1,1'-Bis[(alkyl/aryl)phosphino]ferrocenes: Synthesis and Metal Complex Formation. Crystal Structure of Three Metal Complexes of Fe(η^5-C$_5$H$_4$PPh$_2$)$_2$

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The ferrocenylphosphines Fe(η^5-C$_5$H$_4$PR^{1}R^2)(η^5-C$_5$H$_4$PR^{3}R^4) (R^1⋯R^4 = Ph or CMe$_3$) are prepared by reacting ClPR^{1}R^2 with either Fe(η^5-C$_5$H$_4$Li)$_2$ or Fe(η^5-C$_5$H$_4$Li)(η^5-C$_5$H$_4$PR^{3}R^4). The latter reagent is obtained by cleaving the ferrocenophane Fe(η^5-C$_5$H$_4$PR^3)(η^5-C$_5$H$_4$) with R^{4}Li. Best results are obtained when either or both R^3 and R^4 are Ph. A representative range of Pd(L-L)Cl$_2$, [Rh(L-L)NBD]ClO$_4$, and Ni(L-L)X$_2$ complexes has been prepared. Crystal data for the known compounds (R^1⋯R^4 = Ph) (L-L)PdCl$_2$·CH$_2$Cl$_2$, (L-L)NiBr$_2$, and (L-L)Mo(CO)$_4$·C$_6$H$_6$ are as follows: Pd, P2$_1$/c, a = 9.8615 Å, b = 18.2322 Å, c = 19.1540 Å, β = 102.581°, Z = 4; Ni, Pn2$_1$a, a = 20.4163 Å, b = 14.7573 Å, c = 10.2015 Å, Z = 4; Mo, p$\bar{1}$, a = 10.950 Å, b = 18.110 Å, c = 10.3433 Å, α = 101.777°, β = 93.322°, γ = 83.059°, Z = 2; Mo radiation; R = 0.029, 0.069, and 0.033 for 4324, 1870, and 6687 reflections, respectively. The Pd, Ni, and Mo atoms have cis square-planar, tetrahedral, and cis octahedral coordinations, respectively; mean Pd-P = 2.284 (6) Å, Pd-Cl = 2.349 (9) Å, Ni-P = 2.290 (9) Å, Ni-Br = 2.348 (4) Å, Mo-P = 2.560 (16) Å, and Mo-C = 1.974 (5) (trans to P) and 2.038 (3) Å (cis to P). The ferrocene ligands have slightly nonparallel cyclopentadienyl rings, with approximately staggered arrangements in the Pd and Mo compounds but an approximately eclipsed conformation in the Ni complex and with significant displacements of the P atoms from the ring planes. Both the molybdenum compound and its chromium analogue are fluxional in solution to -80 °C.

Introduction

Ferrocenylphosphines have found useful synthetic application as ligands in the rhodium-, ruthenium-, and palladium-catalyzed hydrogenation of olefins[1-7] and the nickel- and palladium-catalyzed Grignard cross-coupling reactions.[8-11] In particular it has been found that cationic rhodium(I) complexes of 1,1'-bis(diphenylphosphino)-ferrocene, 1, are efficient hydrogenation catalysts for olefin reduction.[5] Similarly (di-*tert*-butylphosphino)ferrocene derivatives such as 2 may also be employed as ligands in such reactions; use of optically pure ligand results in unexpectedly high optical yields of product from the reduction of α-(acylamino)acrylic acids.[3,7]

We are interested in the modification of chelating ferrocenylphosphine ligands, particularly 1 to establish the effect of bulky phosphorus substituents on the rate and mechanism of reaction. As part of ongoing studies the preparation of 1,1'-bis(di-*tert*-butylphosphino)ferrocene, 3, and a cationic rhodium(I) complex of 3 were recently described.[4] We now report the synthesis of a series of related 1,1'-bis[(alkyl/aryl)phosphino]ferrocenes designed specifically for use as ligands in hydrogenation and
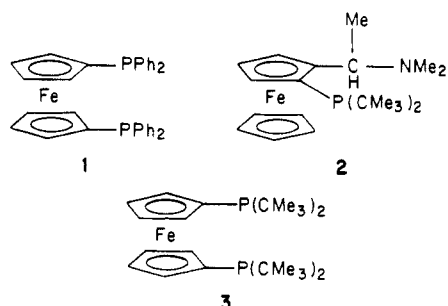

cross-coupling reaction studies.

In earlier studies a series of metal complexes of ligands like 1 has been prepared by the groups of Davison,[12] Kumada,[13] and others,[14] but little X-ray structural data are available.[5,15,16] Thus, it is not known if the cyclopentadienyl rings are always eclipsed (or staggered) as in 4 (or 5) or if structural differences can account for the large differences observed in regioselectivity in cross-coupling reactions catalyzed by M(L-L)Cl$_2$ (L-L = 1 and M = Ni or Pd).[1b] To this end we have carried out some studies of the metal complexes of the series of ligands 1, 3, and 6-9 and in this paper describe the crystal structures of Pd(L-L)Cl$_2$·CH$_2$Cl$_2$, Ni(L-L)Br$_2$, and Mo(L-L)(CO)$_4$·C$_6$H$_6$ (L-L = 1).[16]

Experimental Section

All experimental manipulations were carried out under an N$_2$ or Ar atmosphere using conventional Schlenk tube techniques.

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(16) The crystal structure of Pd(L-L)Cl$_2$·CHCl$_3$ (L-L = 1) was reported[11] during the preparation of this manuscript. We describe the structure of the closely related molecule Pd(L-L)Cl$_2$·CH$_2$Cl$_2$.

5a

4a

4b

5b
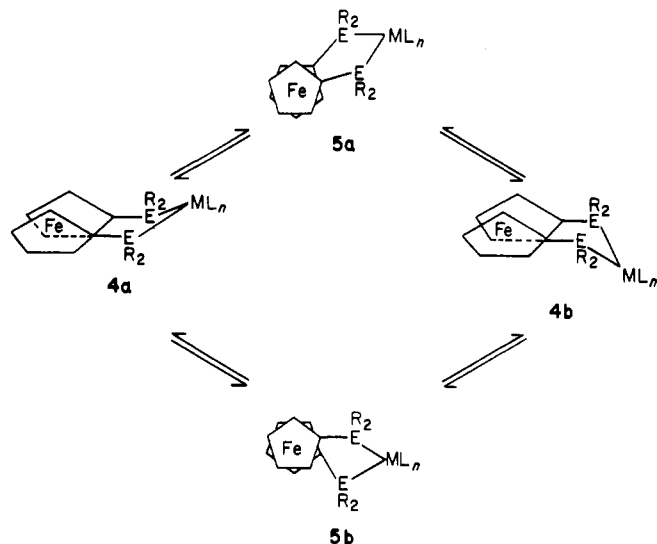
Microanalyses were performed by Mr. Peter Borda of this department. ^{1}H and ^{31}P NMR spectra were recorded in CDCl$_3$ solutions, except where otherwise stated, using a Bruker WP-80, a Varian XL-100, or a Bruker WH-400 spectrometer. Chemical shifts are reported in parts per million downfield from external Me$_4$Si and ^{31}P shifts relative to 85% H$_3$PO$_4$, with P(OMe)$_3$ (δ +141.0) used as external reference. Couplings are given in hertz. All solvents were predried by using conventional techniques and were freshly distilled prior to use. n-Butyllithium in hexane, $tert$-butyllithium in hexane, and phenyllithium in benzene were supplied by the Aldrich Chemical Co. Mass spectra were obtained by using a Kratos MS-50 spectrometer. Petroleum ether refers to the fraction bp 30–60 °C.

Preparation of the Symmetrically 1,1'-Disubstituted Phosphinoferrocenes 1, 3, and 6. Compounds 1 and 3 were prepared according to the literature procedures.[4] Compound 6 was prepared as described for the preparation of 3 replacing di-$tert$-butylchlorophosphine with $tert$-butylchlorophenyl-phosphine. 6 was isolated after chromatography as a deep red oil which solidified slowly on standing at 0 °C (60% yield). The meso and racemic isomers were separated by chromatography on alumina (neutral, Grade 1) eluting with petroleum ether/diethyl ether (70/30): mp 56–58 °C (racemic); ^{1}H NMR (CDCl$_3$) δ 1.20 (d, 18, J = 12 Hz), 4.32 (t, 4), 4.10 (t, 4), 7.80 (m, 4), 7.50 (m, 6). Anal. Calcd for C$_{30}$H$_{36}$FeP$_2$: C, 70.07; H, 7.00. Found: C, 68.91; H, 6.95.

Preparation of 1-(Diphenylphosphino)-1'-(di-$tert$-butyl-phosphino)ferrocene, 7. The ferrocenophane cleavage reaction (eq 2) was carried out essentially by the procedure of Seyferth and Withers[17] with minor modification. A solution containing the [1]ferrocenophane (10) (1.50 g, 5.14 mmol) in diethyl ether ($\sim$30 mL) at -78 °C was added dropwise to a stirred solution of phenyllithium (4 mL of a 1.95 M solution in benzene). The mixture was allowed to warm to room temperature slowly. The solution was then recooled to -78 °C, and excess di-$tert$-butyl-chlorophosphine (3 mL) in diethyl ether (3 mL) was added dropwise. The resulting mixture was slowly warmed to room temperature and was subsequently heated to a gentle reflux for 10 min. Precipitation of LiCl occurred. After being stirred for a further 20 min at room temperature, the solution was hydrolyzed (H$_2$O, 20 mL) and the ether layer separated and dried over anhydrous MgSO$_4$ for 90 min. The solvent volume was reduced to a few milliliters following filtration. The residual oil was chromatographed on neutral alumina to give a single orange band which eluted with diethyl ether/petroleum ether (10/90). Crystallization was initially attempted from petroleum ether, but this was unsuccessful; a mixture of acetone and methanol (20/80) was finally used, and a yellow crystalline solid was isolated. This compound was carefully washed with a few milliliters of *cold* petroleum ether and was vacuum dried at room temperature: yield 47%; ^{1}H NMR (CDCl$_3$) δ 1.12 (d, 18, J = 11.5 Hz), 4.30 (t, t), 4.37 (t, 2), 4.48 (t, 2), 4.62 (t, 2), 7.33 (m, 10). Anal. Calcd for

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C$_{30}$H$_{36}$FeP$_2$: C, 70.06; H, 7.00. Found: C, 69.95; H, 6.95.

Preparation of 1-(Diphenylphosphino)-1'-($tert$-butyl-phenylphosphino)ferrocene, 8, and 1-(Di-$tert$-butyl-phosphino)-1'-($tert$-butylphenylphosphino)ferrocene, 9. The title compounds were prepared from 11 by a procedure essentially identical with that used for the preparation of 7 (Scheme I). The alternative preparations of 8 and 9 using $tert$-butyllithium, 10, and di-$tert$-butylchlorophosphine or chlorodiphenylphosphine were also studied. The latter required hexane as a solvent, and the cleavage reaction was much slower.

Complex Preparation. Pd(L-L)Cl$_2$, Ni(L-L)X$_2$, [Rh(L-L)NBD][ClO$_4$], and M(L-L)(CO)$_4$ (L-L = Bis(tertiary phosphine); X = Cl, Br; M = Mo, W). (i) [Pd(L-L)Cl$_2$]. These complexes were prepared by the direct reaction of either Pd-(PhCN)$_2$Cl$_2$, Pd(COD)Cl$_2$, or K$_2$PdCl$_4$ with a slight molar excess of the appropriate ligand in diethyl ether containing a few milliliters of methylene chloride or chloroform. The product complexes formed as red-orange precipitates in each case which were isolated by filtration. For crystallization the product ($\sim$300 mg) was dissolved in methylene chloride or chloroform ($\sim$5 mL), and a top layer of cyclohexane ($\sim$2.5 mL) was carefully added. Slow diffusion of the solvent layers resulted in the formation of crystalline samples. The crystals thus obtained were washed with n-hexane and vacuum dried.

(ii) Ni(L-L)X$_2$. These compounds were prepared by modest adaptations of published procedures and were isolated in all cases as green crystalline solids.[12]

(iii) [Rh(NBD)(L-L)][ClO$_4$]. The procedure of Schrock and Osborn[18] was used, and the compounds were isolated by two phase crystallization (CH$_2$Cl$_2$ or CHCl$_3$ with cyclohexane).

(iv) M(CO)$_4$(L-L). These compounds were prepared by the literature procedure.[12]

X-ray Crystallographic Analyses of (L-L)PdCl$_2$·CH$_2$Cl$_2$, (L-L)NiBr$_2$, and (L-L)Mo(CO)$_4$·C$_6$H$_6$ (L-L = 1). Crystallographic data for all three complexes are given in Table I. Crystals were mounted in nonspecific orientations on an Enraf-Nonius CAD4-F diffractometer. Final unit-cell parameters were obtained by least-squares on (2 sin θ)/λ values for 25 reflections (with 2θ in the ranges 35–45°, 30–40, and 40–47°, respectively, for the Pd, Ni, and Mo compounds) measured with Mo Kα_1 radiation (λ = 0.709 30 Å).

The intensities of three check reflections were monitored every hour of X-ray exposure time throughout the data collections and in each case showed only small random fluctuations. The data were processed[19] and absorption corrections were made (Gaussian integration[20,21]), those reflections for which $I \geq 3\sigma(I)$ were considered observed and employed in the solution and refinement of the structures.

In the cases of the Mo and Ni complexes the space groups $P\bar{1}$ and $Pn2_1a$ were indicated by both the E statistics and the Patterson functions. Each of the structures was solved by conventional heavy-atom techniques; all non-hydrogen atoms not located from the Patterson function were positioned from subsequent Fourier syntheses. In the case of the Pd complex, all hydrogen atoms except those associated with the CH$_2$Cl$_2$ solvent molecule were located on a difference map and were refined with isotropic thermal parameters; the solvent hydrogen positions were calculated (C–H = 0.98 Å) and included as fixed atoms. For the Ni and Mo complexes all hydrogen atoms were placed in idealized positions [C(sp^2)–H = 0.97; C(sp^3)–H = 0.98 Å] and included as fixed atoms in subsequent cycles of refinement. Neutral atom scattering factors from ref 22 were used for the non-hydrogen atoms and those of ref 23 for hydrogen atoms. Anomalous

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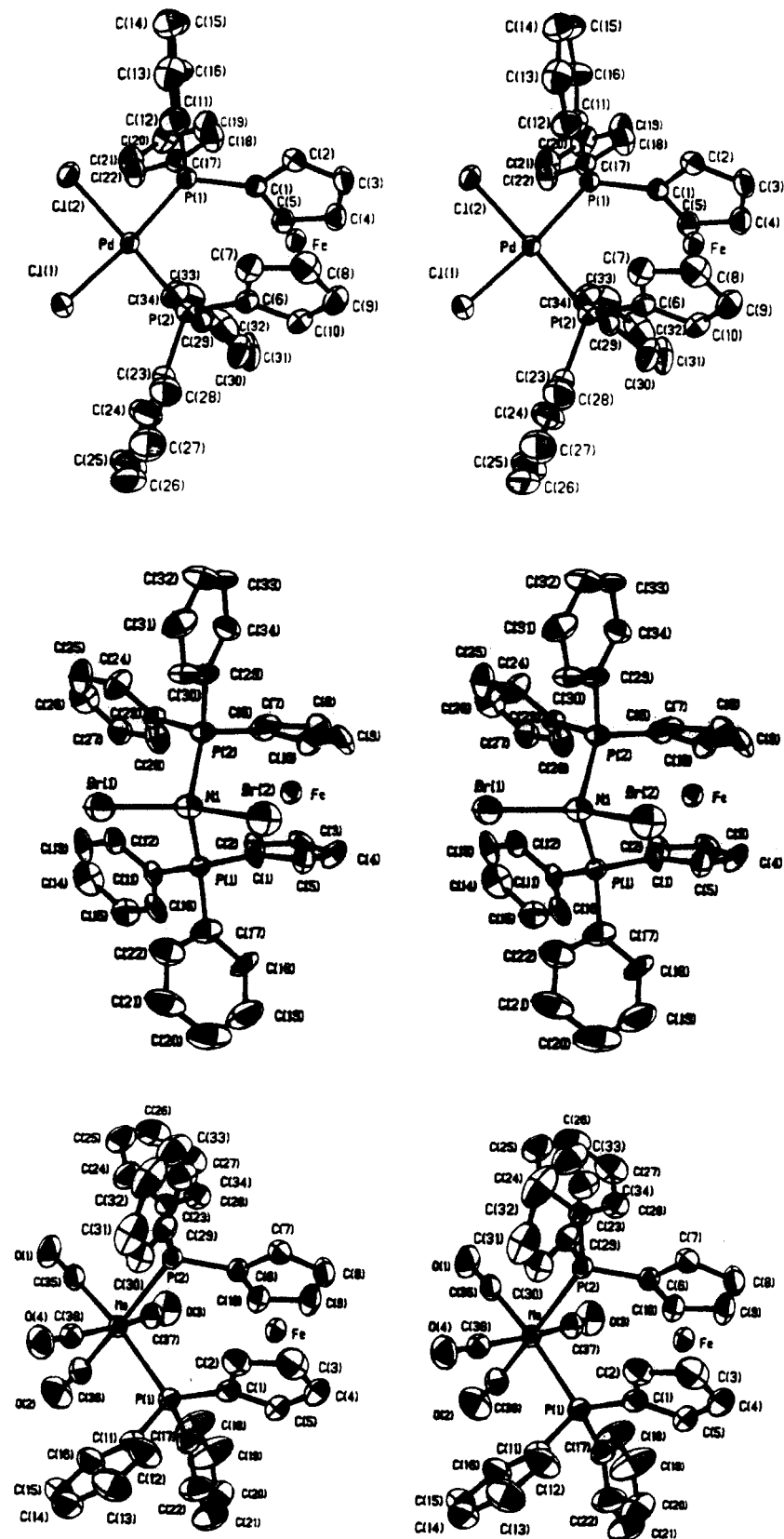(23) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Figure 1. Stereoscopic views of the (L-L)PdCl₂, (L-L)NiBr₂, and (L-L)Mo(CO)₄ complexes (50% probability thermal ellipsoids are shown, and hydrogen atoms are omitted).

scattering factors from ref 24 were employed for Pd, Ni, Mo, Br, Cl, and P atoms. An isotropic type I extinction correction (Thornley–Nelmes definition of mosaic anisotropy with a Lorentzian distribution) was applied for the Ni compound,[25-27] the

final value of g being 13.2 (2) × 10⁴. The polarity of the Ni crystal was checked by parallel refinement, the R and R_w ratios being 1.019 and 1.028, respectively. Maximum fluctuations on the final

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Table I. Crystallographic Data[a]

	(L-L)PdCl$_2$·CH$_2$Cl$_2$	(L-L)NiBr$_2$	(L-L)Mo(CO)$_4$·C$_6$H$_6$
formula[b]	C$_{34}$H$_{28}$Cl$_2$FeP$_2$Pd·CH$_2$Cl$_2$	C$_{34}$H$_{28}$Br$_2$FeNiP$_2$	C$_{38}$H$_{28}$FeMoO$_4$P$_2$·C$_6$H$_6$
fw	816.63	772.91	840.49
cryst system	monoclinic	orthorhombic	triclinic
space group	P2$_1$/c	Pn2$_1$a[c]	P1̄[d]
a, Å	9.8615 (8)	20.4163 (15)	10.950 (2)
b, Å	18.2322 (9)	14.7573 (10)	18.110 (3)
c, Å	19.1540 (15)	10.2015 (6)	10.3433 (12)
α, deg	90	90	101.777 (9)
β, deg	102.581 (4)	90	93.322 (10)
γ, deg	90	90	83.059 (11)
V, Å^3	3361.1 (4)	3073.6 (4)	1992.1 (5)
Z	4	4	2
D$_{calcd}$, g/cm^3	1.614	1.670	1.401
F(000)	1640	1544	856
cryst dimens, mm	0.05 × 0.26 × 0.42	0.15 × 0.41 × 0.46	0.18 × 0.35 × 0.36
μ(Mo Kα), cm^{-1}	13.99	37.89	7.89
transmissn factors	0.721–0.941	0.243–0.587	0.744–0.925
scan type	ω–2θ	ω–2θ	ω–2θ
scan speed, deg/min	1.01–10.06	1.68–10.06	1.44–10.06
scan range, deg in ω	0.65 + 0.35 tan θ	0.80 + 0.35 tan θ	0.65 + 0.35 tan θ
data collected	±h,+k,+l	+h,+k,+l	±h,±k,+l
2θ$_{max}$, deg	55	55	55
unique reflctns	7675	3680	9096
reflctns with I ⩾ 3σ(I)	4324	1870	6687
no. of variables	500	361	439
R	0.029	0.069	0.033
R$_w$	0.035	0.074	0.045
goodness of fit	1.483	3.014	1.799
max Δ/σ	0.43	0.29	1.8[e]
residual density, e/Å^3	±0.8	−1.7, +1.3	−0.8, +0.7

[a] Temperature 22 °C; Mo Kα radiation (λ = 0.710 73 Å); graphite monochromator; takeoff angle 2.7°; aperture (2.0 + tan θ) × 4.0 mm at a distance of 173 mm from the crystal; scan range extended by 25% on both sides for background measurement; $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$ (S = scan count, B = normalized background count); function minimized $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$, $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$, and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w |F_o|^2)^{1/2}$. [b] Names: dichloro[1,1'-bis(diphenylphosphino)ferrocene-P,P]palladium(II); dibromo[1,1'-bis(diphenylphosphino)ferrocene-P,P]nickel(II); tetracarbonyl[1,1'-bis(diphenylphosphino)ferrocene-P,P]molybdenum(0); L-L = 1,1'-bis(diphenylphosphino)ferrocene, (C$_5$H$_4$PPh$_2$)$_2$Fe. [c] Nonstandard setting of Pna2$_1$, equivalent positions: x, y, z; $^1/_2 - x$, $^1/_2 + y$, $^1/_2 + z$; $-x$, $^1/_2 + y$, $-z$; $^1/_2 + x$, y, $^1/_2 - z$. [d] Reduced cell. [e] Associated with the solvent molecule, parameter shifts associated with the complex did not exceed 0.09σ.

difference maps for all three structures were near heavy atoms.

Atomic positional parameters are given in Table II, selected bond lengths and angles in Table III, and complete lists of molecular dimensions and structure factors are included in the supplementary material.

Discussion

Crystal Structures. The three molecules studied by X-ray methods (Figure 1) contain 1,1'-bis(diphenylphosphino)ferrocene, 1, coordinated via the two P atoms to PdCl$_2$, NiBr$_2$, and Mo(CO)$_4$ moieties, thus completing cis square-planar, tetrahedral, and cis octahedral coordinations for Pd, Ni, and Mo atoms, respectively. The crystals of the Pd complex contain dichloromethane solvate,[11,16] crystals of the Ni complex are unsolvated, and the Mo crystals contain benzene solvate. The data for the Ni complex are somewhat less accurate, as a result of poorer crystal quality, than those for the Pd and Mo compounds.

The Pd coordination group is slightly distorted from exact planarity, with a fold about the Cl(2)···P(2) axis; the Cl and P atoms are alternately above and below the Cl$_2$P$_2$ plane by 0.046–0.058 (1) Å, with Pd displaced by 0.0714 (3) Å. Bond lengths and angles are as follows: Pd–P = 2.278 and 2.289 (1) Å, mean 2.284 (6) Å, Pd–Cl = 2.340 and 2.358 (1) Å, mean 2.349 (9) Å, and P–Pd–P = 97.98 (4)° and Cl–Pd–Cl = 89.96 (4)° (Table III).

These dimensions are close to those reported for the chloroform solvate: mean 2.292 and 2.348 Å and 99.07 and 87.8°.[11] The small, but statistically significant, differences in the geometry about Pd in the two solvates probably arise

from packing effects and are not chemically important. In the chloroform solvate[11] the PdCl$_2$P group is planar to within 0.01 Å with the second P atom displaced 0.21 Å from this plane in contrast to the arrangement described above. The pairs of Pd–Cl and Pd–P bond lengths in the chloroform solvate differ by 0.001 and 0.018 Å compared with corresponding differences of 0.018 and 0.012 Å in the dichloromethane solvate. The shorter mean Pd–P and (marginally) longer Pd–Cl distances in the present structure are consistent[11] with the smaller P–Pd–P and larger Cl–Pd–Cl angles.

Molecules of the type Br$_2$Ni(PR$_3$)$_2$ usually exhibit square-planar geometry at Ni with small R groups, e.g., R = Me,[28] but the steric influence of bulkier R groups results in tetrahedral geometry, e.g., R = Ph.[29] In some examples both geometries are found, e.g., for the chelating ligand Ph$_2$PCH$_2$PPh$_2$ both square-planar and tetrahedral isomers are found in the same crystal.[30] Consiglio and co-workers[31] have pointed out that most of the conventional chelating ligands used in catalysis afford diamagnetic nickel(II) complexes. It may be the bulk of the 1,1'-bis(diphenylphosphino)ferrocene ligand (1) in the present Ni complex which produces the tetrahedral coordination at Ni. The Ni–P bonds, mean 2.290 (9) Å (Table III), are

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Table II. Final Positional ($\times 10^4$ for C and O, $\times 10^5$ for Heavy Atoms) and Isotropic Thermal Parameters ($U \times 10^3$, Å^2) for (L·L)PdCl₂·CH₂Cl₂, (L·L)NiBr₂, and (L·L)Mo(CO)₄·C₆H₆ with Estimated Standard Deviations in Parentheses

atom	x	y	z	U_{eq}/U_{iso}	atom	x	y	z	U_{eq}/U_{iso}
				(L·L)PdCl₂·CH₂Cl₂					
Pd	22751 (3)	27778 (2)	30560 (1)	28	C(15)	7203 (6)	1406 (4)	2677 (3)	72
Fe	49749 (5)	30104 (3)	50995 (3)	34	C(16)	6064 (5)	1367 (3)	2992 (3)	57
Cl(1)	3887 (10)	34341 (6)	23929 (5)	48	C(17)	3325 (4)	1050 (2)	3568 (2)	34
Cl(2)	26508 (10)	22423 (6)	19939 (5)	44	C(18)	4033 (5)	532 (2)	4043 (2)	51
Cl(3)	25219 (23)	47238 (11)	8692 (15)	141	C(19)	3544 (6)	−178 (3)	4034 (3)	63
Cl(4)	40431 (29)	44135 (12)	23084 (15)	155	C(20)	2359 (6)	−378 (3)	3569 (3)	58
P(1)	39840 (10)	19891 (5)	36040 (5)	30	C(21)	1640 (6)	132 (3)	3110 (3)	59
P(2)	18208 (10)	33051 (5)	40591 (5)	33	C(22)	2120 (5)	838 (2)	3106 (2)	47
C(1)	4862 (4)	2072 (2)	4534 (2)	33	C(23)	722 (4)	4121 (2)	3942 (2)	45
C(2)	6290 (4)	2264 (2)	4808 (2)	42	C(24)	−678 (6)	4079 (4)	3934 (3)	70
C(3)	6516 (5)	2293 (3)	5565 (2)	48	C(25)	−1471 (8)	4727 (5)	3838 (4)	96
C(4)	5262 (4)	2120 (2)	5772 (2)	45	C(26)	−881 (10)	5375 (4)	3743 (3)	95
C(5)	4243 (4)	1979 (2)	5141 (2)	38	C(27)	501 (9)	5422 (3)	3755 (4)	86
C(6)	3355 (4)	3636 (2)	4672 (2)	36	C(28)	1302 (6)	4794 (3)	3856 (3)	65
C(7)	4564 (5)	3875 (2)	4424 (3)	43	C(29)	929 (4)	2643 (2)	4501 (2)	38
C(8)	5588 (5)	4086 (2)	5033 (3)	52	C(30)	690 (5)	2741 (4)	5186 (3)	67
C(9)	5040 (5)	3987 (2)	5645 (3)	51	C(31)	103 (5)	2194 (5)	5513 (3)	78
C(10)	3671 (5)	3725 (2)	5432 (2)	44	C(32)	−307 (6)	1561 (4)	5157 (4)	80
C(11)	5451 (4)	2006 (2)	3163 (2)	37	C(33)	−150 (6)	1457 (4)	4481 (4)	78
C(12)	5978 (5)	2670 (3)	2995 (3)	48	C(34)	476 (5)	1998 (3)	4153 (3)	52
C(13)	7113 (5)	2694 (3)	2691 (3)	58	C(35)	2837 (10)	4172 (4)	1552 (5)	128
C(14)	7730 (5)	2067 (3)	2533 (3)	64					
				(L·L)NiBr₂					
Ni	60391 (14)	57748	67900 (31)	37	C(9)	6058 (15)	8451 (23)	3531 (26)	65
Fe	63743 (17)	83500 (33)	54452 (33)	42	C(10)	5975 (14)	7573 (17)	3994 (29)	53
Br(1)	64212 (15)	44337 (27)	77713 (28)	56	C(11)	6990 (10)	6964 (14)	9133 (22)	30
Br(2)	49755 (14)	60662 (33)	60349 (32)	66	C(12)	7490 (11)	6341 (15)	8885 (26)	42
P(1)	62343 (27)	69462 (43)	81950 (60)	31	C(13)	8097 (12)	6415 (21)	9565 (31)	60
P(2)	67227 (27)	61006 (46)	50619 (58)	33	C(14)	8207 (15)	7055 (25)	10459 (31)	68
C(1)	6213 (13)	8028 (16)	7361 (25)	43	C(15)	7662 (15)	7661 (19)	10759 (27)	59
C(2)	6744 (12)	8674 (16)	7283 (22)	39	C(16)	7105 (15)	7603 (18)	10086 (25)	52
C(3)	6500 (16)	9451 (18)	6631 (22)	54	C(17)	5613 (11)	7018 (20)	9455 (26)	50
C(4)	5790 (19)	9323 (19)	6397 (30)	77	C(18)	5279 (12)	7811 (21)	9790 (30)	57
C(5)	5648 (13)	8443 (18)	6801 (27)	53	C(19)	4862 (19)	7811 (39)	10820 (45)	108
C(6)	6597 (13)	7215 (16)	4313 (24)	40	C(20)	4751 (16)	7076 (46)	11547 (36)	102
C(7)	7077 (12)	7919 (17)	4153 (24)	43	C(21)	5102 (14)	6225 (31)	11249 (28)	777
C(8)	6740 (16)	8697 (19)	3595 (29)	60	C(22)	5495 (14)	6232 (21)	10213 (27)	61
				(L·L)NiBr₂					
C(23)	7598 (10)	5950 (15)	5415 (22)	34	C(29)	6579 (11)	5339 (17)	3703 (24)	35
C(24)	7889 (12)	5146 (16)	5083 (28)	54	C(30)	6241 (12)	4524 (18)	3896 (24)	43
C(25)	8553 (12)	4998 (19)	5432 (32)	61	C(31)	6170 (12)	3863 (18)	2900 (32)	54
C(26)	8919 (13)	5671 (24)	5983 (32)	62	C(32)	6402 (14)	4078 (20)	1692 (28)	55
C(27)	8606 (13)	6482 (20)	6354 (26)	50	C(33)	6715 (13)	4870 (21)	1442 (24)	51
C(28)	7948 (14)	6637 (18)	5936 (30)	57	C(34)	6752 (16)	5495 (18)	2436 (26)	53
				(L·L)Mo(CO)₄·C₆H₆					
Mo	37356 (2)	27321 (1)	52042 (2)	33	C(19)	3855 (5)	31 (3)	6446 (7)	117
Fe	26091 (3)	30336 (2)	94286 (4)	39	C(20)	2934 (5)	−420 (2)	6344 (5)	93
P(1)	21011 (6)	21327 (4)	62198 (7)	37	C(21)	1729 (5)	−102 (2)	6204 (5)	99
P(2)	40268 (6)	37700 (4)	72269 (6)	33	C(22)	1476 (4)	667 (2)	6170 (5)	78
O(1)	5575 (2)	3384 (2)	3649 (3)	79	C(23)	5572 (2)	4077 (1)	7287 (3)	39
O(2)	3881 (3)	1422 (2)	2714 (3)	87	C(24)	5830 (3)	4540 (2)	6453 (4)	61
O(3)	6186 (2)	1884 (2)	6223 (3)	77	C(25)	7002 (4)	4751 (2)	6425 (4)	72
O(4)	1591 (2)	3538 (1)	3627 (2)	65	C(26)	7918 (3)	4498 (2)	7234 (5)	77
C(1)	1573 (2)	2509 (2)	7888 (3)	42	C(27)	7692 (3)	4042 (2)	8068 (4)	71
C(2)	1044 (2)	3279 (2)	8382 (3)	48	C(28)	6510 (2)	3824 (2)	8085 (3)	51
C(3)	767 (3)	3343 (2)	9723 (3)	63	C(29)	3048 (2)	4680 (1)	7441 (3)	40
C(4)	1121 (3)	2639 (2)	10084 (3)	69	C(30)	1904 (3)	4718 (2)	6800 (3)	49
C(5)	1619 (3)	2117 (2)	8958 (3)	56	C(31)	1152 (3)	5396 (2)	6916 (4)	66
C(6)	4000 (2)	3503 (1)	8813 (2)	36	C(32)	1553 (4)	6052 (2)	7690 (4)	71
C(7)	3555 (3)	3957 (2)	10028 (3)	46	C(33)	2681 (4)	6021 (2)	8315 (4)	68
C(8)	3696 (3)	3504 (2)	11002 (3)	54	C(34)	3436 (3)	5338 (2)	8216 (3)	54
C(9)	4234 (3)	2779 (2)	10430 (3)	57	C(35)	4890 (3)	3168 (2)	4245 (3)	49
C(10)	4423 (3)	2765 (2)	9071 (3)	45	C(36)	3779 (3)	1893 (2)	3655 (3)	52
C(11)	659 (2)	2155 (2)	5214 (3)	43	C(37)	5273 (3)	2175 (2)	5914 (3)	48
C(12)	−445 (3)	2551 (2)	5689 (4)	63	C(38)	2324 (3)	3267 (2)	4244 (3)	42
C(13)	−1486 (3)	2588 (2)	4856 (5)	76	C(39)	7576 (11)	1556 (7)	9604 (12)	214 (4)
C(14)	−1449 (3)	2226 (2)	3572 (4)	66	C(40)	8602 (12)	1177 (8)	8621 (14)	244 (5)
C(15)	−361 (4)	1821 (2)	3090 (4)	69	C(41)	8347 (18)	391 (13)	8054 (21)	357 (9)
C(16)	684 (3)	1793 (2)	3905 (3)	59	C(42)	8003 (15)	−67 (9)	8858 (17)	271 (6)
C(17)	2416 (3)	1116 (2)	6245 (3)	48	C(43)	6890 (14)	265 (10)	9677 (15)	262 (6)
C(18)	3595 (4)	785 (2)	6356 (6)	88	C(44)	6802 (12)	1057 (9)	9994 (14)	254 (6)

Table III. Summary of Molecular Dimensions (Å and deg) in (L·L)PdCl$_2$, (L·L)NiBr$_2$, and (L·L)Mo(CO)$_4$

	Pd, Ni, Mo Coordinations		
Pd-P	2.278, 2.289 (1)	mean	2.284 (6)
Pd-Cl	2.340, 2.358 (1)	mean	2.349 (9)
Ni-P	2.281, 2.299 (6)	mean	2.290 (9)
Ni-Br	2.344, 2.351 (4)	mean	2.348 (4)
Mo-P	2.544, 2.576 (1)	mean	2.560 (16)
Mo-C	1.969, 1.978 (3)	mean	1.974 (5) (trans to P)
	2.035, 2.041 (3)	mean	2.038 (3) (cis to P)

P-Pd-P	97.98 (4)	P···P	3.447 (1)
Cl-Pd-Cl	89.96 (4)		
P-Ni-P	102.5 (2)	P···P	3.573 (9)
Br-Ni-Br	127.0 (2)		
P-Mo-P	95.28 (2)	P···P	3.783 (1)

	Ferrocene Groups[a]		
mean Fe-Co	1.636 (2)	1.666 (7)	1.646 (1)
Cp-Fe-Cp'	177.3	173.1	179.0
angle between plane normals	6.2	6.2	2.2
rotation from eclipsed conformation	39.5	-6.5	41.9
mean Fe-C(1)	2.002	2.06	2.032
mean Fe-C(2)	2.028	2.05	2.036
mean Fe-C(3)	2.058	2.07	2.057
mean C(1)-C(2)	1.437	1.43	1.434
mean C(2)-C(3)	1.416	1.41	1.422
mean C(3)-C(4)	1.410	1.46	1.403
mean C-C-C			
at C(1)	106.8	108	106.9
at C(2,3)	108.3	108	108.3

[a] Cp = centroid of cyclopentadienyl ring: 1 = 1, 6; 2 = 2,5,7,10; 3 = 3,4,8,9.

Figure 2. Schematic representations of deviations from planarity (Å) and of ring orientations (deg) in the Pd, Ni, and Mo complexes.

marginally shorter than those in NiBr$_2$(PPh$_3$)$_2$, 2.334 (11) Å,[29] and Ni-Br and Br-Ni-Br are very similar in the two molecules, mean 2.348 (4) Å and 127.0 (2)° in the present compound vs. 2.338 (9) Å and 126.3° in ref 29. The P-Ni-P angle in the present structure is significantly smaller than in NiBr$_2$(PPh$_3$)$_2$, 102.5 (2) vs. 110.4 (2)°, presumably as a result of the steric constraints of the chelating ferrocene ligand.

In the Mo coordination sphere the Mo-P bond lengths, mean 2.560 (16) Å, are at the upper end of the range usually found. The Mo-C bond lengths are normal for those involving carbonyl ligands but show a pronounced trans effect of the phosphine ligands, mean Mo-C being 1.974 (5) Å for bonds trans to P and 2.038 (3) Å for bonds cis to P.

The ferrocene ligands in the three molecules have roughly similar geometries, with each iron atom sandwiched between two cyclopentadienyl rings and both phosphino groups on one side of the ligand (Figure 1). The cyclopentadienyl rings are planar within experimental error (maximum displacement 2.45σ) but deviate slightly from being parallel, the angles between the plane normals being 6.2, 6.2, and 2.2° in the Pd, Ni, and Mo compounds, respectively. In the Pd and Mo compounds the noncoplanarity is such that the spacing between the rings decreases toward the phosphine substituents; in addition the P atoms are slightly displaced from the planes toward the Fe atom, by 0.062 (1) and 0.035 (1) Å in the Pd compound and by 0.017 (1) and 0.026 (1) Å in the Mo compound (Figure 2). In the Ni compound, in contrast, the spacing between the rings increases toward the phosphine substituents: one P is displaced from its ring plane by 0.157(6) Å away from the Fe atom and the other P by 0.087 (6) Å toward Fe.

The two cyclopentadienyl rings are approximately staggered in the Pd and Mo compounds (rotations of 14.5 and 12.1°, respectively, from exact staggered conformations (Table III)); in contrast, the conformation in the Ni com-
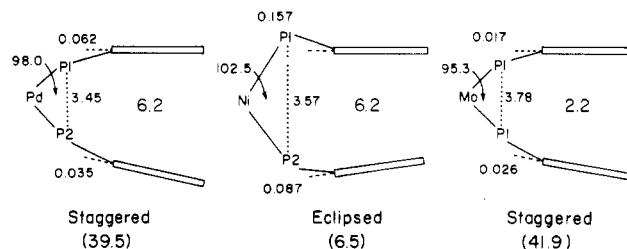
pound is nearly eclipsed (6.6° from an exactly eclipsed position).

These differences in ring tilt, P displacement, and conformation (Figure 2) are probably related to the steric requirements of bonding to the Pd, Ni, and Mo atoms, the P···P distances being 3.45, 3.57, and 3.78 Å, respectively. The configurations at the metal centers are distorted from normal geometry, with P-M-P angles of 97.98 (4) and 95.28 (2)° for M = Pd and Mo, increased from the ideal values of 90°; in the Ni complex the angle is decreased from the ideal 109.5° tetrahedral value to 102.5 (2)°. The exact geometries adopted are presumably compromises between the various bonding and steric forces. Similar variations in geometry have been found in a series of related Rh complexes.[5]

The C-C bond lengths and C-C-C angles in the cyclopentadienyl rings show substituent-induced variations. For the more accurately determined Pd and Mo structures, the mean C-C distances involving the substituted C(1) and C(6) atoms are the longest in the rings at 1.437 and 1.434 Å, respectively; adjacent C-C bonds are 1.416 and 1.422 Å, with the final C(3)-C(4) and C(8)-C(9) lengths being 1.410 and 1.403 Å. C-C-C angles at substituted atoms average 106.8 and 106.9°, slightly reduced from the ideal 108°, with the other angles averaging 108.3°. Fe-C distances are shortest for the substituted C(1) and C(6) atoms, mean 2.002 and 2.032 Å for the Pd and Mo compounds, respectively; Fe-C(2) types average 2.028 and 2.036 Å and Fe-C(3) types 2.058 and 2.057 Å, respectively. All these bond and angle variations are very similar to those observed in phosphine-bridged ferrocenophanes.[32] Similar variations within the cyclopentadienyl rings are observed in a tris(di-*tert*-butylphosphino)[(dimethylamino)ethyl]-ferrocene,[7] where C-C bonds and angles average 1.426 Å and 106.5° at substituted C atoms and 1.416 Å and 109.0° at unsubstituted C atoms; however, in that compound the Fe-C bonds are longer at substituted C atoms, mean 2.092 Å vs. 2.044 Å for unsubstituted atoms, with substituent P and C atoms displaced away from the Fe atoms as a result of steric interactions. The results for the Ni compounds are less accurate, and bond length and angle variations cannot be considered significant.

P-C bond lengths are in the ranges 1.804-1.828 (4), 1.81-1.84 (2), and 1.805-1.842 (3) Å, in the Pd, Ni, and Mo compounds, respectively; those bonds involving the cyclopentadienyl C atoms seem to be slightly shorter in the Pd and Mo compounds, means 1.807 and 1.814 Å vs. 1.822 and 1.838 Å for P-C(phenyl) bonds (differences for the Ni compound are again not statistically significant). Angles at P are 101.3-123.1 (1), 102-119 (1), and 101.0-122.0 (1)° in the Pd, Ni, and Mo compounds, respectively. Bond lengths and angles in the phenyl rings are within the ranges

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<div align="center">Table IV. Analytical and Spectroscopic Data for Complexes</div>

	X	L-L	anal. found (calcd) C	anal. found (calcd) H	^{1}H NMR,^{a} δ
Pd(L-L)X$_2$	Cl	3	47.31 (47.91)	6.88 (7.00)	1.68 (d, 36, J = 12 Hz), 4.49 (bs, 4), 4.85 (bs, 4)
	Cl	6	51.98 (52.08)	4.96 (5.21)	1.53 (d, 18, J = 16 Hz), 4.0–4.4 (m, 8), 7.68 (m, 6), 8.45 (m, 4)
	Cl	7^b	45.80 (45.90)	4.60 (4.59)	1.63 (d, 18, J = 9 Hz), 3.85–4.40 (bm, 4), 7.32–7.52 (m, 6), 7.88–8.23 (m, 4)
	Cl	8^c			1.40 (d, 9, J = 16 Hz), 3.80 (m, 2), 4.25 (m, 1), 4.40 (m, 2), 4.65 (m, 2), 4.80 (m, 1), 7.25–8.60 (m, 15)
Ni(L-L)X$_2$	Br^d	1	52.76 (52.82)	3.72 (3.62)	
	Cl^d	3	51.25 (51.69)	6.95 (7.29)	
	Br^d	3	45.53 (45.06)	6.53 (6.35)	
[Rh(L-L)NBD]ClO$_4$		6	54.24 (54.95)	5.28 (5.44)	1.10 (d, 18, J = 14 Hz), 1.80 (bm, 2), 4.00 (bm, 2), 4.00–4.30 (bm, 8), 5.25 (bm, 2), 5.68 (bm, 2), 7.78 (m, 6), 8.78 (m, 4)
		7	53.70 (54.93)	5.25 (5.44)	1.50 (d, 18, J = 12 Hz), 1.70 (bm, 2), 3.90 (bm, 2), 4.62 (bm, 2), 4.48 (bm, 2), 4.35 (bm, 2), 4.20 (bm, 2), 5.70 (bm, 4), 7.65 (m, 6), 7.85 (m, 4)
		8	56.49 (56.20)	4.86 (4.98)	1.30 (d, 9), J = 10 Hz), 1.60 (bd, 2), 1.82 (bd, 2), 3.88 (q, 1), 4.00–4.60 (m, 9 includes sharp resonances at 4.02, 4.07, 4.20, 4.32, 4.39, 4.45, 4.57), 5.43 (bs, 1), 5.50 (bs, 1), 7.24 (m, 2), 7.48 (m, 3), 7.70 (m, 6), 8.32 (m, 2) 8.62 (m, 2)

^{a} CDCl$_3$. ^{b} CHCl$_3$ solvate. ^{c} CD$_2$Cl$_2$. ^{d} Paramagnetic.

Scheme I
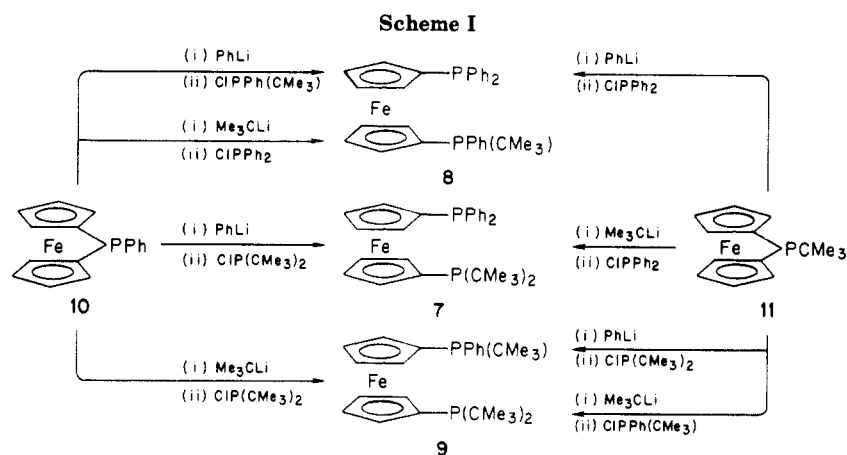
usually found, with slightly shorter outer bond lengths, even after libration corrections.

Intermolecular distances correspond to normal van der Waals interactions. The solvent molecules, dichloromethane (in the Pd complex) and benzene (in the Mo complex), exhibit fairly large thermal motion, with root-mean-square displacements of up to 0.4 and 0.6 Å, respectively.

NMR Studies. The metal complexes of the 1,1′-ferrocenylbis(tertiary phosphines) can be regarded as [3]ferrocenophanes and as such have a formal analogy with cyclohexane, **4** and **5** being equivalent to the chair and half-chair forms.

Apart from this work in which one of the three derivatives has been found to have the eclipsed confirmation, two others with this structural feature have been established by X-ray crystallography, namely, Fe(η^5-C$_5$H$_4$)$_2$S$_3$ and Fe(η^5-C$_5$H$_4$)$_2$S$_2$Se.[34,35]

Variable-temperature NMR studies have indicated that the eclipsed conformation exists in solution for most [3]-ferrocenophanes with group 4 and 6 atoms in the

bridge,[36,37] one exception being the compound with an S$_2$CPh$_2$ bridge when the rings appear to be staggered as in **5**.

The barrier to chair-to-chair reversal analogous to **4a** ⇌ **4b** can be high as in the S$_3$ bridge ($\Delta G^\ddagger$ = 80.1 kJ mol^{-1}) resulting in a limiting ABCD NMR spectrum for the η^5-C$_5$H$_4$ groups at ambient temperatures. In other cases, e.g., with (–CH$_2$)$_2$S ($\Delta G^\ddagger$ = 34.6 kJ mol^{-1})[37c] or (–S)$_2$GeMe$_2$[37a] bridges the molecules are fluxional at ambient temperatures and limiting NMR spectra are obtained only on strong cooling (ca. –100 °C).

The ^{1}H NMR spectra of the compounds M(L-L)(CO)$_4$ (L-L = **1**; M = Cr, Mo) at 400 MHz exhibit the typical pair of multiplets, in the η^5-C$_5$H$_4$ region, of a fluxional [3]-ferrocenophane, the main distinction between the two compounds being a slightly greater chemical shift difference between the triplets for the Cr compound. Since the molybdenum compound has a staggered conformation in the solid state, it is probable that in solution both molecules are fluxional in the sense **5a** ⇌ **5b**. On cooling the

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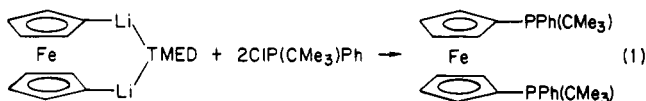(36) Bishop, J. J.; Davison, A. *Inorg. Chem.* **1971**, *10*, 826.

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solutions to −85 °C only a slight broadening is seen in the ^1H NMR spectrum. The (L-L)M(CO)$_4$ complexes of 1,1'-bis(dimethylarsino)ferrocene are also fluxional in solution, probably in the same manner, although Davison and co-workers[36] speculated that the equilibrium would be of the type **4a** ⇌ **4b**. The barriers to ring reversal are low as would be expected from the bulk of the ring substituents.[36,37]

Ligand Preparation. The symmetrically substituted ligands **1** and **3** have been prepared previously from the appropriate chlorophosphine and the dilithioferrocene/ TMED adduct (TMED = tetramethylethylenediamine).[4,9,12] The same procedure has now been applied to the synthesis of **6** as meso and racemic isomers as shown in eq 1.

The unsymmetrically substituted ligands **7–9** were

6, R^1 = R^3 = Ph; R^2 = R^4 = CMe$_3$
7, R^1 = R^2 = Ph; R^3 = R^4 = CMe$_3$
8, R^1 = Ph; R^2 = R^3 = R^4 = CMe$_3$
9, R^1 = CMe$_3$; R^2 = R^3 = R^4 = Ph
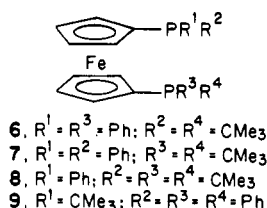
synthesised as shown in Scheme I. A route to **7** is outlined in more detail in eq 2. The first step utilizes the bridge
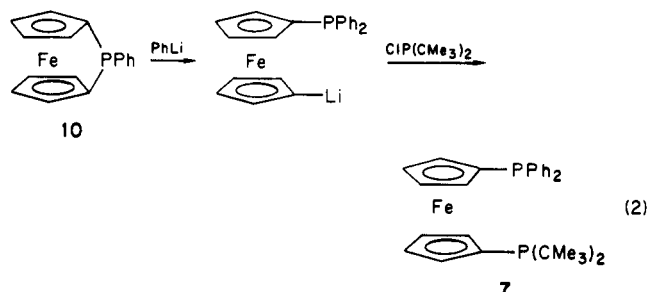
cleavage reaction of the [1]ferrocenophane (**10**) discovered by Seyferth and Withers.[17] This is an extremely effective method of activating the second ring for further substitution. In our hands the bridge cleavage reactions are best carried out a low temperature (−78 to −10 °C) in either diethyl ether or *n*-hexane solution.[38]

All routes shown in Scheme I give the anticipated products, however, the most convenient syntheses of the compounds **7–9** were found to be from **10**. This is largely because the starting compound can be prepared relatively easily from commercially available materials and because the bridge cleavage reaction of **10** gives cleaner product mixtures compared with similar cleavage reactions of **11**.

The preferred lithium reagent to effect bridge cleavage is phenyllithium rather than *tert*-butyllithium since the latter reagent often affords *tert*-butylphosphine containing byproducts which are difficult to separate from the desired product by chromatography.

Some byproducts actually isolated include the known[39] (diphenylphosphino)ferrocene (**12a**) isolated during the synthesis of **7** from **10** and (*tert*-butylphenylphosphino)-ferrocene (**12b**) isolated during the synthesis of **8** from **11**.[40]

12a, R^1 = R^2 = Ph
b, R^1 = Ph; R^2 = CMe$_3$

13
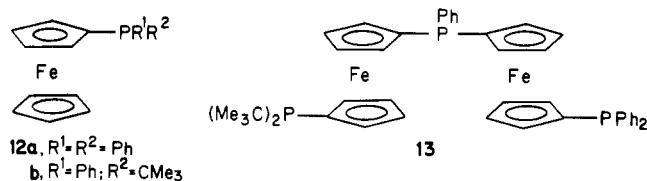
Another byproduct obtained during the synthesis of **7** from **10** is probably the tris(tertiary phosphine) **13**[41] which could be formed following an alternative bridge cleavage reaction of **10** by the initial lithium derivative shown in eq 2. Similar bridge cleavage reactions by the lithiated products have been described.[42]

The analytical and spectroscopic data for **6–8** are in accord with the proposed structures. Compounds **8** and **9** were found to be difficult to obtain pure even after repeated chromatography, however, the NMR spectrum and mass spectra[43] are in accord with the expected structures. The racemic isomer of **6** showed only one PCMe$_3$ resonance in both ^1H and ^{31}P NMR spectra,[44] the ^{31}P resonance at 7.77 ppm being almost halfway between that of **1** (−17.61 ppm) and **3** (26.48 ppm). ^1H NMR spectra of compounds containing P(Ph)(CMe$_3$) groups, **6**, **8**, and **9**, show broadened phenyl resonances split into a 2:3 multiplet. In contrast a broad singlet is observed for the PPh$_2$ groups in **1**, **7**, and **8**.

Metal Complexes. The reaction of ligands **1**, **3**, **6**, **7**, and **8** with either Pd(PhCN)Cl$_2$, K$_2$PdCl$_4$, or Pd(COD)Cl$_2$ gives the Pd(L-L)Cl$_2$ compounds (L-L = **1**, **3**, *rac*-**6**, **7**, and **8**) in essentially quantitative yield based on palladium. The analytical data and spectroscopic properties[46] support of the formulation, and all should have structures analogous to that of the derivative of **1** described above (Figure 1). Ligand coordination results in significant ^1H chemical shifts in the resonances of the ferrocenyl protons. This is particularly evident in the data for **7** where there is a considerable downfield shift associated with the 2,5,2′,5′ protons on the cyclopentadienyl rings resulting in an unusually broad range of ring proton resonances (>1 ppm).

The new rhodium(I) species [Rh(L-L)NBD]ClO$_4$ have been prepared for the ligands *rac*-**6**, **7**, and **8**. The analogous complexes of **1** and **3** have been described previously, and crystal structures of the derivatives of **1**, **3**, **6**, and **7** have been determined.[4,5] Basically all have a more or less distorted cation with "square-planar" coordination around the Rh atom. The NMR spectra are in accord with this formulation.[46] The complex of *rac*-**6** shows a doublet at

(38) *n*-Hexane was used as solvent in reactions involving Me$_3$CLi since Seyferth and Withers report[17] a reaction with diethyl ether under these conditions.

(39) Sollott, G. P.; Mertway, H. H.; Portnoy, S.; Snead, J. L. *J. Org. Chem.* **1963**, *28*, 1040.

(40) Compound **12b** was previously isolated as the sulfide by Seyferth and Withers.[17] **12b**: ^1H NMR (CDCl$_3$) δ 1.05 (d, 9, J_{P-H} = 12 Hz), 3.90 (s, 5), 4.00 (bs, 2), 4.45 (bs, 2), 7.25–7.80 (m, 5); MS, *m/e* 350 (M$^+$). This compound readily oxidizes. Oxide of **12b**: ^1H NMR δ 1.10 (d, 9, J_{P-H} = 12 Hz), 4.00 (s, 5), 4.43 (m, 3), 4.82 (m, 1), 7.50–7.70 (m, 3), 7.90–8.20 (m, 2); MS, *m/e* 366 (M$^+$).

(41) **13**: MS *m/e* 806 (M$^+$). Similar compounds have been isolated as byproducts from the reactions of **10** with ClPPh$_2$ or ClP-*i*-Pr$_2$ as in eq 2.

(42) (a) Butler, I. R.; Cullen, W. R. *Can. J. Chem.* **1983**, *61*, 147. (b) Withers, H. P.; Seyferth, D.; Fellmann, J. D.; Garrow, P. E. *Organometallics* **1982**, *1*, 1283.

(43) **8**: ^1H NMR (CDCl$_3$) δ 1.00 (d, 9, J_{P-H} = 12 Hz), 3.71 (m, 1), 3.90–4.50 (m, 7), 7.23–7.50 (m, 13), 7.50–7.80 (m, 2); MS, *m/e* 534 (M$^+$). A trace of phosphine oxide <0.5% was observed as an impurity by mass spectroscopy. **9** was identified by mass spectroscopy, *m/e* 494 (M$^+$), and is readily air oxidized. All NMR samples prepared contained a variety of trace impurities in spite of repeated attempts at purification by chromatography.

(44) Distinction between the isomers of **6** was made on the basis of the crystal structures of the derivatives [Rh(L-L)NBD]ClO$_4$[5] and [(L-L)HRh(H)$_3$RhH(L-L)]ClO$_4$.[45] The ligand is the rac isomer in both cases.

(45) Butler, I. R.; Cullen, W. R.; Kim, T.-J.; Einstein, F. W. B.; Willis, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 719.

(46) The NMR spectra in Table V are qualitatively all as expected. Because some ligands have low symmetry, extensive decoupling experiments would be required for precise assignments to be made.

32.51 ppm (J_{RhH} = 155 Hz) in its ^{31}P NMR spectrum. Thus the coordination shift for this complex is 24.74 ppm. The corresponding ^{31}P data for the complexes of 1 and 3 are respectively 14.8 ppm, J = 161 Hz, and Δ = 32.45 ppm and 45.81 ppm, J = 148 Hz, and Δ = 18.73 ppm. As is the case for the uncomplexed ligand the ^{31}P NMR shift for the complex of 6 is approximately midway between those of 1 and 3. Again the ^{1}H NMR spectra of the rhodium complex of 7 and other ligands show that a downfield shift of the ligand resonance occurs on complexation, although the magnitude is less than is found for the palladium derivatives.

The nickel(II) complexes of 1 and 3 are easily prepared. They are paramagnetic, indicating a tetrahedral structure which has been confirmed as described above, L-L = 1.

It is possible that the origin of the discrimination observed in reactions catalyzed by nickel and palladium complexes of 1 is the difference in structure, tetrahedral vs. square planar, of the two catalyst precursors in the catalytic cycle.

Rotational Barriers in Substituted (Cycloheptatriene)Cr(CO)$_3$ Complexes

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The barriers of rotation about the cycloheptatriene–Cr axis have been determined for six (7-substituted cycloheptatriene)Cr(CO)$_3$ complexes. The barriers were determined from a complete line-shape analysis of the ^{13}C spectra for the carbonyl region as a function of temperature. The values of ΔH^* for the cycloheptatriene (CHT), 7-*exo*-MeCHT, 7-*endo*-MeOCHT, and 7,7-di-MeOCHT complexes are essentially identical (9.9 ± 0.2, 10.4 ± 0.5, 9.9 ± 0.3, and 9.9 ± 0.4 kcal/mol, respectively) and the values of ΔS^* cluster around zero. On the other hand, ΔH^* values for 7-*exo*-CNCHTCr(CO)$_3$ (8.9 ± 0.2 kcal/mol) and 7-*exo*-*t*-BuCHTCr(CO)$_3$ (10.9 ± 0.3 kcal/mol) are, respectively, slightly lower and higher than these values. This appears to be consistent with arguments concerning the electronic origin of these rotational barriers, namely, that the magnitude of the barrier is related to the cycloheptatriene–norcaradiene equilibrium. Estimates of the rotational barriers in three (1,6-methanoannulene)Cr(CO)$_3$ complexes are also consistent with this theory. Finally the barrier in (tropone)Cr(CO)$_3$ was found to be very small (∼6 kcal/mol); extended Hückel molecular orbital calculations predict a barrier of 5.8 kcal/mol. A rationale why the barrier in this complex is much lower than the other cycloheptatriene complexes is given.

Introduction

A theoretical study of the electronic origin for rotational barriers about the polyene–metal axis in (polyene)ML$_3$ complexes was undertaken some time ago.[2] One prediction[2b] from this body of work was that the ground state conformation of the Cr(CO)$_3$ group in (cycloheptatriene)Cr(CO)$_3$ complexes should be tied to the cycloheptatriene–norcaradiene equilibrium. Namely, if the ligand lies on the cycloheptatriene side of the equilibrium,

the ground state of the complex will be given by 1. On

1   2   3
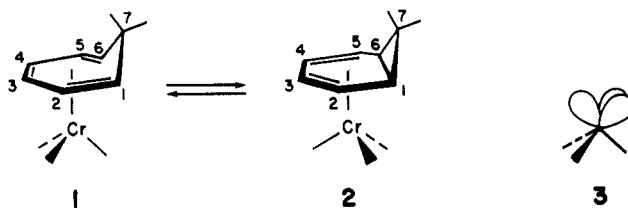
the other hand, if the ligand is forced to be at the norcaradiene extreme, then the Cr(CO)$_3$ group adopts the geometry shown in 2. There are a number of ways to view this pattern[2b,e] perhaps the easiest is to recall that there are three vacant hybrids in a Cr(CO)$_3$ fragment.[2a] They are hybridized away from the carbonyl ligands, and with use of a localized perspective shown in 3 they complete an

(1) Camille and Henry Dreyfus Teacher-Scholar, 1979–1984; Alfred P. Sloan Research Fellow, 1982–1984.
(2) (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* 1977, *99*, 7546. (b) Albright, T. A.; Hoffmann, R.; Hofmann, P. *Chem. Ber.* 1978, *111*, 1591. (c) Albright, T. A.; Hoffmann, R. *Ibid.* 1978, *111*, 1578. (d) Hoffmann, R.; Albright, T. A.; Thorn, D. L. *Pure Appl. Chem.* 1978, *50*, 1. (e) Albright, T. A. *Trans. Am. Crystallogr. Assoc.* 1980, *16*, 35. (f) Albright, T. A. *Acc. Chem. Res.* 1982, *15*, 149.