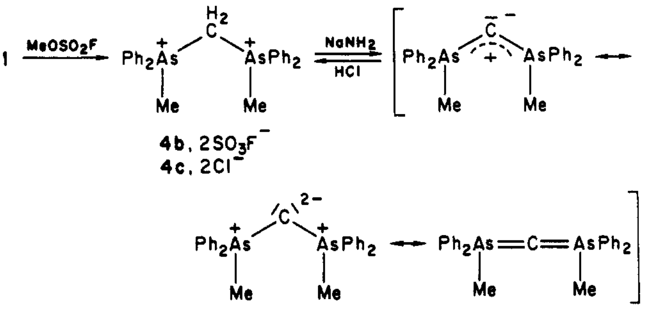
nificant deviation from planarity.[14,15,20,21]

Double quaternization of 1 can be achieved with the more powerful methylating agent CH_3OSO_2F in dichloromethane as a solvent. Yields of the bisquaternary salt **4b** are again close to 80%. The product is soluble in trifluoroacetic acid without decomposition, and ^1H and ^{13}C NMR spectra are thus available (Experimental Section).

After a series of unsuccessful attempts for the conversion of **4b** into a carbodiarsorane, **5**, favorable conditions for its synthesis were found with the system $NaNH_2$/liquid ammonia at −40 °C, followed by a workup at temperatures below −20 °C. A yellow microcrystalline material thus obtained was characterized as **5** by its elemental analyses, NMR spectra, and a reprotonation reaction with anhydrous HCl, yielding the precursor cation (**4c**, Cl for SO_3F in 4).



4b, $2SO_3F^-$
4c, $2Cl^-$

5

3 is thermally unstable both in the solid state and even more so in solution (tetrahydrofuran, toluene).

The ^1H and ^{13}C NMR spectra of cooled solutions give signals attributable to four equivalent phenyl and two equivalent methyl groups. The resonance of the central carbon atom could not be observed, even after prolonged signal accumulation under different pulse conditions, due to unfavorable relaxation conditions and/or line broadening caused by the presence of two As quadrupolar nuclei. Carbodiphosphoranes are also known to give no or very weak P=C=P signals.[7]

The chemical properties of 3 and 5 are presently under investigation with special attention directed toward carbon-transfer reactions to other substrates.

Acknowledgment. We are indebted to Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, and Fonds der Chemischen Industrie, Frankfurt/Main, for continuous generous support.

Registry No. 1, 21892-63-7; 2, 92219-85-7; 3, 92219-86-8; 4b, 92219-88-0; 4c, 92240-98-7; 5, 92219-89-1; MeI, 74-88-4; $MeOSO_2F$, 421-20-5.

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Structures of Three Hydrogenation Catalysts $[(P\text{-}P)Rh(NBD)]ClO_4$ and Some Comparative Rate Studies Where (P-P) = $(\eta^5\text{-}R^1R^2PC_5H_4)(\eta^5\text{-}R^3R^4PC_5H_4)Fe$ ($R^1 = R^2 = R^3 = R^4$ = Ph; $R^1 = R^2$ = Ph, $R^3 = R^4 = CMe_3$; $R^1 = R^3$ = Ph, $R^2 = R^4 = CMe_3$)

William R. Cullen* and Tae-Jeong Kim

Chemistry Department, University of British Columbia, Vancouver, British Columbia V6T 1Y6, Canada

Frederick W. B. Einstein* and Terry Jones

Chemistry Department, Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada

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The compounds $[(P\text{-}P)RhNBD]ClO_4$ [(P-P) = $(\eta^5\text{-}R^1R^2PC_5H_4)Fe(\eta^5\text{-}R^3R^4PC_5H_4)$; $R^1 = R^2 = R^3 = R^4 = CMe_3$, 1, or Ph, 4; $R^1 = R^2 = CMe_3$, $R^3 = R^4$ = Ph, 2; $R^1 = R^3 = CMe_3$, $R^2 = R^4$ = Ph, 3] are catalyst precursors for the hydrogenation of a range of olefins (1 atm of H_2, 30 °C). The presence of bulky *t*-Bu groups enhances reaction rates except when bulky olefins are the substrates. The most promising combination of steric and electronic effects is seen with *rac*-3. 2 crystallizes in the monoclinic space group $P2_1/c$ with a = 12.894 (3) Å, b = 13.913 (2) Å, c = 20.775 (4) Å, β = 113.51 (2)°, Z = 4, and V = 3417.55 Å^3. The structure was refined to a conventional R value of 0.031. 3 crystallizes in the monoclinic space group Cc with a = 18.335 (2) Å, b = 10.123 (2) Å, c = 19.683 (4) Å, β = 102.35 (1)°, Z = 4, and V = 3568.73 Å^3. The structure was refined to a conventional R factor of 0.019. 4 crystallizes in the orthorhombic space group $Pna2_1$ with a = 20.070 (4) Å, b = 10.665 Å, c = 16.747 (5) Å, Z = 4, and V = 3584.64 Å^3. The structure was refined to a conventional R factor of 0.026. The bulky *t*-Bu groups cause a lengthening of P–Rh distances, wider P–Rh–P angles, and a rotation of the NBD out of the P–Rh–P plane. Generally the effects range from a maximum in 1 (previously determined) to a minimum in 4.

Recently we reported[1] the structure of the hydrogenation catlayst precursor $\{[(\eta^5\text{-}((CH_3)_3C)_2PC_5H_4)_2Fe]Rh(NBD)\}ClO_4$, 1, containing a bulky ferrocene-bridged bis(tertiary phosphine) ligand. The cation shows a very distorted

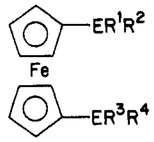
0276-7333/85/2304-0346$01.50/0

Table I. Crystallographic Data[a]

	2	3	4
formula	$C_{37}H_{44}ClFeO_4P_2Rh$	$C_{37}H_{44}ClFeO_4P_2Rh$	$C_{41}H_{36}FeO_4P_2Rh$
fw	808.91	808.91	848.89
cryst system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	Cc	$Pna2_1$
a, Å	12.894 (3)	18.335 (2)	20.070 (4)
b, Å	13.913 (2)	10.123 (2)	10.665 (4)
c, Å	20.775 (4)	19.683 (4)	16.747 (5)
β, deg	113.51 (2)	102.35 (1)	
V, Å^3	3417.55	3568.73	3584.64
Z	4	4	4
D_{calcd}, g cm^{-3}	1.572	1.506	1.573
$F(000)$	1663	1663	1728
cryst dimens, mm	0.13 × 0.13 × 0.13	0.17 × 0.08 × 0.20	[b]
μ(Mo Kα), cm^{-1}	11.09	10.62	10.62
transmissn factors	0.75–0.83	0.84–0.92	0.80–0.88
scan type	ω-2θ	ω-2θ	ω-2θ
2θ scan speed, deg min^{-1}	2.00	2.00	2.00
scan range, deg in 2θ	(1.3 + 0.692 tan θ)	(1.3 + 0.692 tan θ)	(1.3 + 0.692 tan θ)
data collected	$\pm h,k,l$	$\pm h,k,l$	h,k,l
2θ_{max}, deg	45	45	45
cryst decay	negligible	negligible	4%
measd reflctns	4479	2342	2943
obsd reflctns	3680	2098	2226
R	0.031	0.019	0.026
R_w	0.050	0.027	0.033

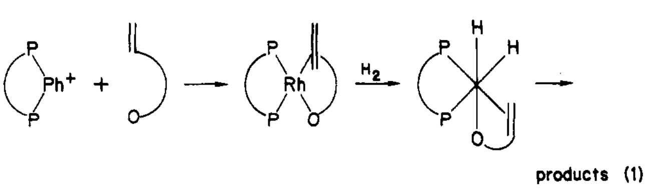
[a] Temperature 293 K; Mo Kα radiation, graphite monochromator, λ = 0.709 26 Å (α_1), 0.713 59 Å (α_2); function minimized: $\Sigma w(|F_o| - |F_c|)^2$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2)^{1/2}$, and $w = 1/(\sigma^2(F) + kF^2)$ where k = 0.0008 for 1 and 0.0006 for 2 and 3. [b] The crystal was a triangular plate: thickness = 0.12 mm, perpendicular distance from each edge to crystal center = 0.22 mm.

square-planar arrangement. This paper presents the structures of three related complexes **2**, **3**, and **4** in which the ligand (P-P) in [(P-P)Rh(NBD)]ClO$_4$ is the ferrocene derivative **5c**, **5d**, or **5f**, respectively. (This whole range of bis(tertiary phosphines) is now available.[2]) The work was carried out in order to probe the origin of the distortions in **1** and to attempt to correlate the structures of the catalyst precursors with their catalytic activity. We had previously found that when **1** and **4** are compared for olefin hydrogenation, faster rates are obtained with **1** when simple olefins **5a–f** (nonchelating) are the substrates.[1]



	R^1	R^2	R^3	R^4
5a	CMe$_3$	CMe$_3$	CMe$_3$	CMe$_3$
5b	CMe$_3$	CMe$_3$	CMe$_3$	Ph
5c	CMe$_3$	CMe$_3$	Ph	Ph
5d	CMe$_3$	Ph	CMe$_3$	Ph
5e	CMe$_3$	Ph	Ph	Ph
5f	Ph	Ph	Ph	Ph

The probable mechanism of these reactions is as delinated in eq 1.[3-6] Here the symbol =⌒O is used to represent a "chelating" olefin such as the commonly used substrate α-(acylamino)cinnamic acid. The rate of the reaction seems to be governed by the ease of oxidative addition of hydrogen in the second step. In the absence of substrate rhodium hydride formation on reaction of the precursor with hydrogen is enhanced by the presence of electron-releasing alkyl groups on the ligand;[7] thus our earlier results could be interpreted in terms of a maximized electronic effect coupled with a minimized steric requirement of the olefin.



(1)

The present investigation in addition to providing more structural information relating in this aspect of catalysis also provides more kinetic data covering a wider range of ligands **5a**, **5c**, **5d**, and **5f** and olefins.

Experimental Section

Ligands and complexes were prepared by literature methods.[1,2,8] Hydrogenation reactions were carried out by using a gas-uptake apparatus as described by James and Rempel.[9]

Structure Determination of [(P-P)Rh(NBD)]ClO$_4$ (2–4). Crystal data for compounds **2–4** are given in Table I. Precession and Weissenberg photographs (Cu Kα, λ = 1.5418 Å) were used to determine the approximate cell dimensions and space group of each compound. For **3** and **4**, where there was abiguity in space group assignment (*Cc* or *C*2/*c* and *Pnma* or *Pna*2$_1$, respectively), correct space groups were confirmed during subsequent structure solution. Accurate cell dimensions (Table I,) were determined by least-squares refinement of the diffractometer angles of a number (20, 20, and 16, respectively, for **2**, **3**, and **4**) of relatively high-angle reflections (with 30 < 2θ < 32°, 28 < 2θ < 32°, and

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[1] Cullen, W. R.; Kim, T.-J.; Einstein, F. W. B.; Jones, T. *Organometallics* **1983**, *2*, 714.

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[8] Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merril, R. E.; Smart, J. C. *J. Organomet. Chem.* **1971**, *27*, 241.

[9] James, B. R.; Rempel, G. L. *Can. J. Chem.* **1966**, *44*, 233.

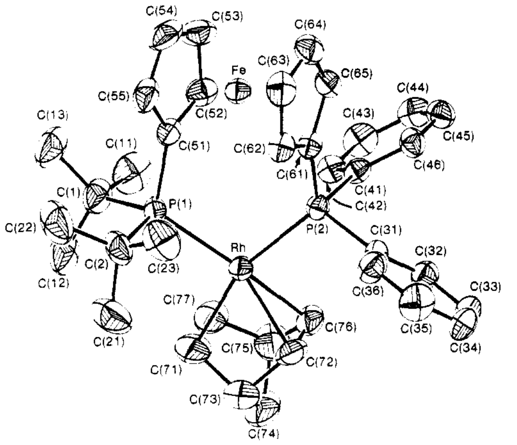

Figure 1. ORTEP diagram and numbering scheme for the $[\{(\eta^5\text{-}(C_6H_5)_2PC_5H_4)Fe(\eta^5\text{-}[(CH_3)_3C]_2PC_5H_4)\}Rh(NBD)]^+$ cation (2). Atoms are represented by 50% probability thermal ellipsoids.

$29 < 2\theta < 30°$ for 2, 3, and 4, respectively) chosen from a variety of points in reciprocal space and measured with Mo $K\alpha_1$ radiation ($\lambda = 0.709\,26$ Å). Data were collected by using a Picker FACS-I four-circle diffractometer with, graphite monochromator, scintillation detector with pulse-height discrimination and a takeoff angle of 3°. For each structure stationary-crystal, stationary-counter counts of 10% of the scan time were taken at each side of a scan. Peak profile analyses were performed on each reflection in each data set and their intensities and associated errors determined by the method of Grant and Gabe.[10] Measurement of two standards every 70 reflections enabled steady monitoring of crystal decomposition and detection chain stability (Table I) throughout each data collection. Lorentz, polarization, and absorption corrections have been applied for 2, 3, and 4.

The structures were solved by conventional Patterson and Fourier methods. All non-hydrogen atoms were easily located. For 3, in space group *Cc*, the x and y coordinates for the Rh atom from the Patterson map were arbitrarily set at $x = {}^1/_2$ and $y = {}^3/_4$. Furthermore, for 4, in space group $Pna2_1$, the z coordinate for Rh from the Patterson map was arbitrarily set at $z = {}^3/_4$. For each structure the positions of aryl and methylene hydrogen atoms were calculated; these hydrogens were included in refinement initially as fixed contributions [C–H = 0.95 Å; $B_{iso}(H) \propto B_{eq}$(parent carbon)]. Subsequent difference Fourier syntheses revealed the positions of remaining hydrogen atoms. During the intermediate stages of refinement of each structure, when the number of variables was relatively low, the coordinates of all hydrogen atoms were allowed to refine. In the case of 2, final cycles of block-diagonal least-squares refinement were performed with the coordinates of all atoms, anisotropic temperature factors for all non-hydrogen atoms, and fixed isotropic temperature factors ($B_{iso} = 6.0$ Å^2) for hydrogen atoms (547 variables). For 3 and 4 final stages of block-diagonal least-squares refinement[11] were carried out with hydrogen atoms included as fixed contributions and with the coordinates and anisotropic temperature factors of non-hydrogen atoms allowed to vary (415 and 450 variables for 2 and 3, respectively). Weighting schemes were derived on the basis of trends in $w\Delta^2$ as a function of $|F_o|$ and $(\sin\theta)/\lambda$ (Table I). The final difference Fourier maps were essentially clear apart from (i) in the case of 2, quite a large peak of 1.57 (7) e/Å^3 at $x = 0.3185$, $y = 0.2901$, and $z = 0.3061$, which lies in a chemically unreasonable position almost midway between Rh and Fe (the origin of this peak is difficult to explain), and (ii) for 4, a peak of 0.43 (6) e/Å at $x = 0.2201$, $y = 0.0854$, and $z = 0.0104$ in the vicinity of the perchlorate anion. Atomic scattering factors including anomalous dispersion were taken from ref [12]. Final positional and B_{iso} parameters for non-hydrogen atoms are given in Tables II–IV.

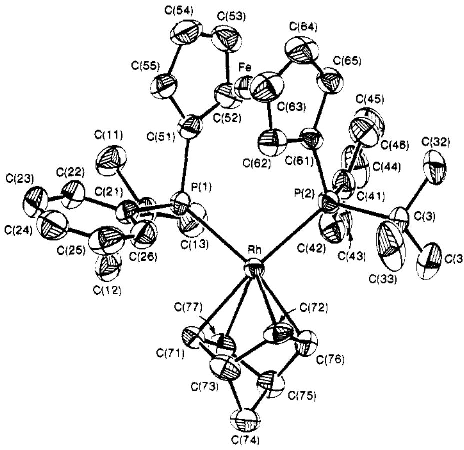

Figure 2. ORTEP diagram and numbering scheme for the $[\{(\eta^5\text{-}C_6H_5[(CH_3)_3C]PC_5H_4)_2Fe\}Rh(NBD)]^+$ cation (3). Atoms are represented by 50% probability thermal ellipsoids.

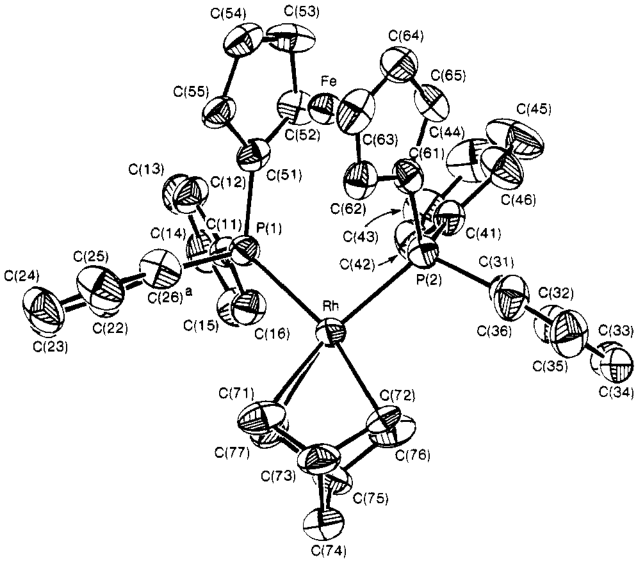

Figure 3. ORTEP diagram and numbering scheme for the $[\{(\eta^5\text{-}(C_6H_5)_2PC_5H_4)_2Fe\}Rh(NBD)]^+$ cation (4). Atoms are represented by 50% probability thermal ellipsoids. (a) In this view of the cation C(21) is totally obscured by C(26).

Anisotropic thermal parameters, mean planes data, hydrogen positional and thermal parameters, and structure factor listing for all three structures have been deposited. The compouter programs used here are those belonging to "The NRC PDP-8e Crystal Structure System".[13]

Results and Discussion

Structures of 1–4. Apart from the importance of these compounds as catalysts they present an interesting series from a purely structural viewpoint. Assuming the double bonds of the norbornadiene ligands occupy single coordination sites, the Rh atom in each structure may be described crudely as lying in a square-planar environment. The progressive change of substitutents joined to the P atoms causes significant changes in this environment. Selected bond parameters for compounds 2–4 are given in Tables V and VI while the structures of their cations are depicted in Figures 1–3. A summary of important bond parameters for 2–4 and 1 is given in Table VII. Previously we noted a number of structural features of 1 that we attributed to steric crowding caused by the bulky *t*-Bu

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[10] Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1977**, *11*, 114.

[11] For compounds 3 and 4, in the noncentric space groups *Cc* and $Pna2_1$ respectively, the coordinates (x, y, z) presented in Tables III and IV gave better agreement than their counterparts $(-x, -y, -z)$ when refined with the "unique" data set collected.

[12] "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[13] Gabe, E. J.; Larson, A. C.; Lee, F. L.; Wang, Y. "The NRC PDP-8e Crystal Structure System"; Chemistry Division, NRC: Ottawa, 1979.

Table II. Final Positional Parameters and B_{eq} Temperature Factors for [(P-P)Rh(NBD)]ClO$_4$, P-P = {(η^5-(C$_6$H$_5$)$_2$PC$_5$H$_4$)Fe(η^5-[(CH$_3$)$_3$C]$_2$PC$_5$H$_4$)} (2)

atom	x	y	z	B_{eq},^{a} Å^2	atom	x	y	z	B_{eq},^{a} Å^2
Rh	0.24429 (2)	0.15779 (2)	0.22058 (1)	2.69 (1)	C(41)	0.2852 (3)	0.3834 (3)	0.1732 (2)	2.7 (2)
Fe	0.26242 (4)	0.28286 (4)	0.38414 (3)	2.73 (2)	C(42)	0.1672 (3)	0.3775 (3)	0.1391 (2)	3.3 (2)
P(1)	0.21028 (8)	0.16813 (7)	0.32542 (5)	2.87 (4)	C(43)	0.1081 (3)	0.4491 (3)	0.0930 (2)	3.9 (2)
P(2)	0.36402 (7)	0.29142 (7)	0.23590 (4)	2.37 (4)	C(44)	0.1627 (4)	0.5250 (3)	0.0797 (2)	4.0 (2)
Cl	0.80642 (9)	0.25232 (8)	0.03072 (6)	4.61 (6)	C(45)	0.2776 (3)	0.5318 (3)	0.1116 (2)	3.5 (2)
O(1)	0.7006 (3)	0.2983 (3)	0.0117 (2)	6.6 (2)	C(46)	0.3392 (3)	0.4623 (3)	0.1582 (2)	3.2 (2)
O(2)	0.8052 (3)	0.1621 (2)	0.0615 (2)	6.8 (2)	C(51)	0.2403 (3)	0.2844 (3)	0.3694 (2)	2.9 (2)
O(3)	0.8872 (4)	0.3125 (4)	0.0789 (3)	9.5 (4)	C(52)	0.1940 (3)	0.3718 (3)	0.3332 (2)	3.5 (2)
O(4)	0.8246 (6)	0.2395 (3)	−0.0298 (3)	15.5 (6)	C(53)	0.2186 (4)	0.4459 (3)	0.3829 (3)	5.4 (3)
C(1)	1.0559 (4)	0.1579 (3)	0.3136 (2)	4.7 (2)	C(54)	0.2797 (4)	0.4086 (4)	0.4486 (2)	4.3 (2)
C(11)	0.9884 (4)	0.2259 (4)	0.2541 (3)	5.9 (3)	C(55)	0.2938 (4)	0.3093 (3)	0.4428 (2)	4.3 (2)
C(12)	1.0111 (4)	0.0563 (4)	0.2934 (3)	6.7 (3)	C(61)	0.4337 (3)	0.3616 (3)	0.3150 (2)	2.8 (2)
C(13)	1.0374 (4)	0.1872 (4)	0.3789 (3)	6.8 (3)	C(62)	0.5070 (3)	0.3267 (3)	0.3827 (2)	3.0 (2)
C(2)	0.3017 (4)	0.0768 (3)	0.3914 (2)	4.3 (2)	C(63)	0.5359 (3)	0.4020 (3)	0.4307 (2)	3.6 (2)
C(21)	0.2913 (5)	−0.0226 (4)	0.3567 (3)	6.4 (4)	C(64)	0.4826 (3)	0.4862 (3)	0.3951 (2)	3.9 (2)
C(22)	0.2718 (5)	0.0622 (4)	0.4552 (3)	6.5 (4)	C(65)	0.4211 (3)	0.4627 (3)	0.3237 (2)	3.5 (2)
C(23)	0.4237 (4)	0.1081 (4)	0.4146 (3)	5.4 (3)	C(71)	0.1655 (4)	0.0158 (3)	0.1856 (3)	5.2 (3)
C(31)	0.4816 (3)	0.2652 (3)	0.2099 (2)	2.8 (2)	C(72)	0.3069 (4)	0.0775 (3)	0.1534 (2)	4.9 (2)
C(32)	0.4720 (3)	0.2756 (3)	0.1413 (2)	3.6 (2)	C(73)	0.2395 (5)	−0.0140 (3)	0.1474 (3)	6.1 (3)
C(33)	0.5614 (4)	0.2525 (3)	0.1230 (2)	4.3 (2)	C(74)	0.1514 (5)	−0.0053 (4)	0.0712 (3)	7.4 (4)
C(34)	0.6605 (4)	0.2193 (3)	0.1731 (2)	4.9 (2)	C(75)	0.1181 (4)	0.0972 (4)	0.0809 (2)	5.2 (3)
C(35)	0.6709 (3)	0.2084 (4)	0.2400 (3)	4.8 (2)	C(76)	0.2323 (4)	0.1452 (3)	0.1125 (2)	4.3 (2)
C(36)	0.5820 (3)	0.2300 (3)	0.2594 (2)	4.1 (2)	C(77)	0.0926 (4)	0.0826 (4)	0.1455 (2)	5.0 (3)

^{a} $B_{eq} = 8\pi^2(U_{11}{}^2 + U_{22}{}^2 + U_{33}{}^2)/3$.

Table III. Final Positional Parameters and B_{eq} Temperature Factors for [(P-P)Rh(NCD)]ClO$_4$, P-P = (η^5-C$_6$H$_5$[(CH$_3$)$_3$C]PC$_5$H$_4$)$_2$Fe

atom	x	y	z	B_{eq},^{a} Å^2	atom	x	y	z	B_{eq},^{a} Å^2
Rh	0.500	0.28293 (3)	0.75000	2.18 (1)	C(41)	0.4726 (3)	0.1560 (6)	0.5907 (3)	3.2 (3)
Fe	0.64313 (4)	0.41040 (8)	0.61348 (4)	3.37 (4)	C(42)	0.4562 (3)	0.0513 (6)	0.6320 (3)	3.7 (3)
P(1)	0.63326 (7)	0.25593 (13)	0.76370 (7)	2.56 (6)	C(43)	0.4619 (4)	−0.0764 (6)	0.6121 (3)	4.7 (4)
P(2)	0.46879 (7)	0.32173 (14)	0.62755 (7)	2.59 (6)	C(44)	0.4833 (4)	−0.1046 (7)	0.5521 (3)	5.1 (4)
Cl	−0.03474 (8)	0.27882 (13)	0.81960 (8)	3.97 (7)	C(45)	0.4970 (5)	−0.0050 (8)	0.5094 (4)	5.1 (3)
O(1)	−0.0086 (3)	0.1949 (4)	0.7720 (3)	6.8 (3)	C(46)	0.4909 (4)	0.1269 (6)	0.5270 (3)	4.3 (3)
O(2)	0.0271 (3)	0.3360 (5)	0.8667 (3)	6.2 (3)	C(51)	0.6803 (3)	0.2839 (6)	0.6928 (3)	3.3 (3)
O(3)	−0.0775 (3)	0.2068 (5)	0.8587 (3)	7.5 (4)	C(52)	0.6646 (3)	0.2151 (6)	0.6280 (3)	3.9 (3)
O(4)	−0.0781 (3)	0.3824 (5)	0.7826 (3)	7.0 (3)	C(53)	0.7093 (4)	0.2672 (8)	0.5854 (3)	5.3 (4)
C(1)	0.6714 (3)	0.0883 (6)	0.7952 (3)	3.4 (3)	C(54)	0.7549 (3)	0.3666 (8)	0.6220 (4)	5.8 (5)
C(11)	0.7494 (3)	0.0595 (7)	0.7835 (4)	4.8 (3)	C(55)	0.7369 (3)	0.3784 (6)	0.6887 (3)	4.1 (3)
C(12)	0.6709 (3)	0.0702 (6)	0.8730 (3)	4.2 (3)	C(61)	0.5323 (3)	0.4321 (5)	0.5969 (3)	2.7 (2)
C(13)	0.6179 (4)	−0.0151 (6)	0.7526 (4)	4.7 (3)	C(62)	0.5678 (3)	0.5375 (5)	0.6417 (3)	3.7 (3)
C(21)	0.6799 (3)	0.3800 (5)	0.8270 (3)	2.9 (3)	C(63)	0.6143 (3)	0.6079 (6)	0.6047 (4)	4.7 (3)
C(22)	0.7531 (3)	0.3703 (6)	0.8627 (3)	3.8 (3)	C(64)	0.6073 (4)	0.5533 (7)	0.5387 (3)	4.9 (3)
C(23)	0.7846 (3)	0.4688 (7)	0.9085 (3)	4.7 (4)	C(65)	0.5564 (3)	0.4447 (6)	0.5327 (3)	3.7 (3)
C(24)	0.7437 (4)	0.5785 (7)	0.9170 (3)	5.2 (4)	C(71)	0.5143 (3)	0.2830 (5)	0.8645 (3)	3.0 (3)
C(25)	0.6717 (4)	0.5933 (7)	0.8808 (4)	5.1 (3)	C(72)	0.4194 (3)	0.4009 (5)	0.7876 (3)	3.3 (3)
C(26)	0.6401 (3)	0.4933 (6)	0.8360 (3)	3.8 (3)	C(73)	0.4515 (3)	0.3829 (5)	0.8650 (3)	3.5 (3)
C(3)	0.3745 (3)	0.3895 (6)	0.5806 (3)	3.6 (3)	C(74)	0.3923 (3)	0.2904 (6)	0.8848 (3)	4.0 (3)
C(31)	0.3136 (4)	0.2851 (10)	0.5805 (4)	7.1 (6)	C(75)	0.3962 (3)	0.1909 (5)	0.8261 (3)	3.3 (3)
C(32)	0.3756 (4)	0.4160 (8)	0.5045 (3)	5.3 (5)	C(76)	0.3857 (3)	0.2846 (6)	0.7639 (3)	3.4 (3)
C(33)	0.3586 (5)	0.5154 (9)	0.6159 (4)	7.4 (6)	C(77)	0.4798 (3)	0.1690 (5)	0.8391 (3)	3.1 (2)

^{a} $B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{23})/3$.

substituents.[1] The most prominent of these features included a very wide P–Rh–P angle, exceptionally long Rh–P(*t*-Bu,*t*-Bu) distances and a large twist angle γ (defined in Table VII). The present results are in accord with this proposal, with trends toward shorter Rh–P bonds, lower P–Rh–P angles, and lower γ angles (Table VII) on substitution of the less sterically imposing Ph groups in place of *t*-Bu groups. It should be pointed out, however, that compound **2** does not fit nicely into this pattern. For instance, its P–Rh–P angle of 100.25 (3)° is larger than that of 98.60 (5)° found for **3**, while its γ angle of 14.4° is less than the value of 20.0° found for **3**. Furthermore, the Rh–P distances in **2**, although internally consistent, i.e., Rh–P(*t*-Bu,*t*-Bu) < Rh–P(Ph,Ph), do not agree with the values found in **1**, **3**, and **4**, e.g., Rh–P(*t*-Bu,*t*-Ph) for **3** is 2.416 (1) Å, whereas Rh–P(*t*-Bu,*t*-Bu) in **2** is only 2.391 (1) Å. Although **2** has the only cation in the series in which each of its P atoms is different, it is difficult to account for these anomalies.

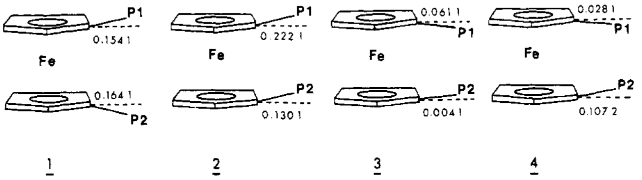

Figure 4. Schematic representation of the deviation of P atoms from cyclopentadienyl planes in compounds 1–4 (deviations have been exaggerated for clarity).

Our previous study on **1** showed a large P–Rh–P angle associated with a relatively large deviation of the P atoms out of the cyclopentadienyl (Cp) ring planes to which they

Table IV. Final Positional Parameters and B_{eq} Temperature Factors for $[(P\text{-}P)Rh(NBD)]ClO_4$, P-P = $(\eta^5\text{-}(C_6H_5)_2PC_5H_4)_2Fe)$ (4)

atom	x	y	z	B_{eq},[a] Å^2	atom	x	y	z	B_{eq},[a] Å^2
Rh	0.04534 (2)	0.10597 (4)	3/4	2.90 (2)	C(35)	0.2744 (3)	−0.1339 (7)	0.7485 (7)	5.5 (4)
Fe	0.16145 (4)	0.43473 (8)	0.79020 (6)	3.10 (4)	C(36)	0.2382 (3)	−0.0234 (7)	0.7551 (5)	4.7 (4)
P(1)	0.00645 (7)	0.31118 (13)	0.76349 (11)	2.84 (8)	C(41)	0.1463 (3)	0.2221 (6)	0.5988 (4,	3.5 (3)
P(2)	0.14911 (8)	0.15643 (16)	0.69859 (11)	3.18 (8)	C(42)	0.0847 (4)	0.2363 (8)	0.5620 (4)	4.6 (4)
Cl	0.13424 (11)	0.04672 (18)	0.02197 (11)	5.0 (1)	C(43)	0.0790 (4)	0.2949 (8)	0.4898 (5)	5.6 (5)
O(1)	0.1569 (4)	−0.0033 (6)	−0.0496 (4)	8.5 (5)	C(44)	0.1336 (5)	0.3412 (8)	0.4522 (5)	6.6 (6)
O(2)	0.0641 (4)	0.0037 (8)	0.0299 (4)	8.9 (5)	C(45)	0.1962 (5)	0.3217 (9)	0.4853 (5)	7.0 (6)
O(3)	0.1298 (3)	0.1777 (5)	0.0213 (4)	7.0 (4)	C(46)	0.2023 (4)	0.2614 (8)	0.5586 (4)	5.1 (5)
O(4)	0.1655 (3)	0.0011 (6)	0.0900 (4)	7.8 (4)	C(51)	0.0619 (3)	0.4446 (5)	0.7705 (4)	3.1 (4)
C(11)	−0.0481 (3)	0.3599 (6)	0.6820 (4)	2.9 (3)	C(52)	0.0979 (3)	0.4974 (6)	0.7061 (4)	3.6 (3)
C(12)	−0.0616 (3)	0.4861 (6)	0.6688 (4)	3.9 (4)	C(53)	0.1358 (3)	0.5981 (6)	0.7354 (5)	4.7 (5)
C(13)	−0.0993 (3)	0.5224 (7)	0.6027 (5)	4.5 (4)	C(54)	0.1254 (3)	0.6095 (6)	0.8170 (4)	4.0 (4)
C(14)	−0.1256 (3)	0.4336 (7)	0.5518 (4)	4.2 (4)	C(55)	0.0790 (3)	0.5156 (5)	0.8398 (4)	3.4 (3)
C(15)	−0.1137 (3)	0.3111 (7)	0.5659 (4)	4.1 (4)	C(61)	0.1962 (3)	0.2632 (5)	0.7602 (4)	3.2 (3)
C(16)	−0.0753 (3)	0.2744 (6)	0.6295 (4)	3.6 (3)	C(62)	0.1855 (3)	0.2712 (6)	0.8440 (4)	3.6 (3)
C(21)	−0.0430 (3)	0.3246 (6)	0.8546 (4)	3.1 (3)	C(63)	0.2262 (3)	0.3668 (7)	0.8744 (4)	4.4 (4)
C(22)	−0.1111 (3)	0.3431 (7)	0.8541 (4)	4.3 (4)	C(64)	0.2614 (3)	0.4206 (6)	0.8113 (5)	4.8 (5)
C(23)	−0.1466 (4)	0.3457 (8)	0.9246 (5)	5.6 (5)	C(65)	0.2443 (3)	0.3572 (7)	0.7406 (5)	4.4 (4)
C(24)	−0.1130 (4)	0.3285 (9)	0.9955 (5)	6.5 (6)	C(71)	−0.0225 (4)	0.0116 (6)	0.8373 (4)	4.6 (4)
C(25)	−0.0468 (4)	0.3049 (9)	0.9978 (4)	5.6 (5)	C(72)	0.0692 (4)	−0.0896 (5)	0.7805 (5)	4.4 (5)
C(26)	−0.0117 (4)	0.3017 (7)	0.9266 (4)	4.4 (4)	C(73)	0.0153 (4)	−0.1106 (6)	0.8409 (5)	4.7 (4)
C(31)	0.2037 (3)	0.0199 (6)	0.6887 (4)	3.3 (3)	C(74)	−0.0312 (4)	−0.1946 (6)	0.7923 (5)	5.0 (4)
C(32)	0.2056 (3)	−0.0511 (7)	0.6191 (5)	4.3 (3)	C(75)	−0.0336 (4)	−0.1064 (7)	0.7206 (4)	4.7 (4)
C(33)	0.2422 (4)	−0.1586 (7)	0.6143 (5)	4.5 (4)	C(76)	0.0396 (4)	−0.0869 (6)	0.7053 (5)	4.8 (4)
C(34)	0.2760 (3)	−0.2019 (6)	0.6798 (5)	4.7 (5)	C(77)	−0.0531 (3)	0.0155 (6)	0.7632 (6)	5.4 (5)

[a] $B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$.

Table V. Selected[a] Interatomic Distances (Å) for 2, 3, and 4

	2	3	4
Rh-P(1)	2.391 (1)	2.416 (1)	2.335 (2)
Rh-P(2)	2.356 (1)	2.388 (1)	2.317 (2)
Rh-C(71)	2.207 (4)	2.219 (5)	2.238 (6)
Rh-C(72)	2.178 (4)	2.151 (5)	2.201 (6)
Rh-C(76)	2.195 (4)	2.171 (5)	2.192 (7)
Rh-C(77)	2.218 (4)	2.196 (5)	2.210 (6)
Fe-C(51)	2.026 (4)	2.022 (5)	2.027 (6)
Fe-C(52)	2.008 (4)	2.024 (6)	2.014 (6)
Fe-C(53)	2.036 (4)	2.040 (7)	2.036 (7)
Fe-C(54)	2.048 (4)	2.068 (6)	2.049 (6)
Fe-C(55)	2.050 (4)	2.040 (6)	2.042 (6)
Fe-C(61)	2.014 (4)	2.000 (5)	2.021 (6)
Fe-C(62)	2.038 (4)	2.049 (6)	2.021 (6)
Fe-C(63)	2.068 (4)	2.066 (6)	2.050 (7)
Fe-C(64)	2.049 (4)	2.068 (6)	2.043 (6)
Fe-C(65)	2.027 (4)	2.024 (6)	2.035 (7)
P(1)-C(1)	1.912 (4)	1.889 (5)	
P(1)-C(11)			1.825 (6)
P(1)-C(2)	1.895 (4)		
P(1)-C(21)		1.845 (5)	1.826 (6)
P(1)-C(51)	1.821 (4)	1.813 (5)	1.810 (6)
P(2)-C(3)		1.905 (5)	
P(2)-C(31)	1.837 (3)		1.829 (6)
P(2)-C(41)	1.820 (4)	1.835 (6)	1.813 (7)

Table VI. Selected[a] Bond Angles (deg) for 2, 3, and 4

	2	3	4
P(1)-Rh-P(2)	100.25 (3)	98.60 (5)	96.82 (6)
P(1)-Rh-MP(1)[b]	101.04	85.40	97.7
P(1)-Rh-MP(2)	165.29	156.92	165.3
MP(1)-Rh-MP(2)	67.96	69.09	68.2
P(2)-Rh-MP(1)	157.11	163.82	165.1
P(2)-Rh-MP(2)	92.31	99.66	97.5
Rh-P(1)-C(1)	116.0 (1)	115.7 (2)	
Rh-P(1)-C(11)			113.3 (2)
Rh-P(1)-C(2)	109.4 (1)		
Rh-P(1)-C(21)		108.1 (2)	109.6 (2)
Rh-P(1)-C(51)	115.5 (1)	122.2 (2)	122.5 (2)
C(1)-P(1)-C(2)	111.0 (2)		
C(1)-P(1)-C(21)		107.7 (3)	
C(11)-P(1)-C(21)			106.1 (3)
C(1)-P(1)-C(51)	97.6 (2)	100.9 (3)	
C(11)-P(1)-C(51)			101.2 (3)
C(2)-P(1)-C(51)	106.6 (2)		
C(21)-P(1)-C(51)		100.7 (3)	102.6 (3)
Rh-P(2)-C(3)		123.1 (2)	
Rh-P(2)-C(31)	112.2 (1)		112.8 (2)
Rh-P(2)-C(41)	108.0 (1)	103.1 (2)	113.8 (2)
Rh-P(2)-C(61)	127.5 (1)	114.0 (2)	113.9 (2)
C(3)-P(2)-C(41)		104.2 (3)	
C(31)-P(2)-C(41)	102.7 (2)		104.0 (3)
C(31)-P(2)-C(61)	101.8 (2)		104.0 (3)
C(3)-P(2)-C(61)		101.4 (2)	
C(41)-P(2)-C(61)	101.8 (2)	110.6 (2)	107.5 (3)
P(1)-C(51)-C(52)	122.1 (3)	124.9 (4)	125.2 (5)
P(1)-C(51)-C(55)	131.3 (3)	128.4 (5)	128.2 (5)
P(2)-C(61)-C(62)	127.1 (3)	119.3 (4)	121.6 (6)
P(2)-C(61)-C(65)	127.0 (3)	133.9 (4)	131.6 (6)
Cp(1)-Fe-Cp(2)[c]	176.9	178.5	179.6

[a] Further bond parameters have been deposited. [b] MP(1) is the midpoint between C(71) and C(77); MP(2) is the midpoint between C(72) and C(76). [c] Cp(1) is the centroid of C(51)-C(55); Cp(2) is the centroid of C(61)-C(65).

are attached. Scematic diagrams of the arrangements found in 1 and the present series together with deviations (Å) of P atoms out of their Cp planes are seen in Figure 4. Bulky P-*t*-Bu$_2$ groups all show repulsive deviations, PPh-*t*-Bu and PPh$_2$ groups the reverse. It seems that in 2 the two effects are synergistic.

The Rh–C distances for each compound are comparable with values reported in related compounds.[1,14-17] Although errors do not allow confident analysis, it appears that Rh–C distances for 1, which contains the least tightly bound bis(teritary phosphine) are shorter than the corresponding values in 4, which contains the most tightly bound one. The MP(1)–Rh–MP(2) angles in all compounds are es-

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Table VII. Summary of Important Bond Parameters for the Series [(P-P)Rh(NBD)]ClO$_4$

	1[a]	2	3	4
Rh-P(*t*-Bu,*t*-Bu)[b]	2.466 (1), 2.458 (1)	2.391 (1)		
Rh-P(*t*-Bu,Ph)			2.416 (1), 2.388 (1)	
Rh-P(Ph,Ph)		2.356 (1)		2.335 (2), 2.317 (2)
Rh-MP(1)	2.069	2.108	2.097	2.113
Rh-MP(2)	2.048	2.077	2.050	2.083
Fe-Cp(1)	1.639	1.641	1.646	1.642
Fe-Cp(2)	1.639	1.646	1.643	1.642
P-Rh-P	103.71 (5)	100.25 (3)	98.60 (5)	96.82 (6)
MP(1)-Rh-MP(2)	68.4	68.0	69.1	68.2
Cp(1)-Fe-Cp(2)	177.2	176.9	178.9	179.6
twist angle γ[c]	36.8	14.4	20.0	5.9

[a] The structure of this compound has been previously reported in ref 1. [b] The notations P(*t*-Bu,*t*-Bu) or P(*t*-Bu,Ph) etc. define the substituents, other than cyclopentadienyl, which are joined to phosphorus. [c] Twist angle γ is defined as the angle between the Rh,P(1),P(2) plane and the Rh,MP(1),MP(2) plane.

sentially constant (Table VII) due to the rigidity imposed by the NBD ligand.

With regard to the ferrocenylphosphine moieties in compounds **2**–**4**, the P–C distances display the not surprising trend P–C(Cp) < P–C(Ph) < P–C(*t*-Bu), while the C–P–C angles do not appear unusual. The cyclopentadienyl and phenyl rings, in each compound, are essentially planar; however, deviations of up to ±0.03 Å are observed in some planes (mean planes data have been deposited). The cyclopentadienyl rings exhibit substituent-induced geomerical distortion similar to that observed in related compounds.[18] The mean C–C bond length, involving the P-substituted carbons is 1.430 (9) Å, the adjacent C–C bonds average 1.410 (13) Å, while the unique C–C bonds average 1.394 (9) Å. Bond angles within the cyclopentadienyl rings are normal, and the angles associated with the substituted carbons are contracted slightly from the "ideal" 108.0° to 105.4 (4)–106.8 (6)°. The bond parameters of the phenyl rings are such that no obvious substituent-induced distortions can be detected. The Fe–Cp distances and Cp–Fe–Cp angles are similar for all compounds. The bond parameters of the norbornadiene ligands are similar to those found in **1** and other similar compounds.[1,15,17,19]

The Cp rings in the complex of **5f** (Figure 3) are staggered. This same conformation is found in (P-P)PdCl$_2$ (square planar) and (P-P)Mo(CO)$_4$ (octahedral), with (P-P) = **5f**.[2,20] These complexes can be regarded as (3)-ferrocenophanes. More conventional variants such as $(\eta^5\text{-}C_5H_4\overline{S)Fe(\eta^5\text{-}C_5H_4S}S)$ have eclipsed Cp rings with variable barriers to bridge reversal[21] that, by analogy with cyclohexane, is believed to proceed via an intermediate with staggered Cp rings. It seems that bulky bridge substituents and/or longer bond lengths favor the staggered conformation over the eclipsed.[2,21] On this basis it is not surprising that staggered Cp rings are found in **1**–**4**.

Catalytic Studies. The cationic rhodium(I) derivatives described above are all catalyst precursors for olefin hydrogenation. The following olefins were hydrogenated under standard conditions:[22] RHC=C(COOH)NHCOMe (R = H, Ph), H_2C=C(COOH)CH_2COOH, PhHC=C(Me)COOH, *n*-C_8H_8, and c-C_6H_{10}. With the exception of one reaction that did not proceed (the combination of **4** with α-methylcinnamic acid) all reactions are rapid and go to completion within 15 min. The most interesting result is that the simple olefins are hydrogenated much faster when *t*-Bu groups are present on the ligand, whereas the chelating substrates (eq 1) react faster when there is less bulk on the ligand.

In the case of catalysis by the widely studied RhX(PR$_3$)$_3$ systems nonchelating olefins are hydrogenated in the order RCH=CH$_2$ > c-C_6H_{10} > R_2C=CH$_2$ > R_2C=CHR. This order of reactivity is maintained approximately for catalysts **3**, **2** and **1**; **4** provides a definite exception. Overall it seems that **3** offers the best balance between steric and electronic effects and further studies with ligands of this type using resolved racemic and meso isomers should be rewarding.

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Registry No. **1**, 84680-98-8; **2**, 92284-07-6; **3**, 92269-95-9; **4**, 84680-96-6; H_2C=C(COOH)NHCOMe, 5429-56-1; PhHC=C(COOH)NHCOMe, 5469-45-4; H_2C=C(COOH)CH_2COOH, 97-65-4; PhHC=C(Me)COOH, 1199-77-5; *c*-C_6H_{10}, 110-83-8.

Supplementary Material Available: Hydrogenation of olefins (experimental data) and tables of bond distances and angles, mean plane calculations, anisotropic thermal parameters, positional and thermal parameters for H atoms, observed and calculated structure factor amplitudes for compounds **2**, **3**, and **4** (87 pages). Ordering information is given on any current masthead page.

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