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Structural Analysis of *o*-Phenylenebis(diisopropylphosphine) Complexes of Nickel(II), Palladium(II), and Platinum(II)[†]

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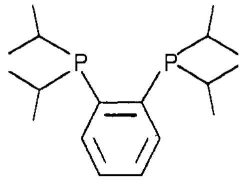
The *o*-phenylenebis(diisopropylphosphine) (**1**) chelated dichloro complexes of group 10 (VIIIB), $[o\text{-}C_6H_4(^iPr_2P)_2]MCl_2$, where M = Ni (**2a**), Pd (**2b**), and Pt (**2c**), were prepared and characterized by NMR spectroscopy and single-crystal X-ray diffraction. The crystal structures of the three complexes are isomorphous. The nickel complex (**2a**) as typical crystallizes in the monoclinic space group $P2_1/c$, with $a = 9.376$ (2) Å, $b = 12.755$ (4) Å, $c = 18.31$ (3) Å, $\beta = 104.39$ (6)°, and $Z = 4$. Least-squares refinement of 3191 observed reflections with $I > 1.5\sigma(I)$ gave final $R = 0.034$ and $R_w = 0.029$. The metal is seated at the center of a square-planar disposition with the phosphine in the cis coordination. The benzene plane of **1** and the complex plane are roughly coplanar with their dihedral angle being 0.49 (8)°. The four isopropyl groups of **1** are symmetrically arranged out of the molecular plane and comprise two sets of methyl groups with each set containing four methyls in magnetic equivalence.

Many chelated ligands are known to be capable of strengthening the stability of their metal complexes; therefore their coordination to the transition-metal ions may lead to the preparation of robust catalysts.[1] *o*-Phenylenebis(tertiary phosphines), having a rigid *o*-phenylene backbone for a strong chelating effect, are among this category.[2] They bind tenaciously with nearly all the transition metals[3,4] and stabilize high oxidation states.[5] The *o*-phenylenebis(diisopropylphosphine) (**1**) (abbreviated as DH for its resemblance to a deer head) is of particular interest because it supposedly possesses the prominent electronic effect as well as the steric effect, in addition to the aforementioned chelating effect. However, data for *o*-phenylenebis(diisopropylphosphine) complexes are very limited.[3c,d] The only DH complex having a structure determination is the Mo(0) system.[4] In this paper, we wish to report the first spectroscopically and structurally characterized dichloro *o*-phenylenebis(diisopropylphosphine) complexes of group 10 d^8 metals.



o-phenylenebis(diisopropylphosphine)
deer head (DH)

1

Results and Discussion

Syntheses. The *o*-phenylenebis(diisopropylphosphine) complexes, (DH)MCl$_2$, where M = Ni (**2a**), Pd (**2b**), and Pt (**2c**), were readily prepared either by direct coordination or by ligand substitution. Complex **2a** was synthesized by mixing a methanol solution of nickel chloride and a methylene chloride solution of **1**. Complex **2c** was prepared in a water/ethanol solution containing potassium tetrachloroplatinate and **1**. And the replacement of benzonitriles in $(PhCN)_2PdCl_2$ by **1** afforded complex **2b**. Unlike the analogous reactions between the metal halides and MPP (*o*-phenylenebis(dimethylphosphine)), which normally give 2:1 complexes,[3] the direct reactions of dichloro complexes with the very bulky DH, even in excess, only resulted in 1:1 products,[6] presumably due to the steric hindrance of DH.

Spectroscopy. All NMR data are listed in Table I. The ^{31}P NMR spectra of complexes **2a–c** are simple, the first two displaying singlets at δ 78.56 and 92.30, respectively, and the last one displaying a triplet in a 1:4:1 pattern at δ 62.24 with $J_{Pt-P} = 3583.4$ Hz. These data indicate that two phosphorus atoms in ligand **1** are magnetically equivalent in those complexes. The coordination chemical shifts of **2a–c** were respectively calculated as δ 83.9, 97.6, and 67.5, on the basis of the chemical shift of the free ligand of **1**, δ −5.3. This order is the same as that in the DPPE (1,2-bis(diphenylphosphino)ethane) system.[7] A linear correlation of the coordination chemical shifts[8] between the DH and the DPPE systems is illustrated in Figure 1.

The proton NMR spectra of complexes **2a–c** exhibit similar patterns, however still characteristic. All three complexes exhibit two sets of doublets of doublets in the region δ 1.2–1.5, which are due to the methyl protons on the four isopropyl groups. This pattern suggests that the isopropyl groups in (DH)MCl$_2$ must be quite symmetrical (vide infra). Peculiarly, the methyl protons in the nickel complex (**2a**) are coupled with the nearer phosphorus atom, and are virtually coupled with the remote phosphorus atom as well. Irradiation at the resonances of the isopropyl methine protons causes the two pairs of the upfield doublets of doublets to collapse to two sets of simple doublets and results in an obvious virtual coupling. This is shown in Figure 2.

The resonances of the isopropyl methine protons (H_α) are intriguing. The symmetrical structure is again supported by the single signal due to four H_α's in each complex. Their $^1H-^1H$ coupling constants are 7.1 Hz, i.e., identical for all. The $^1H-^{31}P$ coupling constants of H_α are 12.8 Hz for **2a**, 10.4 Hz for **2b**, and 10.7 Hz for **2c**. Besides, a $^1H-^{195}Pt$ coupling of 35.7 Hz was observed in the spectrum of **2c**. The distinct coupling patterns of H_α in complexes **2a–c**, as well as their corresponding computer simulations, are in excellent agreement, and are displayed in Figure 3.

[†] This paper is dedicated to Professor Wei-Chuan Lin (NTU) on the occasion of his 70th birthday and his retirement.

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Table I. NMR Data for **2a–c** and Their DPPE Analogues in $CDCl_3$

	M = Ni	M = Pd	M = Pt
		$(DH)MCl_2$	
^1H	1.32 (dd,[a] J = 15.3, 7.1 Hz, 12 H)	1.25 (dd, J = 16.0, 7.1 Hz, 12 H)	1.18 (dd, J = 16.2, 7.1 Hz, 12 H)
	1.55 (dd,[a] J = 17.1, 7.1 Hz, 12 H)	1.47 (dd, J = 18.1, 7.1 Hz, 12 H)	1.41 (dd, J = 17.7, 7.1 Hz, 12 H)
	2.80 (m, J = 12.8, 7.1 Hz, 4 H)	3.02 (m, J = 10.4, 7.1 Hz, 4 H)	3.02 (m, J = 35.7, 10.7, 7.1 Hz)
	7.66 (m, 4 H)	7.76 (m, 4 H)	7.68 (m, 2 H) 7.77 (m, 2 H)
^{31}P	78.56	92.30	62.24 (J_{P-Pt} = 3583.4 Hz)
Δ[b]	83.9	97.6	67.5
		$(DPPE)MCl_2$	
^{31}P	58.9	68.3[c]	45.3[c]
Δ[d]	72.1	81.5	58.5

[a] The virtual coupling with a remote phosphorus atom is shown in Figure 1. [b] Calculated with the chemical shift of DH being δ −5.3. [c] Calculated with the chemical shift of DPPE being δ −13.2. [d] References 6 and 7.

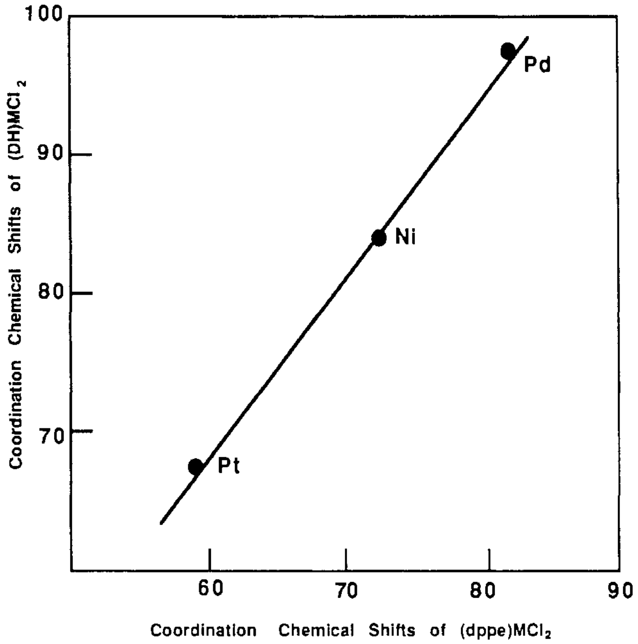

Figure 1. Correlation of ^{31}P NMR coordination chemical shifts between $(DH)MCl_2$ and $(DPPE)MCl_2$ (M = Ni, Pd, Pt).

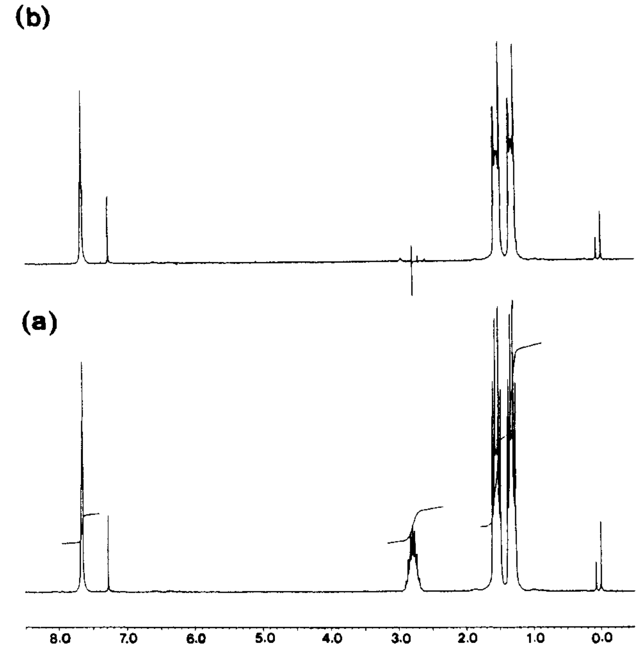

Figure 2. Proton NMR spectrum of **2a**: (a) ^1H-coupled spectrum; (b) decoupled spectrum with the irradiation at δ 2.80.

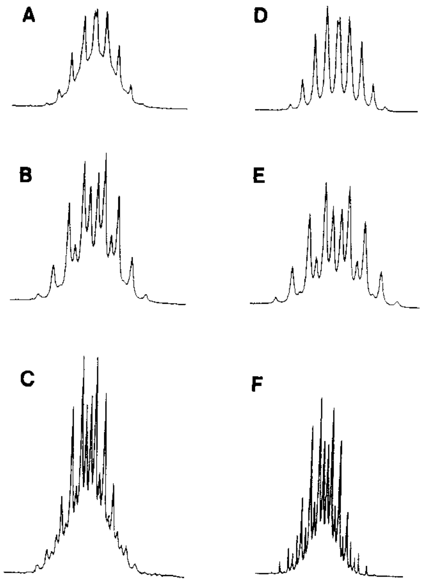

Figure 3. NMR resonances of the isopropyl methine proton for **2a** (A), **2b** (B), and **2c** (C) and their corresponding simulations (D–F).

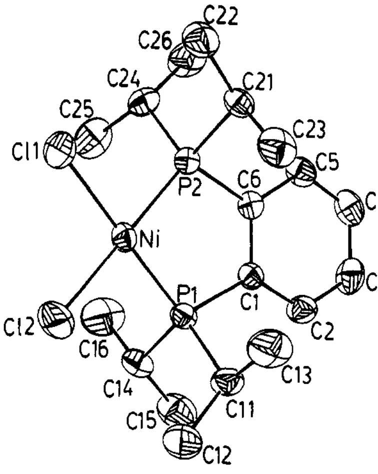

Figure 4. ORTEP drawing of $(DH)NiCl_2$ (**2a**) with hydrogen atoms omitted.

Single-Crystal X-ray Structures. The crystal structures of complexes **2a–c** are isomorphous. The nickel complex (**2a**) as typical crystallizes in the monoclinic space group $P2_1/c$. Other crystal data are summarized in Table II. The metal is seated at the center of the square-planar disposition, with a distance of 0.0390 (6) Å to the complex plane defined by the P and Cl atoms. The DH ligand is cis-coordinated. The chelation of DH is obviously favored by the formation of a stable five-member ring of a metallacycle, as shown by the ORTEP diagram in Figure 4. The benzene plane and the complex plane are roughly coplanar, with their dihedral angle being 0.49 (8)° (0.7 (1)° for **2b** and 1.2 (2)° for **2c**). The bond lengths D(M–Cl) and D(M–P) are typical and are in good agreement with those in $(DPPE)MCl_2$.[9,10] The selected bonding parameters for all three complexes are shown in Table III. The non-hydrogen atomic coordinates for **2a–c** are collected

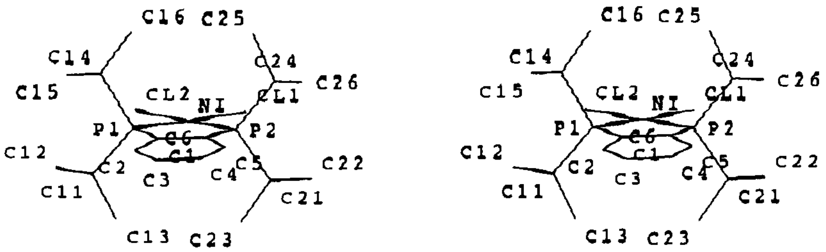

Figure 5. Stereoscopic view of (DH)NiCl$_2$ (**2a**) with hydrogen atoms omitted.

Table II. Crystallographic Data for **2a–c**

compd	(DH)NiCl$_2$	(DH)PdCl$_2$	(DH)PtCl$_2$
formula	NiP$_2$Cl$_2$C$_{18}$H$_{32}$	PdP$_2$Cl$_2$C$_{18}$H$_{32}$	PtP$_2$Cl$_2$C$_{18}$H$_{32}$
fw	440.01	487.70	576.39
a, Å	9.376 (2)	9.336 (2)	9.354 (2)
b, Å	12.755 (4)	12.802 (2)	12.838 (5)
c, Å	18.31 (3)	18.467 (3)	18.472 (7)
β, deg	104.39 (6)	104.60 (1)	104.82 (3)
V, Å^3	2121.03	2136.00	2144.39
Z	4	4	4
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
T, °C	25 (2)	25 (2)	25 (2)
λ, Å	0.7093	0.7093	0.7093
ρ(obsd), g cm^{-3}	1.37 (2)	1.52 (2)	1.78 (1)
ρ(calcd), g cm^{-3}	1.378	1.517	1.785
μ, cm^{-1}	0.132	0.126	0.701
transm coeff	0.96–0.99	0.93–0.99	0.54–1.00
$R(F_o)$	0.034	0.034	0.038
$R_w(F_o)$	0.029	0.030	0.037

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for **2a–c**

	2a (M = Ni)	**2b** (M = Pd)	**2c** (M = Pt)
M–P1	2.157 (1)	2.234 (1)	2.227 (3)
M–P2	2.157 (3)	2.233 (1)	2.214 (2)
M–Cl1	2.204 (1)	2.356 (1)	2.365 (3)
M–Cl2	2.204 (3)	2.352 (1)	2.346 (3)
P1–C1	1.822 (3)	1.816 (4)	1.850 (8)
P1–C11	1.846 (3)	1.843 (5)	1.85 (1)
P1–C14	1.852 (3)	1.834 (5)	1.82 (1)
P2–C6	1.827 (3)	1.824 (4)	1.817 (9)
P2–C21	1.853 (3)	1.833 (4)	1.820 (9)
P2–C24	1.839 (4)	1.838 (5)	1.85 (1)
C1–C6	1.405 (4)	1.403 (6)	1.38 (1)
P1–M–P2	89.41 (5)	87.79 (4)	88.62 (9)
P1–M–Cl1	176.94 (4)	175.77 (5)	176.3 (1)
P1–M–Cl2	88.86 (5)	90.46 (5)	91.34 (9)
P2–M–Cl1	88.50 (5)	89.88 (4)	90.57 (9)
P2–M–Cl2	177.54 (4)	177.36 (5)	177.8 (1)
Cl1–M–Cl2	93.16 (5)	91.74 (5)	89.3 (1)
M–P1–C1	108.6 (1)	108.4 (1)	107.3 (3)
M–P1–C11	119.4 (1)	118.7 (2)	118.7 (3)
M–P1–C14	112.0 (1)	111.2 (2)	111.7 (3)
M–P2–C6	108.78 (9)	108.3 (1)	107.9 (3)
M–P2–C21	117.5 (1)	117.0 (1)	117.3 (3)
M–P2–C24	114.2 (1)	112.8 (2)	113.2 (3)
P1–C1–C6	116.7 (2)	117.8 (3)	117.0 (7)
P2–C6–C1	116.2 (2)	117.5 (3)	119.1 (6)

Table IV. Non-Hydrogen Atomic Coordinates for **2a** with Esd's in Parentheses

	x	y	z	B_{iso}, Å^2
Ni	0.23337 (4)	0.81213 (3)	0.172640 (20)	2.441 (16)
P1	0.30441 (9)	0.65320 (6)	0.20104 (4)	2.45 (4)
P2	0.19116 (9)	0.77246 (6)	0.05466 (4)	2.21 (3)
Cl1	0.15043 (11)	0.97115 (6)	0.13925 (5)	4.12 (5)
Cl2	0.27168 (13)	0.84638 (7)	0.29395 (5)	5.45 (5)
C1	0.2987 (3)	0.58170 (21)	0.11419 (14)	2.26 (13)
C2	0.3579 (4)	0.48239 (23)	0.11160 (15)	3.12 (16)
C3	0.3573 (4)	0.43572 (24)	0.04332 (17)	3.60 (17)
C4	0.2963 (4)	0.48797 (25)	−0.02348 (16)	3.44 (16)
C5	0.2386 (4)	0.58655 (23)	−0.02242 (15)	2.94 (15)
C6	0.2392 (3)	0.63494 (21)	0.04624 (15)	2.18 (12)
C11	0.4940 (4)	0.62860 (24)	0.25716 (16)	3.07 (15)
C12	0.5208 (4)	0.6512 (3)	0.34125 (17)	4.77 (19)
C13	0.6058 (4)	0.6849 (3)	0.22451 (19)	5.37 (21)
C14	0.1815 (4)	0.58379 (25)	0.24997 (16)	3.32 (15)
C15	0.2154 (4)	0.4676 (3)	0.26429 (18)	4.88 (20)
C16	0.0223 (4)	0.5988 (3)	0.20879 (21)	5.97 (22)
C21	0.3068 (3)	0.83621 (22)	−0.00116 (15)	2.60 (13)
C22	0.2634 (4)	0.9483 (3)	−0.02467 (18)	4.16 (18)
C23	0.4683 (4)	0.8289 (3)	0.04197 (18)	4.31 (18)
C24	0.0013 (4)	0.79849 (24)	0.00051 (17)	3.06 (14)
C25	−0.1100 (4)	0.7681 (3)	0.04531 (20)	4.67 (20)
C26	−0.0392 (4)	0.7518 (3)	−0.07974 (19)	4.87 (18)

Table V. Non-Hydrogen Atomic Coordinates for **2b** with Esd's in Parentheses

	x	y	z	B_{iso}, Å^2
Pd	0.23505 (4)	0.81397 (3)	0.172738 (18)	2.209 (14)
P1	0.30810 (13)	0.64972 (9)	0.20185 (6)	2.32 (5)
P2	0.19568 (13)	0.76921 (9)	0.05247 (6)	2.12 (5)
Cl1	0.14133 (15)	0.98215 (9)	0.13678 (7)	3.84 (7)
Cl2	0.27045 (17)	0.85424 (11)	0.30030 (6)	4.82 (7)
C1	0.3028 (5)	0.5797 (3)	0.11570 (21)	2.30 (19)
C2	0.3602 (5)	0.4795 (4)	0.11420 (23)	3.06 (23)
C3	0.3606 (6)	0.4320 (4)	0.04730 (25)	3.45 (24)
C4	0.3008 (5)	0.4831 (4)	−0.01893 (23)	3.23 (23)
C5	0.2433 (5)	0.5815 (3)	−0.01952 (22)	2.64 (21)
C6	0.2437 (5)	0.6317 (3)	0.04786 (21)	2.14 (18)
C11	0.4986 (5)	0.6263 (4)	0.25783 (23)	2.99 (21)
C12	0.5217 (6)	0.6532 (5)	0.34049 (24)	4.6 (3)
C13	0.6110 (6)	0.6804 (5)	0.2241 (3)	5.0 (3)
C14	0.1836 (5)	0.5831 (4)	0.24939 (23)	2.99 (22)
C15	0.2175 (6)	0.4677 (4)	0.2663 (3)	4.7 (3)
C16	0.0240 (6)	0.5973 (5)	0.2075 (3)	5.5 (3)
C21	0.3142 (5)	0.8307 (3)	−0.00076 (21)	2.59 (21)
C22	0.2750 (6)	0.9447 (4)	−0.0218 (3)	4.1 (3)
C23	0.4771 (5)	0.8201 (4)	0.04139 (25)	3.8 (3)
C24	0.0052 (5)	0.7955 (4)	−0.00161 (24)	2.86 (21)
C25	−0.1056 (5)	0.7680 (4)	0.0415 (3)	4.5 (3)
C26	−0.0343 (6)	0.7470 (4)	−0.0802 (3)	4.7 (3)

in Tables IV–VI, respectively.

The steric features of the isopropyl groups in DH are also worthy of some comments. Figure 5 illustrates a stereoscopic view of complex **2a**, in which the isopropyl groups are symmetrically disposed out of the complex plane. The whole molecule, therefore, essentially is in a C_{2v} symmetry. This is consistent with observations by NMR spectroscopy. The bulkiness of the isopropyl arms and the rigid benzene backbone in DH are likely to block the entering channels of external substrates from all directions, except from the trans side of DH. Therefore, the DH complexes are supposed to favor the dissociative type of substitutions,[11] in particular in the presence of large ligands. Indeed, treatment of **2a** with DPPE in solution did not give any replaced product.[6] Of course, the chelating stability of DH might also be a contribution to the inertness of **2a**.

Experimental Section

NMR Spectra. Nuclear magnetic resonance spectra were recorded on either a Bruker AC-E 200 or a Bruker AM-300WB spectrometer. For the phosphorus-31 NMR spectra, spectrometer frequencies of 81.01 and 121.49 Hz were employed respectively, and the chemical shifts were given in parts per million (δ) relative to 85% H_3PO_4 in $CDCl_3$. The upfield of the standard was defined as negative. The computer simulation was

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Table VI. Non-Hydrogen Atomic Coordinates for **2c** with Esd's in Parentheses

	x	y	z	B_{iso}, Å^2
Pt	0.23633 (4)	0.81275 (3)	0.171561 (20)	1.955 (15)
P1	0.3093 (3)	0.64987 (20)	0.20193 (13)	2.22 (12)
P2	0.1980 (3)	0.76938 (19)	0.05211 (13)	1.93 (11)
Cl1	0.1430 (3)	0.98185 (20)	0.13735 (14)	3.74 (14)
Cl2	0.2677 (4)	0.85678 (23)	0.29793 (14)	4.52 (16)
C1	0.3006 (10)	0.5791 (7)	0.1137 (4)	1.9 (4)
C2	0.3570 (12)	0.4794 (8)	0.1127 (5)	2.9 (5)
C3	0.3593 (12)	0.4323 (8)	0.0485 (5)	3.3 (6)
C4	0.2986 (12)	0.4828 (8)	−0.0194 (5)	3.3 (5)
C5	0.2432 (11)	0.5819 (7)	−0.0200 (5)	2.7 (5)
C6	0.2462 (10)	0.6328 (7)	0.0479 (4)	1.9 (4)
C11	0.5006 (11)	0.6271 (7)	0.2583 (5)	2.7 (4)
C12	0.5253 (13)	0.6568 (9)	0.3406 (5)	4.1 (6)
C13	0.6126 (12)	0.6795 (10)	0.2239 (6)	4.7 (6)
C14	0.1866 (11)	0.5835 (8)	0.2495 (5)	2.8 (5)
C15	0.2235 (14)	0.4687 (9)	0.2670 (6)	4.7 (7)
C16	0.0279 (13)	0.5950 (10)	0.2082 (7)	5.5 (7)
C21	0.3156 (11)	0.8302 (7)	−0.0006 (5)	2.5 (5)
C22	0.2753 (13)	0.9441 (8)	−0.0215 (6)	4.3 (6)
C23	0.4767 (12)	0.8188 (9)	0.0415 (5)	4.1 (6)
C24	0.0070 (12)	0.7950 (8)	−0.0032 (5)	3.2 (5)
C25	−0.1047 (12)	0.7665 (9)	0.0390 (6)	4.7 (6)
C26	−0.0320 (13)	0.7488 (9)	−0.0824 (6)	4.5 (6)

done with a Bruker built-in PANIC program. The J values are according to the data in Table I, and LW = 1.6 Hz. All NMR data are summarized in Table I.

All of the reactions, manipulations, and purification steps involving phosphines were performed under a dry nitrogen or argon atmosphere. Other chemicals and solvents from commercial sources were used without further purification, except as noted.

Syntheses. ***o*-Phenylenebis(diisopropylphosphine) (1)**[2c] **and dichloro[*o*-phenylenebis(diisopropylphosphine)]nickel(II) (2a)** were prepared according to the literature methods.[3d]

Dichloro[*o*-phenylenebis(diisopropylphosphine)]palladium(II) (2b). A mixture of DH (0.0723 mmol) and $(PhCN)_2PdCl_2$ (0.0723 mmol) in degassed dichloromethane (4 mL) was stirred at room temperature for 5 h, during which the solution became brown. Methanol (3 mL) was added to the reaction mixture, and the resulting solution was allowed to sit overnight. A colorless crystalline solid was collected (27.6 mg, 78%; mp 275 °C dec). Anal. Calcd for $C_{18}H_{32}P_2Cl_2Pd$: C, 44.33; H, 6.61. Found: C, 44.35; H, 7.00.

Dichloro[*o*-phenylenebis(diisopropylphosphine)]platinum(II) (2c). A flask was charged with DH (0.59 mmol) and K_2PtCl_4 (0.59 mmol), followed by a mixture of degassed water (5 mL) and ethanol (5 mL). The resulting suspension was stirred for 3 h, after which white precipitates were collected by filtration. The filtrate was extracted with CH_2Cl_2 to recover the remaining product, and the combined product was recrystallized from CH_2Cl_2/methanol. A colorless crystalline solid was obtained (195.2 mg, 57%; mp 280–285 °C dec). Anal. Calcd for $C_{18}H_{32}P_2Cl_2Pt$: C, 37.51; H, 5.60. Found: C, 38.03; H, 5.70.

Crystallography. Crystals of **2a–c** were obtained by recrystallization from cosolvents (vide supra). Cell parameters were determined on a CAD-4 diffractometer at 300 K and by a least-squares treatment. Atomic scattering factors are from ref 12. The computing program was the NRCC SDP VAX package.[13] The crystal data are listed in Table II, and the non-hydrogen atomic coordinates are listed in Tables IV–VI. The ORTEP diagram of complex **2a** is shown in Figure 4. Other crystallographic data are supplied as supplementary material.

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Supplementary Material Available: Figures S2 and S3, showing ORTEP drawings of complexes **2b,c** respectively, and Tables S1–S13, listing atomic coordinates and thermal parameters, complete bond distances and bond angles, anisotropic thermal parameters, and detailed crystal data (15 pages); listings of structure factors for **2a–c** (36 pages). Ordering information is given on any current masthead page.

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Exchange Interactions in a Novel Copper(II) Linear-Chain Compound with Ladderlike Structure: $Cu_2(1,4\text{-diazacycloheptane})_2Cl_4$[1]

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The synthesis, crystal structure, and magnetic properties are reported for the novel compound $Cu_2(1,4\text{-diazacycloheptane})_2Cl_4$. The blue compound, $Cu_2C_{10}H_{24}N_4Cl_4$, crystallizes in the monoclinic space group $P2_1/c$. Cell dimensions are as follows: a = 13.406 (3), b = 11.454 (2), c = 12.605 (3) Å; β = 115.01 (2)°; Z = 4. The structure was solved at room temperature by Patterson and direct methods and refined to an R value of 0.037 (R_w = 0.040), for 2089 observed reflections and 183 parameters. The binuclear unit of the complex is roughly centrosymmetric, and the coordination environments around the two copper atoms are very similar. Each metal center shows distorted (4 + 1) square-pyramidal geometry. The four short bonds involve the two nitrogens of 1,4-diazacycloheptane, a terminal chlorine atom, and a bridging chlorine atom. The long, apical bond involves a basal chlorine atom of the other copper atom. The binuclear units are packed along the [101] direction. Each dimer is related to its two nearest neighbors along this axis by cristallographic inversion symmetry and is connected to each of them by two Cu–Cl···H–N–Cu hydrogen bonding interactions. As a result of this 1-D network of hydrogen bonds, the binuclear units are connected into infinite ladderlike chains. The X-ray analysis of the compound does not reveal any close contacts between chains that may be regarded as bonding interactions. The magnetic susceptibility vs temperature curve for the compound exhibits a maximum at about 8 K, strongly indicative of antiferromagnetic exchange. Comparisons between theory and experiment with use of approximate Heisenberg models have been made. The results indicate that, in order to account for the magnetic properties of the compound, both interactions between nearest neighbors and interactions between next nearest neighbors must be considered explicitly in the spin Hamiltonian, since they are of the same order of magnitude.

Introduction

Exchange-coupled magnetic systems that display large amounts of order in but one dimension, owing to their unique physical properties, have occupied considerable experimental and theoretical work.[2]

In the realm of copper(II) crystal chemistry, there has recently

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