 cp *H*), 3.61 (m, cp *H*), 2.09 (s, pz*Me*), 1.95 (d, $J = 7$, CH*Me*N), 1.68 (s, pz*Me*). ^{13}C NMR ($CDCl_3$): δ 191 (dd, J(C,Rh) = 71, J(C,P) = 17, *C*O), 139–127 (10 ar *C*H), 109.2 (pz *C*H), 72.9 (cp *C*H), 70.5 (5 cp *C*H), 69.9 (cp *C*H), 67.8 (cp *C*H), 58.0 (*C*HMeN), 16.4 (CH*Me*N), 13.1 (pz*Me*), 12.1 (pz*Me*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.4 (d, $J = 168$). IR (CH_2Cl_2-film): s, 1989.2 cm^{-1} (C≡O). MS: *m/z* 676 ($M^+ + H_2O$), 658 (M^+), 630 ($M^+ - CO$), 445 (630 − PPh_2, 100%), 297 (445 − RhCl), 259, 183 (PPh_2), 78 (Ph − H), 47 (PO^+). Anal. Calcd for $C_{30}H_{29}ClFeN_2OPRh$: C, 54.70; H, 4.44; N, 4.25. Found: C, 54.55; H, 4.29; N, 4.16.

X-ray Crystallographic Studies of 3a, 3h, 5k, and 5n. Selected crystallographic and relevant data collection parameters are listed in Tables 1 and 3. Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. One standard reflection was measured every 120 reflections; no significant variation was detected.

The structures were solved by direct methods and refined by full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms. The contribution of the hydrogen atoms in their idealized positions (Riding model with fixed isotropic $U = 0.080$ Å^2) was taken into account but not refined. All calculations were carried out by using the Siemens SHELXTL PLUS system.

Acknowledgment. We are grateful to U. Burckhardt and V. Gramlich for their valuable help with the X-ray structural analyses.

Supporting Information Available: Text giving experimental details for the preparation and characterization of [RhCl(P,N)CO] complexes (**5**) and tables of crystal data and refinement details, atomic coordinates, all bond distances and angles, anisotropic displacement coefficients for non-carbon atoms, and coordinates of hydrogen atoms for compounds **3a, 3h, 5k,** and **5n** (42 pages). Ordering information is given on any current masthead page. Tables of calculated and observed structure factors for all four compounds may be obtained from the authors upon request.

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