following unpaired spin densities at carbon atoms: α-pyrrole, 0.016; β-pyrrole, 0.017; meso, 0.019. Application of the Karplus–Fraenkel relationships to combined carbon-13 and proton NMR data could in principle be used to evaluate the theoretical predictions. Unfortunately, such calculations for the $S = 2$ system appear unreliable perhaps as a consequence of both σ- and π-spin delocalization mechanisms. Estimations of spin density at carbon atoms are possible, however, if it is assumed that the proton hyperfine coupling constant, A^H, is proportional to the unpaired spin density, ρ_C^π, centered on the π-orbital of the carbon atom to which it is attached.[33]

$$A^H = \frac{Q_{CH}{}^H \rho_C{}^\pi}{2S} \qquad (4)$$

The empirical value of $Q_{CH}{}^H$ is taken as −63 MHz. The value for A^H is obtained from the contact shift by (downfield shift given a positive sign)

$$\frac{\Delta H_{con}}{H} = A^H \frac{|\gamma_e|}{|\gamma_H|} \frac{S(S + 1)}{3kT} \qquad (5)$$

For contact shifts of −30.6 ppm (pyrrole H) and +41.4 ppm (meso H) previously reported by La Mar and Walker,[21] carbon spin density values of 0.0094 (β-pyrrole carbon) and −0.013 (meso carbon) are found. An extreme mismatch is apparent for the calculated meso carbon value and the theoretical prediction in that the signs are reversed. Further theoretical calculations that permit direct inclusion of electron correlation effects are clearly needed.

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Registry No. (TPP)MnCl, 32195-55-4; (TPP(m-CH$_3$))MnCl, 56811-40-6; (TPP(p-OCH$_3$))MnCl, 62769-24-8; (TPP(p-OCH$_3$))MnI, 88271-89-0; (TPP(p-OCH$_3$))MnF, 88271-90-3; (TPP(p-OCH$_3$))-Mn(4-MePy)$^+$, 88271-91-4; (OEP)MnCl, 28265-17-0; (ETIO)MnCl, 58675-99-3.

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A Nickel Complex Containing an Extremely Long Nickel–Phosphorus Bond. Syntheses and X-ray Structures of $[Ni(CN)_2[P(CH_2OH)Ph_2]_3](C_6H_6)_{0.5}$ and *trans*-$[Ni(CN)_2[P(CH_2OH)Ph_2]_2]$

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The syntheses and crystal and molecular structures of two derivatives of Ni(II) with (hydroxymethyl)diphenylphosphine, a potentially bidentate ligand, are reported. These compounds are dicyanotris((hydroxymethyl)diphenylphosphine)nickel(II)–0.5-benzene ($[Ni(CN)_2[P(CH_2OH)Ph_2]_3](C_6H_6)_{0.5}$, **1**) and *trans*-dicyanobis((hydroxymethyl)diphenylphosphine)nickel(II) (*trans*-$[Ni(CN)_2[P(CH_2OH)Ph_2]_2]$, **2**). Complex **1**, which was synthesized in good yield by the reaction of $Na_2[Ni(CN)_4]\cdot 3H_2O$ with $PHPh_2$ and aqueous formaldehyde in benzene solution at 60 °C, crystallizes as red needles, space group $P\bar{1}$ (No. 2), unit cell dimensions $a = 12.323$ (9) Å, $b = 12.844$ (10) Å, $c = 15.507$ (10) Å, $\alpha = 111.38$ (5)°, $\beta = 90.39$ (6)°, $\gamma = 119.85$ (6)°, $Z = 2$. The structure has been refined to an R index of 0.057 on the basis of 2855 unique reflections. The potentially bidentate ligand coordinates through phosphorus only. The inner coordination about nickel is closer to square-pyramidal than to trigonal-bipyramidal geometry. The metal is coordinated to three phosphorus and two cyano carbon atoms. One of the Ni–P bonds is extremely long, with a Ni–P distance of 2.400 (3) Å. Complex **1** readily dissociates a phosphine under mild conditions to afford **2** in quantitative yield. The structure of **2** has the simple trans-square-planar geometry at nickel. The orange-yellow crystals belong to the orthohombic space group *Pbca* (No. 61) with unit cell dimensions $a = 10.258$ (2) Å, $b = 16.173$ (5) Å, $c = 15.055$ (3) Å, and $Z = 4$. The structure has been refined to $R = 0.038$ on the basis of 1765 unique reflections. The Ni–P bond lengths are normal, and there is no interaction between the OH groups and the metal atom. The free ligand $P(CH_2OH)Ph_2$ may be isolated in ca. 70% yield from either complex by treatment with excess CN^- in aqueous solution.

Introduction

We are currently interested in ligands of the type $P(CH_2X)Ph_2$ where X = OH, SH, NHR, or PHR, and R = alkyl or aryl group. These ligands can behave as uninegative or neutral mono- or bidentate donors. Our initial work has concentrated on the ligand $P(CH_2OH)Ph_2$. A previous report has dealt with some rhodium, palladium, and platinum complexes,[1] but no structure of any complex involving this ligand has appeared.

In this paper we report the first X-ray crystal structures of such complexes. In addition, we describe a novel high-yield synthetic route involving the reaction of a metal salt with a secondary phosphine in the presence of aqueous formaldehyde.

Experimental Section

Materials. Sodium tetracyanonickelate trihydrate was synthesized according to literature procedures.[2] Diphenylphosphine (Strem), formaldehyde (37% in water), benzene, and sodium cyanide (Mallinckrodt) were used as purchased.

Preparation and Characterization of Complexes. All syntheses were performed under an atmosphere of nitrogen with modified Schlenk techniques. Both products **1** and **2** are air-stable crystalline materials, but **1** dissociates to **2** and free ligand at room temperature in solvents such as C_6H_6 or $CHCl_3$. ^1H NMR spectra were recorded on a Varian EM-390 spectrometer and ^{31}P NMR spectra on a Nicolet NT-200

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Table I. Crystal Data and Experimental Details of the X-ray Diffraction Studies

	[Ni(CN)$_2$-[P(CH$_2$OH)Ph$_2$]$_3$·0.5C$_6$H$_6$]	*trans*-[Ni(CN)$_2$-[P(CH$_2$OH)Ph$_2$]$_2$]
M_r	798.39	543.19
cryst dimens, mm	0.3 × 0.3 × 0.6	0.1 × 0.1 × 0.2
color	red	yellow
unit cell at 140 K		
a, Å	12.323 (9)	10.258 (2)
b, Å	12.844 (10)	16.173 (5)
c, Å	15.507 (10)	15.055 (3)
α, deg	111.38 (5)	-
β, deg	90.39 (6)	-
γ, deg	119.85 (6)	-
d_{calcd}(140 K), g cm^{-3}	1.38	1.44
d_{measd}(298 K), g cm^{-3}	1.35	1.41
space group	$P\bar{1}$	*Pbca*
Z	2	4
radiatn, λ, Å (graphite monochromator)	Mo Kα, 0.71069	Mo Kα, 0.71069
$\mu_{\text{Mo K}\alpha}$, cm^{-1}	6.65	9.33
cryst temp, K	140	140
scan type	ω	ω
scan range, deg	1.5	2.2
scan speed, deg min^{-1}	59	15
bkgd offset, deg	1.5	1.5
bkgd/scan time	1	1
$2\theta_{\text{max}}$, deg	45	50
no. of unique reflcns	5029	2553
no. of reflcns with $F > 6\sigma(F)$	2855	1765
no. of parameters	222	160
R	0.057	0.038
R_w	0.052	0.035

spectrometer operating at 80.988 MHz. ^{1}H and ^{31}P NMR chemical shifts are relative to Me$_4$Si and external 85% H$_3$PO$_4$, respectively.

[Ni(CN)$_2$[P(CH$_2$OH)Ph$_2$]$_3$](C$_6$H$_6$)$_{0.5}$. Diphenylphosphine (3.75 mL, 19 mmol) in benzene (50 mL) was added dropwise to a stirred solution of formaldehyde (37%, 4.8 mL, 60 mmol) and Na$_2$[Ni(CN)$_4$]·3H$_2$O (1.30 g, 5 mmol) in water (10 mL) at 50 °C. After the addition was completed, stirring was continued for 1 h. The benzene layer was then separated and allowed to cool, whereupon red crystals formed; these were removed by filtration, washed 3 times with 20-mL portions of ether, and dried in vacuo. The yield of 1 was 3.4–3.6 g, 85–90%; mp 118–122 °C (red to yellow), 131–135 °C dec.

***trans*-[Ni(CN)$_2$[P(CH$_2$OH)Ph$_2$]$_2$].** A solution of 1 (1 g) in benzene (50 mL) was refluxed for 1 h during which the color changed from red to yellow with concomitant precipitation of the product as a yellow solid. Recrystallization from the minimum volume of refluxing methanol afforded the pure product in high yield as yellow crystals, mp 157–161 °C dec.

P(CH$_2$OH)Ph$_2$. A solution of [Ni(CN)$_2$[P(CH$_2$OH)Ph$_2$]$_3$] (3.05 g, 0.146 mol) in benzene (100 mL) and a saturated aqueous solution (100 mL) of NaCN were heated at 50 °C for 4 h. The benzene layer was separated and dried over Na$_2$SO$_4$. Removal of the benzene in vacuo afforded P(CH$_2$OH)Ph$_2$ (1.91 g, 73%) as a colorless oil, ^{31}P NMR -10.1 ppm, in CDCl$_3$.

Data Collection and Structure Determination. Suitable dark red crystals of 1 were grown by using a larger volume (100 mL) of benzene than described in the Experimental Section and allowing the reaction mixture to cool slowly.

Diffraction data were collected on a Syntex P2$_1$ diffractometer equipped with a modified LT-1 low-temperature apparatus, following a philosophy described by Hope and Nichols.[3a] Crystal data are given in Table I.

The structure of 1 was solved with Patterson–heavy-atom techniques, using programs in the Nicolet SHELXTL system. Although the stoichiometry was initially unknown, the X-ray data together with the synthetic history provided the information required for a straightforward assignment of structure and stoichiometry. An empirical absorption correction[3b] was applied to the intensity data. All H atoms were found in a difference electron density map. Their parameters were refined with the fixed geometry schemes of SHELXTL; all C–H distances were set to 1.0 Å at idealized geometry; the three O–H distances were held near 0.85 Å (imposed esd 0.03 Å), but with otherwise free geometry. All atoms were assigned isotropic thermal parameters. A trial refinement with anisotropic heavy atoms resulted in no changes in geometry and only a slight improvement in R and was therefore discontinued. H atoms were assigned U's of 1.2U_{iso}(anchor) for C–H and 1.3U_{iso}(anchor) for O–H. Isotropic refinement converged with R = 0.057. Final parameters are listed in Tables I and IIa. Selected distances and angles are given in Tables IIIa and IVa. The molecule is illustrated in Figure 1.

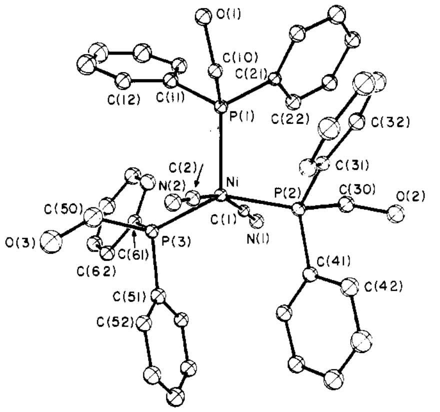

Figure 1. Computer-generated diagram of **1**, [Ni(CN)$_2$[P(CH$_2$OH)Ph$_2$]$_3$].

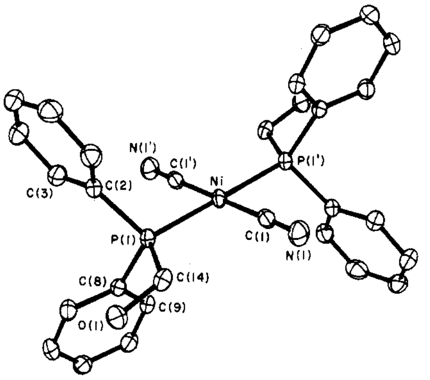

Figure 2. Computer-generated diagram of **2**, *trans*-[Ni(CN)$_2$[P(CH$_2$OH)Ph$_2$]$_2$].

The structure of 2 was solved by placing the Ni atom at the origin. The remaining non-hydrogen atoms were located on a difference Fourier map. In the final block-cascade least-squares refinement, non-hydrogen atoms were assigned anisotropic thermal parameters while each H atom was assigned an isotropic thermal parameter equal to 1.2U_{iso} of its C atom. The hydroxyl H atom was included in the structure factor calculation at the position found on the last difference map with U_{iso} = 0.03 Å^2. The remaining hydrogen atoms were included at calculated positions assuming a fixed C–H distance of 0.96 Å and idealized geometry. A final difference map was essentially flat, with a maximum peak of 0.13 e Å^{-3}. Additional details are presented in Table I. Atom coordinates are presented in Table IIb. Selected bond distances and angles are given in Tables IIIb and IVb. The molecule is illustrated in Figure 2.

The remainder of the bond distances and angles, anisotropic thermal parameters, H parameters, and F_o/F_c tables are available as Supplementary Material.

Description of the Structures

The major structural feature common to both complexes is that the phosphine ligand behaves as a monodentate donor. There is no interaction between the metal and the –OH group in either compound. The geometry at nickel in 1 can be regarded as closer to square pyramidal (spy) than to trigonal bipyramidal (tbp) due to the wide P(2)–Ni–P(3) (144.1 (1)°)

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Table II. Atom Coordinates (×10^4) and Thermal Parameters (Å^2 ×10^3)

atom	x	y	z	U^a
(a) $[Ni(CN)_2[P(CH_2OH)Ph_2]_3](C_6H_6)_{0.5}$				
Ni	2624 (1)	3349 (1)	2238 (1)	13 (1)
C(1)	3241 (7)	4747 (7)	3439 (5)	12 (2)
N(1)	3641 (6)	5649 (6)	4174 (4)	19 (2)
C(2)	2334 (7)	2325 (7)	941 (5)	17 (2)
N(2)	2175 (6)	1735 (6)	129 (4)	20 (2)
P(1)	951 (2)	1595 (2)	2554 (1)	15 (1)
C(10)	445 (7)	−52 (7)	1590 (5)	15 (2)
O(1)	−717 (5)	−1134 (5)	1597 (3)	20 (1)
C(11)	−586 (7)	1495 (7)	2611 (5)	19 (2)
C(12)	−1364 (8)	1161 (7)	1785 (5)	22 (2)
C(13)	−2501 (9)	1170 (8)	1833 (6)	34 (2)
C(14)	−2791 (9)	1597 (8)	2702 (6)	37 (2)
C(15)	−2020 (8)	1948 (8)	3518 (6)	34 (2)
C(16)	−923 (8)	1893 (7)	3491 (5)	22 (2)
C(21)	1329 (7)	1486 (7)	3653 (5)	14 (2)
C(22)	1991 (7)	2654 (7)	4513 (5)	21 (2)
C(23)	2263 (8)	2613 (8)	5360 (5)	22 (2)
C(24)	1922 (8)	1418 (7)	5385 (5)	23 (2)
C(25)	1266 (8)	259 (8)	4541 (5)	28 (2)
C(26)	968 (8)	288 (7)	3685 (5)	22 (2)
P(2)	4304 (2)	3169 (2)	2505 (1)	14 (1)
C(30)	5042 (8)	3879 (7)	3766 (5)	21 (2)
O(2)	6109 (5)	3735 (5)	3878 (4)	25 (1)
C(31)	3945 (7)	1483 (7)	2056 (5)	14 (2)
C(32)	3769 (7)	862 (7)	2675 (5)	20 (2)
C(33)	3478 (8)	−416 (7)	2344 (5)	23 (2)
C(34)	3383 (8)	−1120 (8)	1386 (6)	30 (2)
C(35)	3573 (8)	−516 (8)	776 (6)	29 (2)
C(36)	3834 (7)	758 (7)	1088 (5)	20 (2)
C(41)	5702 (7)	4080 (7)	2069 (5)	17 (2)
C(42)	6566 (8)	3685 (8)	1815 (5)	24 (2)
C(43)	7681 (9)	4480 (8)	1573 (6)	33 (2)
C(44)	7942 (8)	5689 (8)	1620 (5)	28 (2)
C(45)	7095 (7)	6091 (7)	1891 (5)	22 (2)
C(46)	5957 (8)	5272 (7)	2091 (5)	19 (2)
P(3)	1994 (2)	4465 (2)	1789 (1)	15 (1)
C(50)	760 (8)	3515 (8)	662 (6)	30 (2)
O(3)	389 (6)	4288 (6)	396 (4)	43 (2)
C(51)	3371 (8)	5748 (7)	1590 (5)	20 (2)
C(52)	3680 (8)	5496 (7)	706 (5)	20 (2)
C(53)	4792 (8)	6459 (7)	572 (6)	25 (2)
C(54)	5614 (8)	7674 (8)	1325 (5)	28 (2)
C(55)	5306 (8)	7925 (8)	2204 (5)	24 (2)
C(56)	4208 (7)	6972 (7)	2354 (5)	18 (2)
C(61)	1309 (7)	5319 (7)	2576 (5)	18 (2)
C(62)	1341 (7)	6372 (7)	2487 (5)	22 (2)
C(63)	748 (8)	6958 (8)	3055 (5)	25 (2)
C(64)	117 (8)	6510 (8)	3692 (6)	30 (2)
C(65)	92 (8)	5469 (8)	3774 (6)	29 (2)
C(66)	690 (7)	4865 (8)	3218 (5)	24 (2)
C(1B)	4646 (8)	909 (8)	5121 (5)	22 (2)
C(2B)	5918 (8)	1291 (8)	5195 (5)	25 (2)
C(3B)	6279 (9)	394 (8)	5090 (6)	32 (2)
(b) *trans*-$[Ni(CN)_2[P(CH_2OH)Ph_2]_2]$				
Ni	0	0	0	19 (1)
P(1)	1382 (2)	468 (1)	1008 (1)	20 (1)
O(1)	1388 (2)	1278 (1)	2623 (1)	29 (1)
N(1)	−2319 (3)	280 (1)	1186 (2)	31 (1)
C(1)	−1422 (3)	159 (2)	745 (2)	22 (1)
C(2)	2522 (3)	−329 (2)	1360 (2)	22 (1)
C(3)	3702 (3)	−437 (2)	909 (2)	28 (1)
C(4)	4516 (3)	−1091 (2)	1124 (2)	34 (1)
C(5)	4165 (3)	−1647 (2)	1784 (2)	34 (1)
C(6)	3006 (3)	−1538 (2)	2235 (2)	36 (1)
C(7)	2182 (3)	−885 (2)	2026 (2)	28 (1)
C(8)	2356 (2)	1342 (2)	639 (2)	21 (1)
C(9)	1982 (2)	1783 (2)	−116 (2)	24 (1)
C(10)	2619 (3)	2510 (2)	−340 (2)	28 (1)
C(11)	3656 (3)	2784 (2)	175 (2)	29 (1)
C(12)	4065 (3)	2332 (2)	902 (2)	30 (1)
C(13)	3411 (3)	1614 (2)	1144 (2)	25 (1)
C(14)	566 (2)	860 (2)	2023 (2)	25 (1)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Lengths (Å)

(a) $[Ni(CN)_2[P(CH_2OH)Ph_2]_3](C_6H_6)_{0.5}$			
Ni-C(1)	1.859 (6)	Ni-C(2)	1.869 (7)
Ni-P(1)	2.400 (3)	Ni-P(2)	2.246 (4)
Ni-P(3)	2.229 (4)	C(1)-N(1)	1.160 (8)
C(2)-N(2)	1.163 (9)	P(1)-C(10)	1.863 (8)
P(1)-C(11)	1.838 (11)	P(1)-C(21)	1.836 (9)
C(10)-O(1)	1.418 (9)	P(2)-C(31)	1.820 (9)
P(2)-C(30)	1.825 (8)	C(30)-O(2)	1.433 (14)
P(2)-C(41)	1.838 (8)	P(3)-C(50)	1.849 (8)
P(3)-C(51)	1.813 (8)	P(3)-C(61)	1.835 (10)
C(50)-O(3)	1.454 (16)		
(b) *trans*-$[Ni(CN)_2[P(CH_2OH)Ph_2]_2]$			
Ni-P(1)	2.210 (1)	Ni-C(1)	1.858 (3)
P(1)-C(2)	1.819 (3)	P(1)-C(8)	1.818 (3)
P(1)-C(14)	1.855 (3)	O(1)-C(14)	1.409 (3)
N(1)-C(1)	1.152 (4)		

Table IV. Selected Bond Angles (deg)

(a) $[Ni(CN)_2[P(CH_2OH)Ph_2]_3](C_6H_6)_{0.5}$			
C(1)-Ni-C(2)	163.8 (4)	C(1)-Ni-P(1)	100.0 (3)
C(2)-Ni-P(1)	96.1 (2)	C(1)-Ni-P(2)	89.7 (3)
C(2)-Ni-P(2)	88.6 (3)	P(1)-Ni-P(2)	101.6 (1)
C(1)-Ni-P(3)	85.4 (3)	C(2)-Ni-P(3)	86.7 (4)
P(1)-Ni-P(3)	114.3 (1)	P(2)-Ni-P(3)	144.1 (1)
Ni-C(1)-N(1)	177.7 (8)	Ni-C(2)-N(2)	177.2 (8)
Ni-P(1)-C(10)	110.7 (3)	Ni-P(1)-C(11)	118.2 (3)
C(10)-P(1)-C(11)	102.4 (4)	Ni-P(1)-C(21)	117.2 (2)
C(10)-P(1)-C(21)	104.3 (4)	C(11)-P(1)-C(21)	102.1 (4)
Ni-P(2)-C(30)	113.7 (4)	Ni-P(2)-C(31)	115.4 (3)
C(30)-P(2)-C(31)	103.4 (4)	Ni-P(2)-C(41)	115.5 (4)
C(30)-P(2)-C(41)	100.8 (3)	C(31)-P(2)-C(41)	106.3 (4)
Ni-P(3)-C(50)	116.7 (4)	Ni-P(3)-C(51)	108.4 (4)
C(50)-P(3)-C(51)	104.6 (4)	Ni-P(3)-C(61)	120.0 (3)
C(50)-P(3)-C(61)	100.6 (5)	C(51)-P(3)-C(61)	105.0 (4)
(b) *trans*-$[Ni(CN)_2[P(CH_2OH)Ph_2]_2]$			
P(1)-Ni-C(1)	92.4 (1)	P(1)-Ni-P(1A)	180.0
C(1)-Ni-P(1A)	87.6 (1)	P(1)-Ni-C(1A)	87.6 (1)
C(1)-Ni-C(1A)	180.0	P(1A)-Ni-C(1A)	92.4 (1)
Ni-P(1)-C(2)	111.7 (1)	Ni-P(1)-C(8)	114.1 (1)
C(2)-P(1)-C(8)	106.7 (1)	Ni-P(1)-C(14)	113.1 (1)
C(2)-P(1)-C(14)	107.0 (1)	C(8)-P(1)-C(14)	103.5 (1)
Ni-C(1)-N(1)	177.5 (2)		

and C(1)–Ni–C(2) (163.8 (4)°) angles (Figure 1). The nickel–phosphorus distances have the values 2.400 (3), 2.246 (4), and 2.229 (4) Å (Table IIIa). Thus the apical Ni–P(1) distance, 2.400 (3) Å, is unique, and this supports the distorted spy view of the structure. All three Ni–P bond lengths are significantly longer than those found in other similar complexes (see Discussion). Within the phosphine ligand, the angles at phosphorus are unremarkable and the P–C bond distances are within the reported range. For the cyanide ligands the Ni–C distances of 1.859 (6) and 1.869 (7) Å are very close to those reported in ref 3–6. The same comment applies to the N–C distances, average value 1.161 (8) Å. A curious structural feature in **1** is that the Ni—C≡N links deviate slightly from linearity, away from the apex of the square pyramid. The relevant angles are 177.7 (8) and 177.2 (8)°. This type of bending could be due to interelectronic repulsion as a result of the presence of the axial phosphine ligand. This bending has been noted in $[Ni(CN)_5]^{3-}$ [6a] and has been discussed in more detail elsewhere.[6b]

The structure of **2**, the square-planar complex *trans*-$[Ni(CN)_2[P(CH_2OH)Ph_2]_2]$, is useful for the purpose of comparing with **1** and assisting in the evaluation of the importance

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Table V. Comparison of Bond Lengths and Angles in Some 5-Coordinate Cyano(phosphine)nickel Complexes

	Ni-P bond dist, Å		apical – basal diff, Å	bond angles P_bNiP_b and C_bNiC_b, deg	ref
	apical	basal			
$[Ni(CN)_2[P(CH_2OH)Ph_2]_3]$	2.400 (3)	2.231 (4)	0.162	164.0 (3)[c]	this work
		2.244 (3)		144.1 (1)[d]	
$[Ni(CN)_2(PC_{13}H_{11})_3]$[a]	2.32	2.178	0.142	161.3[c]	18
		2.177		140.2[d]	
$[Ni(CN)_2[P(OEt)_2Ph]_3]$	2.289 (5)	2.189 (5)	0.092	170.8 (6)[c]	4
		2.205 (6)		133.5 (2)[d]	
$[Ni(CN)_2(PMe_2Ph)_3]$	2.261 (3)	2.223 (3)	0.04	176.5 (4)[c]	5
		2.223 (3)		127.0 (1)[d]	
$[Ni(CN)_5]^{3-}$	2.168 (14)	1.862 (6)[b]	0.306	159.5 (2)[c]	6, 13
	2.140 (11)	1.877 (9)	0.263	161.5 (3)[c]	
	2.101 (9)	1.877 (7)	0.224	159.7 (3)[c]	

[a] $PC_{13}H_{11}$ = 9-methyl-9-phosphafluorene. [b] These distances are Ni-C bonds; the elongation here is very large, but $[Ni(CN)_5]^{3-}$ is unstable in solution except in the presence of a large excess of CN^- and can only be crystallized if large cations such as $[Co(en)_3]^{2+}$ are used.[6,20] The complexes can be prepared in the presence of a small excess of phosphine ligand. [c] P_bNiP_b. [d] C_bNiC_b.

of steric and electronic factors in the determination of the geometry in **1**. The molecule is centrosymmetric, as crystallographically required, with Ni located at (0,0,0). A feature of the structure is the coplanarity of the atom sequence Ni, P(1), C(14), O(1), C(1), and N(1) (Figure 2), with deviations from the least-squares plane of 0.065 (1), –0.069 (3), –0.052 (4), 0.070 (3), –0.008 (4), and –0.006 (4) Å, respectively. There are no short nonbonding interactions between nickel and any other atoms in the molecule. As in **1**, the nitrogens are intermolecularly hydrogen bonded to the OH group of an adjacent molecule. The calculated N(1)···H distance is 1.86 Å and the N(1)···H–O(1) angle is 177°. The Ni–P distance of 2.210 (1) Å is on the high end of the range reported for square-planar nickel complexes. The Ni–C and C–N distances are normal and almost identical with those found in **1**.

Discussion

The features of this work involve (a) the high yield synthesis of both nickel complexes, which includes the alteration of the phosphine ligand during the synthesis, (b) the degree of structural distortion of the pentacoordinated nickel complex, and (c) the first structural report of a simple phosphine ligand with an OH group in the α position.

Phosphines of the formula $P(CH_2OH)_nR_{3-n}$, where $n = 1$, 2 or 3, are well-known.[8-11] Due to difficulties in crystallization, no structures have been reported and generally such ligands are thermally unstable and rearrange during distillation. For example, attempted distillation of $P(CH_2OH)Ph_2$ affords $PHPh_2$ as the major phosphorus-containing product. Rearrangements forming other products have been noted elsewhere.[8-11] Our results show that metal complexes of such ligands can be made in >90% yield in a single-step synthesis. We are at present working on an extension of this reaction to other metals and primary phosphines.

A considerable number of 5-coordinate nickel complexes have been described.[4-6,12-15] They can adapt tbp, spy, or some intermediate geometry. Many of the tbp complexes have tripod ligands. There are relatively few spy complexes, and most of these are high spin and involve hard donor atoms; the complex $[Ni[MeC(CH_2PPh_2)_3]SO_4]$[16] is a notable exception. The factors that govern the choice of 5-coordination, spy or tbp geometry, in the absence of an imposed symmetry by polydentate ligands are not yet fully understood.[12-17] Clearly the steric and electronic properties of the ligands play a major role in influencing the geometry at nickel. For example, CN^- is particularly likely to induce 5-coordination and is the only anion whch appears to be able to stabilize 5-coordination by itself. The tendency to form pentacoordinate nickel(II) complexes has been correlated with the electronegativity or polarizability of the anions,[15-17] and it is believed that, generally speaking, electronic effects play a greater role than steric effects in determining the stability and overall geometry of the complex.[4-6,14-17] In phosphine complexes it appears that the greater σ-donor character of the phosphine ligands favors the tbp geometry. Steric effects tend to decrease the overall stability of the tbp complex and favor dissociation to a square-planar complex and free ligand. From this point of view steric effects would probably favor spy geometry since this is closer to square planar than tbp. In the limit, large phosphines such as PPh_3 and $P(C_6H_{11})_3$ preclude pentacoordination.[12]

We believe that, for a pentacoordinate Ni(II) complex, **1** represents the closest reported approach to dissociation while maintaining overall structural integrity. We hold this view for several reasons: (i) the Ni–P(1) distance in **1** is the longest reported Ni–P bond length for a nickel(II) phosphine complex, (ii) the difference between the apical and basal Ni–P distances (ca. 0.16 Å) is the largest which has been reported, (iii) the structure of the complex is closer to spy than the similar bis(cyano)tris(phosphine) complexes (arguably spy, which is structurally nearer to square-planar geometry, is more likely to be a precursor for dissociation than is a tbp complex), (iv) $P(CH_2OH)Ph_2$ is one of the largest phosphine substituents in known 5-coordinate nickel complexes of formula $Ni(CN)_2P_3$ (P = phosphine). Table V lists some other known 5-coordinate nickel cyano/phosphine complexes for comparison purposes.

With regard to the relative importance of electronic and steric effects in the geometry of **1**, we believe that both factors play a significant role. Consideration of both **1** and **2** shows that, in both complexes, all the Ni–P distances are long. Since it is unlikely that steric forces come into play in **2** we feel that the slight elongation of the Ni–P bonds may be a result of the poorer donor properties of the ligand. In **1**, since the Ni center is more electron rich due to the higher number of donors, the increase in length of all Ni–P bonds is to be expected. However, the magnitude of the apical Ni–P bond elongation is

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significantly greater than that of other similar complexes (Table V). We feel that the extra lengthening is due, primarily, to increased ligand size, which results in a weaker Ni–P apical bond.

Further support for the weak nature of apical ligand bonding comes from ^{31}P NMR studies. Preliminary qualitative ^{31}P NMR data on our complexes show that for **1** in C_6D_6 the spectrum at room temperature shows two peaks at 29.9 and 1.8 ppm. These have been assigned to **1** and **2**, respectively. The ratio of the two peaks indicates that about 7% of **2** is present at 21 °C. Heating the sample at 70 °C for 15 min affords a sample in which **1** and **2** are present in about equal amounts. Further heating for 1 h affords **2** almost exclusively.

The dissociation of pentacoordinated nickel(II)–phosphine complexes is well-known. However, pentacoordinated nickel complexes of the formula $[Ni(CN)_2P_3]$ are, in general, quite stable to dissociation.[17] This stability has been attributed to the presence of the cyano group in the complex. For example, it was not possible to isolate square-planar complexes of the type $[Ni(CN)_2P_2]$ where P = PMe_2Ph, $PMePh_2$ or $P(C_6F_5)Me_2$; only the 5-coordinate species $[Ni(CN)_2P_3]$ could be obtained.[17] Also, the ^{31}P NMR spectrum of $[Ni(CN)_2P_3]$ showed the presence of only a small quantity of $[Ni(CN)_2(PMe_3)_2]$ in solution.[19] The dissociation of **1** is then quite remarkable and is similar in magnitude to the dissociaton of $[Ni(CN)_2(PEtPh_2)_3]$ (ca. 20%).[17] The ligand $PEtPh_2$ is very similar in size to $P(CH_2OH)Ph_2$, and the amount of dissociation indicates that the apical Ni–P distance in $[Ni(CN)_2(PEtPh_2)_3]$ should be of similar length to that found in **1**. In conclusion, both our ^{31}P NMR and X-ray data indicate that steric effects play a significant role in determining the stability of 5-coordinated nickel(II) complexes to dissociation. Our results are in agreement with those of Meek[17] on $[Ni(CN)_2(PEtPh_2)_3]$ and related complexes, which show that electronic arguments alone are unable to account for the spectroscopic and structural findings.

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Registry No. **1**, 88158-03-6; **2**, 88179-93-5; $Na_2[Ni(CN)_4]$, 14038-85-8; $P(CH_2OH)Ph_2$, 5958-44-1; diphenylphosphine, 829-85-6; formaldehyde, 50-00-0.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes in addition to complete tables of bond distances, angles, and thermal parameters (24 pages). Ordering information is given on any current masthead page.

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Preparation, Spectra, and Crystal Structures of Two Rhodium(III) Complexes with Short Intramolecular Hydrogen Bonds

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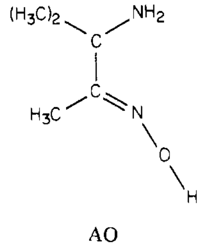
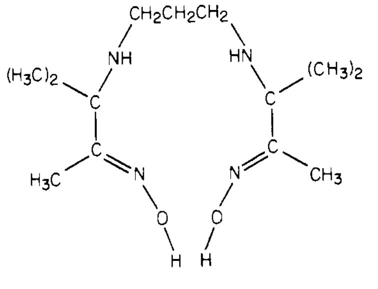
In the reactions of the tetradentate ligand 3,3′-(1,3-propanediyldiimino)bis(3-methyl-2-butanone oxime) (PnAO) and the bidentate ligand 3-amino-3-methyl-2-butanone oxime (AO) with $RhCl_3$ in aqueous ethanol, the neutral *trans*-dichloro complexes $[Rh(PnAO\text{-}H)Cl_2]$ and $[Rh((AO)_2\text{-}H)Cl_2]$, respectively, are formed with the elimination of one hydrogen ion from an oxime group. The resulting complexes have a strong hydrogen bond between cis oxime groups (O---O = 2.474 (7) and 2.459 (2) Å, respectively). This hydrogen bond can be seen as a broad band in the IR spectra at 1792 and 1785 cm^{-1} and in proton chemical shifts of 18.9 and 19.3 ppm downfield from Me_4Si, respectively. The average Rh–ligand distances are Rh–Cl = 2.336 (10) Å, Rh–N(oxime) = 1.988 (2) Å, and Rh–N(amine) = 2.064 (8) Å. $[Rh(PnAO\text{-}H)Cl_2]$ crystallizes in the orthorhombic space group $P2_12_12_1$: a = 8.400 (2) Å, b = 13.149 Å (5) Å, c = 16.065 (3) Å, Z = 4, d_{calcd} = 1.668 (1) g/cm^3. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to a final R value of 0.043 for the 2579 reflections with $I > 2\sigma(I)$. $[Rh((AO)_2\text{-}H)Cl_2]$ crystallizes in the orthohombic space group $Pnam$: a = 11.108 (1) Å, b = 11.993 (1) Å, c = 11.661 (2) Å, Z = 4, d_{obsd} = 1.732 (1) g/cm^3. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to a final R value of 0.020 for the 2609 reflections with $I > 2\sigma(I)$. This complex has a mirror plane containing the rhodium, two chlorines, and the hydrogen-bonded hydrogen atom.

Introduction

Cobalt(III) complexes of the ligands AO and PnAO have been previously reported,[1] and the crystal structures of $[Co((AO)_2\text{-}H)Cl_2]^2$ and of $[Co(PnAO\text{-}H)(NO_2)_2]^3$ have revealed the presence of very strong intramolecular hydrogen bonds (O---O = 2.422 (3) and 2.432 (3) Å, respectively). The purpose of this study was to examine the effect of the larger Rh(III) atom on the hydrogen bond with and without the steric constraint of the propylene bridge between the amine nitrogen atoms. At least in the case of the PnAO complex, some lengthening of the O---O distance might be expected on steric grounds.



AO



PnAO

Experimental Section

Synthesis. Ligands. The ligands 3,3′-(1,3-propanediyldiimino)-

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