Synthesis and Characterization of Diastereomeric Nickel(II) Complexes of 2,2′-Bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)

Ljiljana Solujić,[†] Emil B. Milosavljević,[†] John H. Nelson,[*,†] and Jean Fischer[‡]

Department of Chemistry, University of Nevada, Reno, Nevada 89557, and
Laboratoire de Cristallochimie Structurale (URA 424-CNRS), Université Louis Pasteur,
67070 Strasbourg Cedex, France

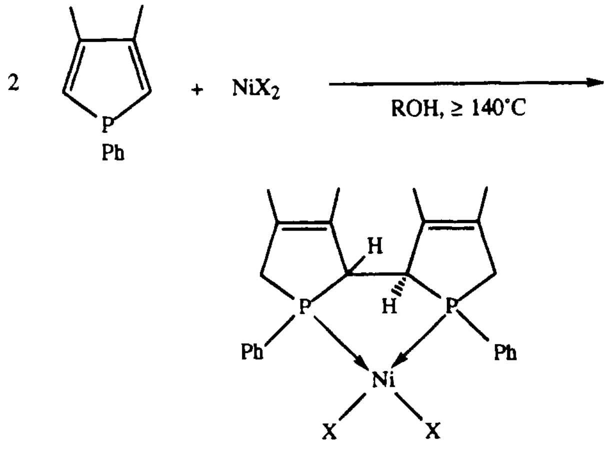
Received June 24, 1994[⊗]

The reaction of dibromo[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II) with silver tetrafluoroborate in dichloromethane/acetonitrile solution leads to the formation of the meso (**1**) and racemic (**2**) diastereomers of bis[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II) tetrafluoroborate and a single diastereomer of bromobis[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II) tetrafluoroborate (**3**). These compounds were separated by fractional crystallization and characterized by elemental analysis, physical properties, ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, electronic spectroscopy, and cyclic voltammetry. The structures of complexes **1** and **2** were determined by X-ray crystallography. Complex **1** crystallizes in the monoclinic space group *C*2/*c* with $a = 18.443(5)$ Å, $b = 14.139(2)$ Å, $c = 18.535(3)$ Å, $\beta = 104.19(2)°$, and $Z = 4$. Complex **2** crystallizes in the monoclinic space group *P*2 with $a = 17.108(4)$ Å, $b = 9.512(3)$ Å, $c = 14.78(3)$ Å, $\beta = 90.59(2)°$, and $Z = 2$. Refinements converged to $R(F) = 0.084$ and 0.051 for 3572 and 2068 independent observed ($I \geq 3\sigma(I)$) reflections, respectively.

Introduction

Palladium and platinum complexes of the type $[M(R_3P)_2(solvent)_2](Y)_2$ have been shown to be catalysts for olefin isomerization and hydrogenation.[1] They are also useful starting materials for the synthesis of a variety of complexes because the weakly coordinated solvent molecules are readily displaced.[2] These complexes are typically synthesized by reacting complexes of the type $(R_3P)_2MX_2$ (X = Cl, Br, I) with AgY (Y = BF_4^-, ClO_4^-, PF_6^-, $CF_3SO_3^-$).

We have previously shown[3] that thermolysis of 1-phenyl-3,4-dimethylphospholes in alcoholic solvents in the presence of anhydrous NiX_2 (X = Cl, Br) results in the formation of dihalo[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II), $Ni(dpple)X_2$ (reaction 1). This reaction occurs with

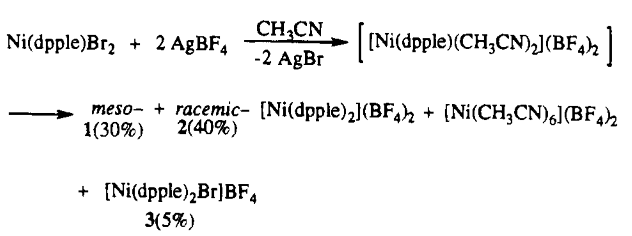


(1)

$Ni(dpple)X_2$

remarkable stereoselectivity producing exclusively a racemic mixture of a single diastereomer, despite the possibility of forming eight diastereomers. Accordingly, we have investigated the reaction of $Ni(dpple)Br_2$ with $AgBF_4$ in order to ascertain whether this reaction would provide a route to synthetically useful nickel complexes containing the chiral dpple ligand and report the results herein.

Scheme 1



$$Ni(dpple)Br_2 + 2\,AgBF_4 \xrightarrow[-2\,AgBr]{CH_3CN} \left[[Ni(dpple)(CH_3CN)_2](BF_4)_2\right]$$

$$\longrightarrow \underset{1(30\%)}{meso\text{-}} + \underset{2(40\%)}{racemic\text{-}}\ [Ni(dpple)_2](BF_4)_2 + [Ni(CH_3CN)_6](BF_4)_2 + \underset{3(5\%)}{[Ni(dpple)_2Br]BF_4}$$

Experimental Section

A. Reagents and Physical Measurements. All chemicals were reagent grade and were used as received or synthesized as described below. Solvents were dried by standard procedures and were stored over Linde Type 4A molecular sieves. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Conductance measurements were carried out at 25 °C on 1×10^{-3} M nitromethane solutions by using a Yellow Springs Instruments conductivity cell, Model No. 3403, and were measured with a Tektronix Type 310 oscilloscope. Conductance ranges were taken from published values.[4] Electronic spectra were recorded on a GBC, UV/VIS 911A spectrophotometer using 1 cm quartz cells at ambient temperature. Cyclic voltammograms were recorded as previously described.[5] The $^{31}P\{^1H\}$, ^1H, $^1H\{^{31}P\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded at 121.56, 300, 300 and 75 MHz respectively on a General Electric GN-

---

[*] To whom correspondence should be addressed.

[†] University of Nevada.

[‡] Université Louis Pasteur.

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1994.

(1) Hartley, F. R.; Murray, S. G.; Wilkinson, A. *Inorg. Chem.* **1989**, *28*, 549.

(2) Fallis, S.; Anderson, G. K.; Rath, N. P. *Organometallics* **1991**, *10*, 3180.

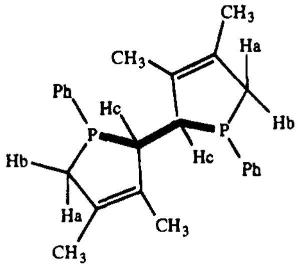
(3) Mercier, F.; Mathey, F.; Fischer, J.; Nelson, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 425. Mercier, F.; Mathey, F.; Fischer, J.; Nelson, J. H. *Inorg. Chem.* **1985**, *24*, 4141.

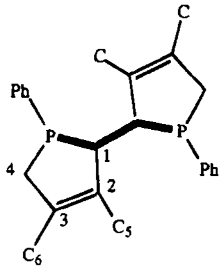
(4) Geary, W. J. *Coord. Chem. Rev.* **1971**, *81*, 7.

(5) Milosavljević, E. B.; Solujić, Lj.; Krassowski, D. W.; Nelson, J. H. *J. Organomet. Chem.* **1988**, *352*, 177.

0020-1669/94/1333-5654$04.50/0

Table 1. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}^a$ NMR Data for the Obtained Compounds





Cmpd	δ(CH$_3$)	δ(CH)	δ(Ph)	δ(CH$_2$)(J$_{HH}$)		δ^{31}P
				H$_a$	H$_b$	
1	1.62,1.90	3.11	7.20-7.70	3.93(19.8)	3.22(19.8)	81.6
2	1.61,1.71	2.92	7.20-7.75	3.73(18.9)	1.96(18.9)	83.9
3	1.66,1.81	3.12	7.00-7.50	3.57(17.5)	3.16(17.5)	82.8

	C$_1$	C$_2$	C$_3$	C$_4$	C$_5$	C$_6$	C$_i$	C$_o$	C$_m$	C$_p$
1	61.35,5L (27.4)	131.23,5L (6.7)	131.85	32.21	16.27	16.89	126.86,5L (24.0)	131.62	129.52	130.74
2	60.80,5L (27.4)	131.36,5L (7.6)	131.75	32.56	16.61	16.80	127.40,5L (25.0)	132.65	129.69	131.61
3	61.16,5L	132.05	131.99	39.10	16.43d (6.2)	16.81d (5.2)	130.04	130.76	128.59	130.90

[a] AXX'X"X"' spin system; coupling constants given are separations equivalent to $|^nJ_{PC} + {}^{n+2}J_{PC}|$ in the AXX' spin system.

Table 2. Crystallographic Data and Data Collection Parameters for **1** and **2**

	1	2
formula	$C_{48}H_{56}B_2F_8NiP_4$	$C_{48}H_{56}B_2F_8NiP_4{\cdot}0.5H_2O$
fw	989.20	998.20
space group	*C2/c*	*P2*
a, Å	18.443(5)	17.108(4)
b, Å	14.139(2)	9.512(3)
c, Å	18.535(3)	14.78(3)
β, deg	104.19(2)	90.59(2)
V, Å^3	4686	2399
Z	4	2
d(calcd), g/cm^3	1.402	1.381
abs coeff, cm^{-1}	6.131	24.155
λ, Å	0.710 73	1.5418
T, K	293 ± 1	173 ± 1
R(*F*)^a	0.084	0.051
R$_w$(*F*)^b	0.095	0.071

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$; $w = 1/(\sigma^2(F)^2 + (0.08I)^2)$.

300 spectrometer. Proton and carbon chemical shifts are relative to internal Me_4Si and phosphorus chemical shifts are relative to external 85% H_3PO_4, with positive values being downfield of the respective reference.

B. Synthesis. Reaction of Dibromo[2,2′-bi-(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II) with Silver Tetrafluoroborate. To a solution of 1.19 g (2.0 mmol) of dibromo[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II)[3] in 30 mL of dichloromethane was added a solution of 0.78 g (4.0 mmol) of silver tetrafluoroborate in 30 mL of acetonitrile. The reaction mixture was heated at reflux for 30 min, cooled to ambient temperature and filtered to remove silver bromide. The filtrate was concentrated to half-volume on a rotary evaporator and after addition of ethanol (~20 mL) left at ambient temperature for 48 h. During this time, from the solution there separated out 0.30 g (30%) of *meso*-bis[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II) tetrafluoroborate, **1**, in the form of pale yellow crystals. These were recrystallized from CH_2Cl_2/EtOH and vacuum dried; dec > 320 °C. Anal. Calcd for $NiC_{48}H_{56}P_4B_2F_8$: C, 58.28; H, 5.66; P, 12.52. Found: C, 58.34; H, 5.70; P, 12.91. $\lambda_m(CH_3NO_2) = 219\ \Omega^{-1}\ cm^2\ mol^{-1}$. To the filtrate obtained, after the separation of **1**, diethyl ether (~10 mL) was added and the solution was left at ambient temperature for 2d. By this time, 0.40 g (40%) of yellow crystals of *rac*-bis[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II) tetrafluoroborate, **2**, which formed, was isolated by filtration, recrystallized from CH_2Cl_2/EtOH and vacuum dried; dec > 290 °C. Anal. Calcd for $NiC_{48}H_{56}P_4B_2F_8{\cdot}0.5H_2O$: C, 57.73; H, 5.71; P, 12.41. Found: C, 57.59; H, 6.27; P, 12.37. H_2O was detected in the ^1H NMR spectrum in approximately the correct ratio. $\lambda_m(CH_3NO_2) = 208\ \Omega^{-1}\ cm^2\ mol^{-1}$. The volume of the filtrate obtained, after the separation of **2**, was reduced on a rotary evaporator to 2 mL, diethyl ether (~2 mL) was added, and the solution was left in a refrigerator for several hours. The resultant orange crystals, 0.05 g (5%), of bromobis[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II) tetrafluoroborate, **3**, were isolated by filtration, recrystallized from CH_2Cl_2/Et_2O and vacuum dried; mp 242−4 °C. Anal. Calcd for $NiC_{48}H_{56}P_4BrBF_4$: C, 58.69; H, 5.75; P, 12.62. Found: C, 58.70; H, 5.80; P, 12.30. $\lambda_m(CH_3NO_2) = 107\ \Omega^{-1}\ cm^2\ mol^{-1}$.

C. X-ray Data Collection and Processing. Yellow crystals of **1** and **2** were obtained by slow evaporation of CH_2Cl_2 solutions at ambient temperature. For both complexes, a single crystal was cut out from a cluster of crystals and mounted on a rotation-free goniometer head. Systematic searches in reciprocal space using an Enraf-Nonius CAD4-F for **1** and a Philips PW1100/16 automatic diffractometer for **2** showed that both crystals belonged to the monoclinic system. Quantitative data for **1** were obtained at room temperature, whereas for **2** they were obtained at −100 °C achieved by using a locally built gas flow device. The resulting data sets were transferred from the X-ray instrument computers to a VAX computer, and for all subsequent calculations the

Table 3. Atomic Coordinates for *meso*-[Ni(dpple)$_2$](BF$_4$)$_2$, **1**[a]

atom	*x*	*y*	*z*	*B*, Å^2
Ni	1.000	0.2046(1)	0.750	1.98(3)
P1	1.0846(1)	0.3163(2)	0.7631(1)	2.32(4)
C1	1.1554(6)	0.3295(8)	0.8507(6)	3.4(2)
C2	1.1196(6)	0.4022(7)	0.8928(6)	3.4(2)
C3	1.0627(6)	0.4526(7)	0.8529(5)	3.2(2)
C4	1.0417(5)	0.4340(6)	0.7687(5)	6.3(2)
C5	1.1565(8)	0.411(1)	0.9747(7)	5.0(3)
C6	1.0219(8)	0.528(1)	0.8826(8)	5.8(3)
C7	1.1239(5)	0.3185(7)	0.6834(6)	2.8(2)
C8	1.0769(6)	0.2910(7)	0.6152(6)	3.4(2)
C9	1.1006(7)	0.2989(8)	0.5497(7)	4.3(3)
C10	1.1723(7)	0.3327(9)	0.5526(7)	4.9(3)
C11	1.2181(6)	0.357(1)	0.6203(7)	5.3(3)
C12	1.1956(6)	0.3518(9)	0.6849(7)	4.5(3)
P2	1.0807(1)	0.0909(2)	0.7853(1)	2.27(4)
C13	1.0950(6)	0.0747(7)	0.8846(5)	3.3(2)
C14	1.0994(6)	−0.0330(7)	0.8939(5)	3.2(2)
C15	1.0761(6)	−0.0850(7)	0.8326(6)	3.1(2)
C16	1.0436(5)	−0.0294(6)	0.7612(5)	5.8(2)
C17	1.1299(8)	−0.067(1)	0.9716(7)	4.9(3)
C18	1.0765(8)	−0.1888(8)	0.8287(8)	4.9(3)
C19	1.1703(5)	0.0926(6)	0.7629(5)	2.6(2)
C20	1.1739(6)	0.0763(8)	0.6915(6)	3.7(2)
C21	1.2400(6)	0.081(1)	0.6696(7)	4.6(3)
C22	1.3047(6)	0.1045(9)	0.7194(8)	4.5(3)
C23	1.3032(6)	0.1228(9)	0.7920(9)	5.1(3)
C24	1.2371(6)	0.1159(8)	0.8150(6)	4.0(2)
B	0.1043(9)	0.174(1)	0.0813(9)	5.7(4)
F1	0.1408(9)	0.1615(9)	0.1585(7)	11.1(4)
F2	0.1640(6)	0.1773(9)	0.0508(6)	9.5(3)
F3	0.0620(6)	0.0931(8)	0.0642(7)	12.0(3)
F4	0.0675(7)	0.2555(9)	0.083(1)	13.1(5)

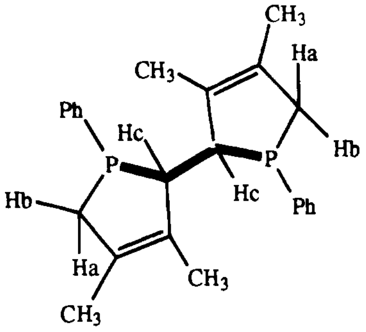
[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Enraf-Nonius Molen package[6] was used with the exception of a local data reduction program. Three standard reflections were measured every hour during the entire data collection periods and showed no significant trends. For **2**, the raw step-scan data were converted to intensities using the Lehman-Larsen method.[7] Both data sets were corrected for Lorentz and polarization factors. The structures were solved by the heavy atom method. After refinement of the non-hydrogen atoms, difference Fourier maps revealed maxima of residual electronic density close to the positions expected for the hydrogen atoms. They were introduced, with the exception of the water hydrogens for **2**, in the structure factor calculations by their computed coordinates (CH = 0.95 Å) with isotropic temperature factors such as B(H) = 1.3B_{eqv}(C) Å^2, but were not refined. At this stage empirical absorption corrections were applied for **2** using the method of Walker and Stuart[8] since face indexation was not possible under the cold gas stream. No absorption corrections were applied to the data for **1**. Otherwise, solutions were obtained with full least-squares refinements with the weighting scheme given in Table 2. Final difference maps revealed no significant maxima (0.19 e/Å^3, **1**; 0.14 e/Å^3, **2**). The absolute structure of **2** was determined by comparing $+x$, $+y$, $+z$ and $-x$, $-y$, $-z$ refinements. The acentricity of the structure was indicated by N_z cumulative tests on $|F_o|$; it was not possible to find and refine a structure solution in space groups *Pm* and *P2/m*. There are two crystallographically independent cation moieties each lying on a 2-fold axis. The scattering factors coefficients and anomalous dispersion coefficients come respectively from parts a and b of ref 9.

Results and Discussion

Reaction of Ni(dpple)Br$_2$ with silver tetrafluoroborate in CH$_3$CN/CH$_2$Cl$_2$ solution produces three new dpple complexes (Scheme 1). Ni(dpple)Cl$_2$ reacts similarly. The expected product of this reaction, [Ni(dpple)(CH$_3$CN)$_2$] (BF$_4$)$_2$, apparently undergoes facile ligand redistribution.[10] Similar redistributions were not observed for reactions of analogous palladium and platinum complexes.[1,2] Compounds **1** and **2** are 2:1 electrolytes[4] in CH$_3$NO$_2$ solutions (λ_m = 219 and 208 Ω^{-1} cm^2 mol^{-1}, respectively) whereas **3** is a 1:1 electrolyte in CH$_3$NO$_2$ (λ_m = 107 Ω^{-1} cm^2 mol^{-1}). The ^{31}P{^{1}H} NMR spectra of all three compounds exhibit singlet resonances (Table 1) showing that their phosphorus nuclei are symmetry equivalent and that the compounds are pure diastereomers. The chemical shifts lie between those of Ni(dpple)Cl$_2$ (δ 80.0) and Ni(dpple)Br$_2$ (δ 87.7).[3]

The ^{1}H NMR spectra of these new compounds, all of which possess the ligand conformation **4**, are second order but deceptively simple. Assignments were made by ^{31}P decoupling experiments together with comparisons with the spectra of Ni(dpple)X$_2$ (X = Cl, Br) and *trans*-(dpple)$_2$RuCl$_2$.[3] Since ^{31}P decoupling does not change any of the line shapes in the 1.0–4.0 ppm regions for all three compounds we conclude that $|^2J(\mathrm{PH_a}) + {}^4J(\mathrm{PH_a})|$, $|^2J(\mathrm{PH_b}) + {}^4J(\mathrm{PH_b})|$, and $|^2J(\mathrm{PH_c}) + {}^4\mathrm{H}(\mathrm{PH_c})|$ are all zero, as is also the case for *trans*-(dpple)$_2$RuCl$_2$.[3] This results in an AB spectral pattern for the H$_a$ and H$_b$ resonances and a singlet for that of H$_c$. The chemical shift difference of the H$_a$ and H$_b$ resonances for the meso diastereomer ($\Delta\delta$ = 0.71 ppm) is significantly less than that for the racemic diastereomer ($\Delta\delta$ = 1.77 ppm) (Table 1). As the crystal structures of these two compounds show (*vide infra*), H$_b$ is situated near the shielding region of an adjacent phenyl ring while H$_a$ is situated near the deshielding region of the same phenyl ring in the racemic diastereomer, whereas both H$_a$ and H$_b$ are remote from phenyl rings in the meso diastereomer. Since the ^{1}H NMR spectrum of *trans*-(dpple)$_2$RuCl$_2$ is very similar to that of *rac*-[Ni(dpple)$_2$](BF$_4$)$_2$, the current data lend support for our previous conclusion[3] that the ruthenium complex is the racemic diasteromer. The ^{1}H NMR data for [Ni(dpple)$_2$Br]BF$_4$, **3**, are very similar to those for *meso*-[Ni(dpple)$_2$](BF$_4$)$_2$, **1**, suggesting that **3** is most likely a square-based-pyramidal complex containing *RR* and *SS* dpple ligands. Were this complex trigonal-bipyramidal, its ^{1}H and ^{31}P{^{1}H} NMR spectra would be more complicated. In particular, the ^{31}P{^{1}H} NMR spectrum would not be a singlet. This compound is then probably structurally similar to {Ni[bis(diethylphosphino)ethane]$_2$I}I which is square-based-pyramidal.[12]



4

---

(6) *Molen: An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.

(7) Lehman, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys. Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 580–584.

(8) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1983**, *A39*, 158.

(9) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2.b. (b) *Ibid.*, Table 2.3.1.

(10) Garrou, P. E. *Adv. Organomet. Chem.* **1984**, *23*, 95.

(11) Moedritzer, K. *Adv. Organomet. Chem.* **1968**, *6*, 171.

(12) Alyea, E. C.; Meek D. W. *Inorg. Chem.* **1972**, *11*, 1029.

Table 4. Atomic Coordinates for *rac*-$[Ni(dpple)_2](BF_4)_2$, **2a**[a]

atom	*x*	*y*	*z*	*B*, Å^2
Ni1	0.500	−0.023	0.000	2.52(5)
P1	0.4252(1)	−0.0139(3)	−0.1207(2)	2.51(5)
P2	0.5967(1)	−0.0061(3)	−0.0936(2)	2.31(5)
C1	0.3893(6)	0.158(1)	−0.1586(8)	3.9(3)
C2	0.3887(6)	0.145(1)	−0.2594(6)	3.4(2)
C3	0.4312(6)	0.041(1)	−0.2946(6)	3.3(2)
C4	0.4789(5)	−0.044(1)	−0.2266(6)	2.6(2)
C5	0.3425(7)	0.256(2)	−0.3100(9)	5.8(3)
C6	0.4389(7)	0.019(2)	−0.3936(8)	6.0(4)
C7	0.5658(5)	0.006(1)	−0.2141(6)	2.5(2)
C8	0.6282(6)	−0.078(1)	−0.2640(6)	2.9(2)
C9	0.6735(6)	−0.158(1)	−0.2121(7)	3.1(2)
C10	0.6579(6)	−0.164(1)	−0.1099(7)	3.3(2)
C11	0.6342(7)	−0.063(1)	−0.3643(7)	4.8(3)
C12	0.7366(8)	−0.256(1)	−0.2433(8)	5.6(3)
C13	0.3402(5)	−0.128(1)	−0.1254(6)	2.3(2)
C14	0.2674(5)	−0.080(1)	−0.1062(7)	2.6(2)
C15	0.2049(6)	−0.170(1)	−0.1014(7)	3.5(3)
C16	0.2164(6)	−0.308(1)	−0.1128(8)	4.2(3)
C17	0.2885(7)	−0.363(1)	−0.1325(8)	4.3(3)
C18	0.3496(7)	−0.272(1)	−0.1374(7)	3.8(3)
C19	0.3387(6)	0.142(1)	0.0781(6)	2.3(2)
C20	0.2590(5)	0.134(1)	0.0755(7)	2.7(2)
C21	0.2159(6)	0.254(1)	0.0652(7)	3.9(3)
C22	0.2498(7)	0.384(1)	0.0562(8)	3.9(3)
C23	0.3287(8)	0.394(1)	0.0583(9)	4.8(3)
C24	0.3744(6)	0.273(1)	0.0688(7)	3.6(3)
Ni2	1.000	0.4822(3)	0.500	2.32(4)
P3	1.1133(1)	0.4823(3)	0.5708(2)	2.55(5)
P4	1.0678(1)	0.4470(3)	0.3777(2)	2.41(5)
C25	1.1439(6)	0.654(1)	0.6101(8)	4.1(3)
C26	1.2318(7)	0.660(1)	0.5824(8)	4.5(3)
C27	1.2573(6)	0.559(1)	0.5278(7)	3.8(3)
C28	1.1975(6)	0.449(1)	0.4973(6)	2.9(2)
C29	1.2764(8)	0.781(2)	0.618(1)	6.3(3)
C30	1.3389(7)	0.545(2)	0.4949(9)	5.9(4)
C31	1.1761(5)	0.448(1)	0.3935(6)	2.7(2)
C32	1.2016(6)	0.320(1)	0.3431(6)	2.7(2)
C33	1.1463(6)	0.223(1)	0.3233(6)	3.1(2)
C34	1.0642(6)	0.260(1)	0.3465(7)	2.9(2)
C35	1.2879(7)	0.301(1)	0.3241(8)	4.9(3)
C36	1.1596(7)	0.083(1)	0.2840(8)	3.9(3)
C37	1.1244(6)	0.359(1)	0.6622(7)	2.9(2)
C38	1.1240(7)	0.399(2)	0.7539(7)	5.0(3)
C39	1.1267(9)	0.308(2)	0.8195(9)	7.2(4)
C40	1.1296(7)	0.174(2)	0.8049(9)	7.8(4)
C41	1.1318(7)	0.117(1)	0.714(1)	7.2(4)
C42	1.1294(6)	0.216(1)	0.6417(8)	4.0(3)
C43	1.0537(5)	0.546(1)	0.2748(6)	2.4(2)
C44	1.0608(6)	0.486(2)	0.1894(6)	4.1(3)
C45	1.0537(7)	0.581(2)	0.1146(7)	6.4(4)
C46	1.0356(7)	0.720(1)	0.1254(8)	4.8(3)
C47	1.0277(7)	0.771(1)	0.2095(8)	4.3(3)
C48	1.0365(6)	0.691(1)	0.2834(7)	3.6(3)
B1	0.4864(9)	0.504(2)	0.2397(9)	5.8(4)
F1	0.5172(6)	0.489(1)	0.1544(7)	11.4(3)
F2	0.4720(6)	0.3732(9)	0.2702(7)	9.6(3)
F3	0.4243(7)	0.580(1)	0.231(1)	16.8(4)
F4	0.5402(5)	0.576(1)	0.2927(6)	9.0(2)
B2	1.000	1.093(3)	0.000	6.3(6)*
F5	0.9368(5)	0.0249(9)	0.0205(6)	6.0(2)
F6	1.027(1)	1.117(2)	0.101(1)	6.1(5)
F7	0.000	0.231(1)	0.000	11.6(5)
B3	0.000	0.930(3)	0.500	12.5(9)
F8	0.079(1)	0.973(3)	0.486(1)	6.5(4)*
F9	−0.009(1)	0.962(2)	0.409(1)	5.2(4)*
F10	0.000	0.773(1)	0.500	5.3(2)
OW	0.500	0.689(2)	0.000	7.2(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

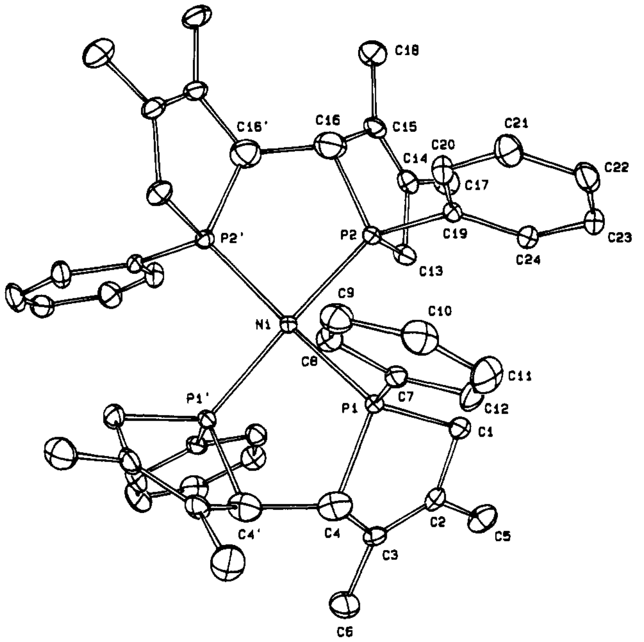


Figure 1. ORTEP drawing of the *meso*-$[Ni(dpple)_2]^{2+}$, **1**, cation (50% probability ellipsoids). Hydrogen atoms are omitted.

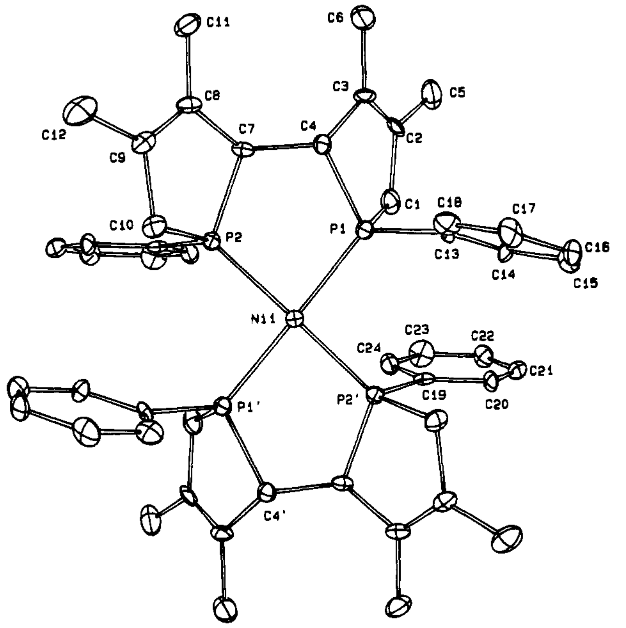


Figure 2. ORTEP drawing of the *SS,SS*-$[Ni(dpple)_2]^{2+}$, **2**, cation (50% probability ellipsoids). Hydrogen atoms are omitted.

The $^{13}C\{^1H\}$ NMR spectra of these complexes (Table 1) display AXX′X″X‴ multiplets, A ≡ ^{13}C, X ≡ ^{31}P, for each carbon resonance and all coupling constants were not calculated. Instead separations equivalent to $|^nJ(PC) + {}^{n+2}J(PC)|$ in the AXX′ spin system are reported to facilitate comparison with previous data[3] on other complexes of dpple.

In order to gain conclusive support for the structural assignments of the meso and racemic diastereomers of $[Ni(dpple)_2](BF_4)_2$ X-ray crystal structures were obtained. Crystal data and collection parameters are given in Table 2 and final atom coordinates are given in Tables 3 and 4 for **1** and **2** respectively. ORTEP diagrams of *meso*- (**1**) and *rac*-$[Ni(dpple)_2](BF_4)_2$ (**2**) are shown in Figures 1 and 2 respectively. Both complexes exist as well separated cations and anions with no unusual interionic contacts. For **1**, each of the four cations lies on a C_2 axis that bisects the P1−Ni−P1′ angle. This compound contains the *RR* and *SS* absolute configurations of dpple and is the meso diastereomer. For **2**, there are two equivalent cations in the unit cell each of which possess a C_2 axis normal to the NiP_4

Table 5. Selected Bond Lengths (Å) and Angles (deg) for *meso*- and *rac*-$[Ni(dpple)_2](BF_4)_2$ (**1, 2**)

Bond Lengths

1		**2**			
Ni−P1	2.192(1)	Ni1−P1	2.184(2)	Ni2−P3	2.192(2)
Ni−P2	2.180(1)	Ni1−P2	2.171(2)	Ni2−P4	2.181(2)
P1−C1	1.826(4)	P1−C1	1.83(1)	P3−C25	1.81(1)
P1−C4	1.857(4)	P1−C4	1.841(8)	P3−C28	1.840(9)
C2−C3	1.332(6)	C2−C3	1.34(1)	C26−C27	1.33(1)
C14−C15	1.334(6)	C8−C9	1.33(1)	C32−C33	1.35(1)
C4−C4′	1.524(6)	C4−C7	1.57(1)	C28−C31	1.57(1)
C16−C16′	1.559(6)				

Bond Angles

1		**2**			
P1−Ni−P2	94.78(3)	P1−Ni1−P2	85.61(7)	P3−Ni2−P4	85.32(8)
P1−Ni−P1′	87.73(5)	P1−Ni1−P2′	94.07(7)	P3−Ni2−P4′	94.69(9)
C1−P1−C4	94.6(2)	C1−P1−C4	92.7(4)	C25−P2−C28	96.9(4)
C13−P2−C16	94.7(2)	C10−P2−C7	94.7(4)	C31−P4−C34	93.9(4)
Ni−P1−C4	110.5(2)	Ni1−P1−C4	113.0(1)	Ni2−P3−C28	114.4(2)
Ni−P2−C16	114.9(2)	Ni1−P2−C7	113.7(2)	Ni2−P4−C31	115.6(2)
P1−C4−C4′	111.7(3)	P1−C4−C7	109.6(5)	P3−C28−C31	113.5(6)
P2−C16−C16′	111.2(3)	P2−C7−C4	110.8(5)	P4−C31−C28	110.1(5)

plane passing through the nickel atom. This complex has spontaneously resolved and the crystal examined contains the *SS* form of the ligand only. The bulk sample is racemic, however, containing equal amounts of the *RR,RR* and *SS,SS* complexes as no CD spectrum is observable for the bulk sample.

Important bond lengths and angles are given in Table 5. The Ni−P distances in **1** and **2** (2.186(1) Å (average), 2.182(2) Å (average) respectively) are both longer than that found for Ni(dpple)Cl_2 (2.126(1) Å)[3] and those for **1** and **2** are essentially the same. The former lengthening results from the combined effects of increased steric encumbrance within the nickel coordination sphere and the greater trans influence of P than Cl.[13] The two $[Ni(dpple)_2]^{2+}$ cations are slightly distorted toward tetrahedral geometry as the NiP_2/P_2Ni dihedral angles are 16.5(1)° and 9.1(1)/17.7(1)° for **1** and **2** respectively. The chelate rings adopt λ configurations[14] in both **1** and **2**. The NiP distances in $[Ni(Ph_2PCH_2PPh_2)_2](BF_4)_2$, $[Ni(dppm)_2](PF_6)_2$ (2.224(9) Å)[15] and $[Ni(Ph_2P\text{-}1,2\text{-}C_6H_4PPh_2)_2](PF_6)_2$, $[Ni(dppb)_2](PF_6)_2$, (2.224(b) Å)[15] are slightly longer than those in **1** and **2**. The P−M−P angles within the chelate rings of the former two compounds 87.73° and 89.92° (average) compare with 94.78° and 85.61° for **1** and **2** respectively.

DuBois and co-workers found that the lowest energy electronic transition for a series of $[Ni(P{\sim}P)_2](BF_4)_2$ complexes decreases in energy as the P−Ni−P angle increases and the half-wave potentials for the Ni(II/I) couples become more positive as the P−Ni−P angle increases. Compounds **1** and **2** undergo well-separated quasi-reversible one-electron reductions to Ni(I) and Ni(0) species with potentials that are not very different for the two diastereomers (Table 6). No oxidations to Ni(III) species in the accessible potential range could be observed for any of these species. In contrast, Ni(dpple)Cl_2 was previously observed[3] to undergo an irreversible ligand-centered two-electron oxidation and an irreversible two electron reduction. Based upon the similarities in P−Ni−P angles for **1**, **2** and $[Ni(dppb)_2](PF_6)_2$ one might expect to observe similar potentials for their Ni(II/I) couples. However, the potentials are quite different (−1.02 V, **1**; −1.09 V, **2**; −0.54 V, $[Ni(dppb)_2](PF_6)_2$) showing that the correlation between the P−Ni−P angle and the Ni(II/I) couple is not general.

Table 6. Reduction Potentials of the Obtained Complexes[a]

	E_{p_c}	
compd	Ni(II) → Ni(I)	Ni(I) → Ni(0)
1	−1.02[b]	−1.68
2	−1.09	−1.82
3	−1.52	

[a] In CH_2Cl_2 containing 0.1 M tetrabutylammonium perchlorate at 25 °C; v = 200 mV s^{-1}; volts *vs* Fc^+/Fc. [b] Quasireversible; $E_{1/2}$ given (ΔE = 150 mV).

The electronic absorption spectra of **1** [λ (nm), ϵ (L mol^{-1} cm^{-1}) in CH_2Cl_2: 295 (1702), 298 (1817), 325 (741)] and **2** [295 (2225), 298 (2319), 327 (1197)], like the reduction potentials, are not very different for the two diastereomers. The electronic spectral correlation with the half-wave potential for the Ni(II/I) couple noted by DuBois and co-workers is reasonably well obeyed by the data for **1** and **2** and the new data extends the reduction potential range for $[Ni(P{\sim}P)_2]^{2+}$ complexes now from −0.12 to −1.09 V.

Acknowledgment. We are grateful to the donors of the Petroleum Resarch Fund, administered by the American Chemical Society, for financial support.

Supplementary Material Available: Listings of crystal and refinement data, bond angles and distances, H atom coordinates, and thermal parameters (U) (17 pages). Ordering information is given on any current masthead page. Listings of observed and calculated structure factors (×10) (25 pages) are available from the authors.

---

(13) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(14) Hawkins, C. J. *Absolute Configuration of Metal Complexes*; Wiley-Interscience: New York, 1971.

(15) Miedaner, A.; Haltiwanger, R. C.; DuBois, D. L. *Inorg. Chem.* **1991**, *30*, 417.