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Synthesis and Characterization of Water-Soluble 1,2-Bis(bis(hydroxyalkyl)phosphino)ethane Ligands and Their Nickel(II), Ruthenium(III), and Rhodium(I) Complexes

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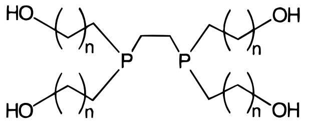
The syntheses of the water-soluble, chelating phosphines 1,2-bis(bis(hydroxybutyl)phosphino)ethane (**1**, $n = 3$; DHBuPE) and 1,2-bis(bis(hydroxypentyl)phosphino)ethane (**1**, $n = 4$; DHPePE) are reported. These ligands (and, in general, other 1,2-bis(bis(hydroxyalkyl)phosphino)ethane ligands) can be used to impart water solubility to metal complexes. As examples of this, the [Ni(DHPrPE)$_2$Cl]Cl (**2**), [Rh(DHPrPE)$_2$][Cl] (**3**), and [Ru(DHBuPE)$_2$Cl$_2$][Cl] (**4**) complexes were synthesized; they are indeed soluble in water (>0.5 M). Crystals of DHPrPE (**1**, $n = 2$) are monoclinic, space group $P2_1/c$, with $a = 9.5935(8)$ Å, $b = 9.353(2)$ Å, $c = 10.655(2)$ Å, $\alpha = 90°$, $\beta = 100.03(1)°$, $\gamma = 90$, $V = 941.5(5)$ Å^3, $R = 0.051$, and $Z = 2$. Crystals of [Ni(DHPrPE)$_2$Cl]Cl (**2**) are monoclinic, space group $I2$, with $a = 15.951(3)$ Å, $b = 11.454(2)$ Å, $c = 20.843(3)$ Å, $\alpha = 90°$, $\beta = 91.24(2)°$, $\gamma = 90°$, $V = 3807(2)$ Å^3, $R = 0.062$, and $Z = 4$. Crystals of [Rh(DHPrPE)$_2$][Cl] (**3**) are triclinic, space group $P\bar{1}$, with $a = 13.900(2)$ Å, $b = 15.378(2)$ Å, $c = 18.058(2)$ Å, $\alpha = 87.71(1)°$, $\beta = 75.03(1)°$, $\gamma = 85.24(1)$, $V = 3715(2)$ Å^3, $R = 0.044$, and $Z = 4$. Crystals of [Ru(DHBuPE)$_2$Cl$_2$][Cl] (**4**) are monoclinic, space group $C2/c$, with $a = 14.310(2)$ Å, $b = 21.630(2)$ Å, $c = 15.459(3)$ Å, $\alpha = 90°$, $\beta = 99.83(1)°$, $\gamma = 90$, $V = 4715(1)$ Å^3, $R = 0.056$, and $Z = 4$.

There is considerable interest in water-soluble phosphines for use in aqueous synthesis,[1] catalysis,[2] and radiopharmaceuticals.[3] Until now, most of the water-soluble phosphines reported in the literature have been sulfonates or amine derivatives of aryl-substituted phosphines.[4] Only a few reports of water-soluble alkylphosphines have appeared.[5] Klötzer et al. reported[6] the synthesis of 1,2-bis(bis(hydroxymethyl)phosphino)ethane (**1**, $n = 0$; DHMPE[⊥]) in 1984, and Boerner and co-workers[7] synthesized several chiral bis(phosphines) bearing hydroxyl groups. Reddy recently described[8] several complexes of DHMPE, and we recently reported[9] the synthesis of 1,2-bis(bis(hydroxypropyl)phosphino)ethane (**1**, $n = 2$) and 1,2-bis(di(sulfonatopropyl)phosphino)ethane. There have been no reports of higher homologs (C$_4$, C$_5$, ...) of the 1,2-bis(bis(hydroxyalkyl)phosphino)ethane ligands. We report here the synthesis and characterization of the hydroxybutyl and the hydroxypentyl homologs of structure **1**. In addition, we report the Ni(II) and Rh(I) complexes of the DHPrPE ligand and a Ru(III) complex of the DHBuPE ligand. X-ray structures of the DHPrPE ligand and the Ni, Ru, and Rh complexes are also included.



1

n = 0, DHMPE;
2, DHPrPE;
3, DHBuPE;
4, DHPePE

Experimental Section

All manipulations of air-sensitive materials were carried out under an argon atmosphere by using standard Schlenk line techniques or by handling the materials and solutions in a Vacuum Atmospheres Co. glovebox.

Materials and Reagents. 1,2-Bis(phosphino)ethane (Strem), 3-buten-1-ol (Aldrich), and 4-penten-1-ol (Aldrich) were used as received. All

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[⊥] The ligand abbreviations used in this paper are based on traditional names for these species; e.g., DHMPE = 1,2-bis(di(hydroxymethyl)phosphino)ethane. The names used in the paper follow IUPAC recommendations.

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(1) (a) Herrmann, W. A.; Brossmer, C.; Ofele, K.; Beller, M.; Fischer, H. *J. Mol. Catal. A: Chem.* **1995**, *103*, 133−146. (b) Monflier, E.; Bourdauducq, P.; Couturier, J. L.; Kervennal, J.; Mortreux, A. *J. Mol. Catal. A: Chem.* **1995**, *97*, 29−33. (c) Casalnuovo, A. L.; Calabrese, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 4324−4330.

(2) (a) Kalck, P.; Monteil, F. In *Advances in Organometallic Chemistry*, Vol. 34; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1992; pp 219−284. (b) Cornils, B.; Kuntz, E. G. *J. Organomet. Chem.* **1995**, *502*, 177−186. (c) *Proceedings of the NATO Advanced Research Workshop on Aqueous Organometallic Chemistry and Catalysis*; Horvath, I. T., Joo, F., Eds.; Kluwer Academic: Norwell, MA, 1995.

(3) (a) Katti, K. V. *Curr. Sci.*, **1996**, *70*, 219−225. (b) Herbowski, A.; Deutsch, E. A. *J. Organomet. Chem.* **1993**, *460*, 19−23.

(4) Herrmann, W. A.; Kohlpainter, C. W. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1524−1544.

(5) (a) Chatt, J.; Leigh, G. L.; Slade, R. M. *J. Chem. Soc., Dalton Trans.* **1973**, 2021−2028. (b) Hoye, P. A. T.; Pringle, P. G.; Smith, M. B.; Worboys, K *J. Chem. Soc., Dalton Trans.* **1993**, 269−274. (c) Heesche-Wagner, K.; Mitchell, T. N. *J. Organomet. Chem.*, **1994**, *468* 99−106. (d) Paetzold, E.; Oehme, G. *J. Prakt. Chem.* **1993**, *335*, 181−184. (e) Ganguly, S.; Mague, J. T.; Roundhill, D. M. *Inorg. Chem.*, **1992**, *31*, 3500−3501. (f) Tsvetkov, E. N.; Bondarenko, N. A.; Malakhova, I. G.; Kabachnik, M. I. *Synthesis* **1986**, *3*, 198−208.

(6) Klõtzer, D.; Mäding, P.; Munze, R. Z. *Z. Chem.* **1984**, *24*, 224.

(7) Holz, J.; Boerner, A.; Kless, A.; Borns, S.; Trinkhaus, S.; Seleke, R.; Heller, D. *Tetrahedron: Asymmetry* **1995**, *6*, 1973−1988.

(8) Reddy, V. S.; Berning, D. E.; Katti, K. V.; Barnes, C. L.; Volker, W. A.; Ketring, A. R. *Inorg. Chem.* **1996**, *35*, 1753−1757

(9) Baxley, G. T.; Weakley, T. J. R.; Miller, W. K.; Lyon, D. K.; Tyler, D. R. *J. Mol. Catal., A*: *Chem.*, in press.

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Table 1. Crystallographic Data

	1	**2**	**3**	**4**
compn	$C_{14}H_{32}O_4P_2$	$C_{28}H_{64}Cl_2NiO_8P_4$	$C_{28}H_{64}ClO_8P_4Rh$	$C_{36}H_{80}Cl_3O_8P_4Ru$
fw	326.4	782.31	791.1	972.35
space group	$P2_{1/c}$	$I2$	$P\bar{1}$	$C2/c$
a, Å	9.5935(8)	15.951(3)	13.900(2)	14.310(2)
b, Å	9.353(2)	11.454(2)	15.378(2)	21.630(2)
c, Å	10.655(2)	20.843(3)	18.058(2)	15.459(3)
α, deg	90	90	87.71(1)	90
β, deg	100.03(1)	91.24(2)	75.03(1)	99.83(1)
γ, deg	90	90	85.24(1)	90
V, Å^3	941.5(5)	3807(2)	3715(2)	4715(1)
Z	2	4	4	4
d_{calc}, g cm^{-3}	1.151	1.365	1.414	1.370
T, °C	22	21	22	21
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
μ, cm^{-1}	2.34	8.6	7.35	6.73
transm coeff (μ)	0.90−1.00	0.88−1.00	0.89−1.00	0.96−1.00
no. of obs rflns	943	2586	6664	2875
$n[I \geq n\sigma(I)]$	1.5	2	2.5	2
$R(F)^a$	0.051	0.062	0.044	0.056
$R_w(F)^b$	0.039	0.056	0.047	0.064

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

Table 2. NMR Data

compound	^{31}P	^1H
DHPrPE (**1**, $n = 2$)	−27.3 (s)^a	1.52 (m, br, 8 H, 4 × PCH_2), 1.57 (m, br, 4 H, PCH_2CH_2P), 1.64 (m, br, 8 H, 4 × CH_2), 3.61 (t, 8 H, 4 × CH_2-OH), 4.8 (s, OH)^b
DHBuPE (**1**, $n = 3$)	−27.8 (s)^a	1.47 (m, br, 20 H), 1.59 (m, br, 8 H), 3.54 (t, 8 H, 4 × CH_2OH), 4.80 (s, OH)^a
DHPePE (**1**, $n = 4$)	−26.4^b	1.38 (m, br, 28 H), 1.47 (m, br, 8 H), 3.46 (t, 8 H, 4 × CH_2OH), 4.8 (OH)^b
[Ni(DHPrPE)$_2$Cl]Cl (**2**)	56.42	
Ni(DHBuPE)$_2$Cl$_2$	58.36	
Ni(DHPePE)$_2$Cl$_2$	58.79	
[Rh(DHPrPE)$_2$]Cl (**3**)	56.2, 57.1 (d, $J_{RhP} = 130$ Hz)	1.7 (m, br, 24 H, 6 × PCH_2), 1.9 (m, br, 16 H, 4 × CH_2), 3.59 (t, 16 H, 4 × CH_2OH), 4.08 (s, OH)^a
[Ru(DHBuPE)$_2$Cl$_2$]Cl		1.8 (m, br), 3.6 (m, br), 4.8 (s, OH)

[a] D_2O. [b] MeOH.

solvents were reagent grade and deoxygenated by an argon purge. Deuterium oxide (D_2O) and methanol-d_4 were purchased from Aldrich. VAZO 67 (2,2′-azobis(2-methylbutyronitrile) was obtained from DuPont and used as received. *Safety note: 1,2-Bis(phosphino)ethane (Stench!) is highly toxic and pyrophoric. Well-ventilated laboratory space and good fume hoods are needed to safely handle this material.* DHPrPE and [Rh^I(DHPrPE)$_2$][Cl] were prepared as previously described.[9]

Instrumentation and Procedures. NMR spectra were collected on a Varian Unity/Inova 300 spectrometer. ^{1}H (299.95 MHz) and ^{13}C (75.43 MHz) signals were referenced to TMS. ^{31}P (121.42 MHz) spectra were referenced to external 1% H_3PO_4 in D_2O. Elemental analyses were performed by E&R Microanalytical Laboratory, Inc., Corona, NY.

X-ray Crystallography. All crystals were mounted in capillaries in the glovebox. The orientation parameters and cell dimensions were in each case obtained from the setting angles of an Enraf-Nonius CAD-4 diffractometer for 25 centered reflections in the range 13−16° θ. Table 1 contains a summary of crystal data and the final residuals. More extensive tables including particulars of data collection and structure refinement are in the supporting data. Intensity data were collected to θ 25° (22.5° for the weakly diffracting **3**). Data for **1** were corrected for *ca*. 5% crystal decay (on I) during data collection, and the data for **2** and **4** were corrected for absorption.[10] MITHRIL *E* maps[11] showed all non-hydrogen atoms of **1** and the metal and phosphorus atoms of **2**−**4**, whose remaining atoms were located from difference syntheses or by use of DIRDIF.[12] Evident disorder in the side chains of the ligands in **2**−**4** produced alternate sites for several oxygen atoms. These “split” atoms were refined isotropically. In addition, the noncoordinated Cl atoms in **2** and **4** appeared from their large and anisotropic thermal motion to be disordered over alternative sites close to a crystal diad axis, though the disorder could not be satisfactorily modeled. Hydrogen atoms of **1** were located from difference syntheses and refined isotropically. Hydrogens attached to carbon atoms in **2**−**4** were included at calculated, updated, positions; those hydroxyl hydrogens that could be located in difference syntheses were also included without refinement. The final difference syntheses confirmed the absence of solvent of crystallization. Refinement of the structure of opposite polarity in the case of **2** gave the same final residuals and standard deviations. The *TEXSAN* program suite,[13] incorporating complex atomic scattering factors,[14] was used in all calculations. The precision of the structural analyses for **2**−**4** was limited by the disorder in the 3-hydroxypropyl or 4-hydroxybutyl side chains.

Synthesis of DHBuPE (1, *n* = 3). 1,2-Bis(phosphino)ethane (6.0 g; 63.8 mmol), 3-butene-1-ol (20.7 g; 287 mmol), and VAZO 67 (1.3 g; 6.84 mmol) were dissolved in 150 mL of methanol in a 500 mL 24/40 single-neck round-bottom flask containing a magnetic stir bar. The flask was sealed with a septum and steel worm clamp. (*Safety note: Because round-bottom flasks are not designed to handle high pressure, it is recommended that the temperature in the flask not exceed 60 °C. Use a blast shield in this procedure.*) The flask was removed from the glovebox and placed in an oil bath at 60 °C for 24 h. After this time, the reaction mixture was cooled to room temperature and

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(10) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158−166.

(11) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42−46.

(12) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; Van Der Hark, T. E. M.; Prick, P. A. J.; Noordik, K. H.; Beurskens, G.; Parthasarathi, V.; Bruins Slot, H. J.; Haltiwanger, R. C.; Strumpel, M.; Smits, J. M. M. DIRDIF: Direct Methods for Difference Structures. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed Nijmegen, The Netherlands, 1984.

(13) *TEXSAN: Texray Program for Structure Analysis*, version 5.0; Molecular Structure Corp.: 3200A Research Forest Dr., The Woodlands, TX 77381, 1989.

(14) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71, 148.

brought into the glovebox. The solvent was removed under vacuum, until about 50 mL remained. With vigorous stirring, 400 mL of anhydrous diethyl ether was added, forming a white precipitate. The precipitate was collected on a glass-fritted funnel, rinsed with 100 mL of diethyl ether, and dried in vacuo. Yield: 61%. ^{31}P NMR (CD_3OD): singlet, −27.8(5) ppm. Anal. Calcd for $C_{18}H_{40}O_4P_2$: C, 56.53; H, 10.54; P, 16.20. Found: C, 56.22; H, 10.61; P, 16.63.

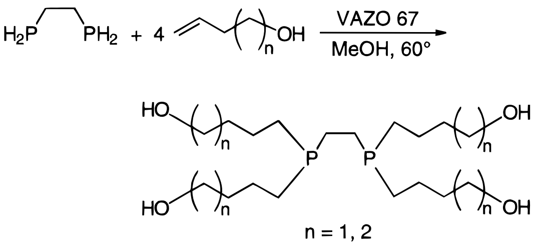
Synthesis of DHPePE (1, *n* = 4). This ligand was prepared by the method above using 9.41 g (109 mmol) of 4-penten-1-ol, 2.42 g (25.7 mmol) of 1,2-bis(phosphino)ethane, and 1.34 g (7.05 mmol) of VAZO 67. Yield: 72%. ^{31}P NMR (CD_3OD): singlet, −26.4 ppm. Anal. Calcd for $C_{22}H_{48}O_4P_2$: C, 60.25; H, 11.03; P, 14.12. Found: C, 60.28; H, 11.00; P, 14.45.

Synthesis of [Ru^{III}(DHBuPE)$_2$Cl$_2$][Cl]. DHBuPE (0.384 g, 1.0 mmol) and $RuCl_3$ (0.104 g, 0.5 mmol) were dissolved in a 100 mL Schlenk flask with 35 mL of ethanol. The red solution was brought to a reflux and stirred for 3 h, gradually turning green. A green solid precipitated upon the addition of 35 mL of diethyl ether. The flask was cooled to −5 °C, and the solid was collected on a glass frit and dried *in vacuo*. A second crop of crystals was obtained after continued cooling of the filtered solution. (Yield: 74% based on DHBuPE.) X-ray diffraction quality crystals were obtained by layering a saturated aqueous solution with diethyl ether. ^{1}H NMR δ (D_2O/CD_3CN): 1.8 (m, br), 3.6 (m, br), 4.8 (s, O*H*). (These resonances are very broad due to paramagnetic Ru^{3+}.) Anal. Calcd for $C_{36}H_{80}Cl_3O_8P_4Ru$: C, 44.47; H, 8.29; Cl, 10.94. Found: C, 44.04; H, 8.37; Cl, 8.18.

Synthesis of [Ni(DHPrPE)$_2$Cl]Cl. DHPrPE (2.00 g, 6.13 mmol) was dissolved in 25 mL of 1-propanol. $NiCl_2 \cdot 6H_2O$ (0.728 g, 3.06 mmol) was added with stirring. The mixture was heated to gentle reflux for 13 h. Initially, a brown solution was obtained, followed by formation of an orange-brown microcrystalline slurry. The mixture was cooled to room temperature and filtered, and the solid product was rinsed with 20 mL of diethyl ether. The solid was dried *in vacuo* for 8 h. Yield: 1.50 g, 62%. Additional product can be obtained by removing additional solvent from the mother liquor. X-ray quality crystals were obtained by cooling a hot saturated 1-propanol solution to room temperature. Anal. Calcd for $C_{14}H_{32}Cl_2NiO_4P_2$: C, 42.99; H, 8.25; Cl, 9.06; Ni, 7.50; P, 15.84. Found: C, 42.78; H, 8.35; Cl, 9.48; Ni, 7.51; P, 15.58.

Results and Discussion

Olefinic alcohols react cleanly with 1,2-bis(phosphino)ethane under free-radical conditions to give the 1,2-bis(bis(hydroxyalkyl)phosphino)ethane ligands in good yields (eq 1).[15] The



(1)

products were identified by ^{31}P and ^{1}H NMR and by elemental analysis. The NMR spectra (Table 2) are consistent with the proposed products and are typical of other tertiary alkylphosphines. X-ray crystallography confirmed the expected structure of the DHPrPE ligand (Figure 1; Tables 3 and 4). It is noteworthy that each OH group participates in two hydrogen bonds [O··O 2.673−2.769(9) Å], so that the molecules are linked in a three-dimensional network. The DHPrPE ligand is highly water-soluble (>1.0 M), but DHBuPE (≈0.02 M) and DHPePE (≈0.002 M) are much less soluble as free ligands.

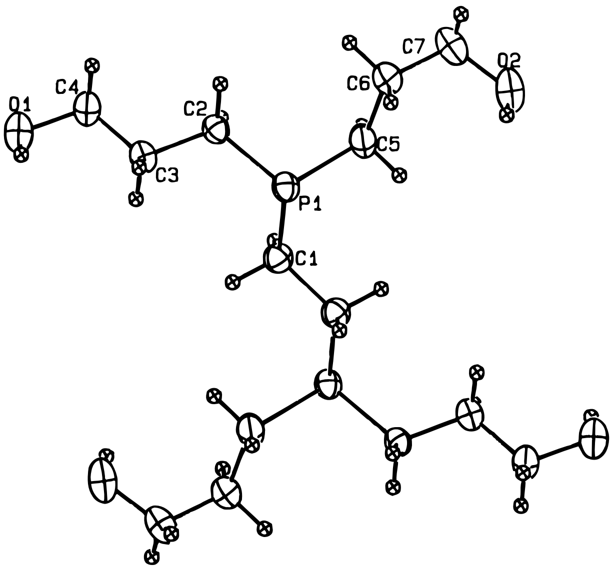


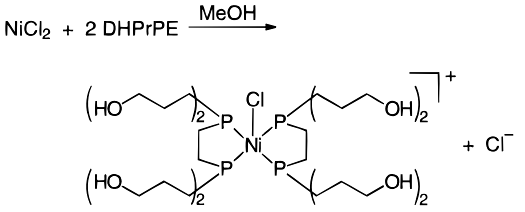
Figure 1. Molecular structure of the DHPrPE ligand (**1**).

Table 3. Atomic Coordinates and Thermal Parameters (Å^2) for **1**[a]

atom	*x*	*y*	*z*	B_{eq}
P(1)	0.46347(11)	0.14599(13)	0.15963(10)	3.90(4)
O(1)	0.9102(4)	0.1036(5)	0.5193(4)	8.7(3)
O(2)	−0.0331(4)	0.1108(6)	0.0747(5)	9.1(3)
C(1)	0.5303(5)	−0.0006(5)	0.0707(4)	4.3(2)
C(2)	0.5427(4)	0.0930(5)	0.3219(4)	3.8(2)
C(3)	0.7004(5)	0.1204(7)	0.3537(5)	4.9(2)
C(4)	0.7632(5)	0.0800(7)	0.4867(5)	5.9(3)
C(5)	0.2807(5)	0.0819(7)	0.1542(6)	5.6(3)
C(6)	0.1879(5)	0.1779(7)	0.2159(5)	6.1(3)
C(7)	0.0390(6)	0.1142(10)	0.2015(7)	7.9(4)

[a] $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$; H isotropic.

To demonstrate the potential use of these ligands in aqueous catalysis and radiopharmaceuticals, several metal complexes were prepared and characterized. The reaction of DHPrPE with $NiCl_2$ in a 2:1 ratio in methanol gave an orange product identified as Ni(DHPrPE)$_2$Cl$_2$ (**2**), eq 2. Recrystallization from



(2)

1-propanol gave X-ray quality crystals. In the solid state, the molecule is square pyramidal, with a Cl atom at the apex and the second Cl atom not bonded to the Ni (Figure 2; Tables 4 and 5). The Ni−P bond lengths are 2.213−2.237(3) Å. For comparison, the average Ni−P bond length in square-planar [Ni(DHMPE$_2$)$_2$]Cl$_2$ is 2.216(1) Å. The Ni atom lies 0.221(2) Å from the mean plane of the P atoms, toward Cl(1), and the conformation of the ligand side chains makes the sixth coordination position less accessible for coordination of the second Cl$^-$. All of the OH groups participate in short intermolecular O··O contacts [2.64−2.77(2) Å] or contacts with noncoordinated Cl$^-$ [Cl··O 3.04−3.35(2) Å].

The structure of Ni(DHPrPE)$_2$Cl$_2$ is notably different from that of Ni(DHMPE)$_2$Cl$_2$, in which the square-planar Ni center is not bonded to either chloride.[16] A possible explanation for this behavior is the following. In the case of Ni(DHPrPE)Cl$_2$,

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[15] The addition of alkenes to phosphines is a well-known reaction. See Lavenot, L.; Bortoletto, M. H.; Roucoux, A.; Larpent, C.; Patin, H. *J. Organomet. Chem.* **1996**, *509*, 9−14 and references therein.

Table 4. Principal Bond Lengths (Å) and Angles (deg)

1, $C_{14}H_{32}O_4P_2$			
P−C(1)	1.844(4)	C(1)−C(1^i)	1.518(8)
P−C(2)	1.832(4)	C(2)−C(3)	1.513(6)
P−C(5)	1.845(6)	C(3)−C(4)	1.489(7)
O(1)−C(4	1.410(6)	C(5)−C(6)	1.496(7)
O(2)−C(7)	1.408(8)	C(6)−C(7)	1.531(8)
C(1)−P−C(2)	99.2(2)	C(2)−C(3)−C(4)	113.1(4)
O(1)−C(4)−C(3)	114.6(5)	C(1)−P−C(5)	99.0(2)
P−C(5)−C(6)	115.2(4)	C(2)−P−C(5)	100.2(3)
C(5)−C(6)−C(7)	109.8(5)	P−C(1)−C(1^i)	113.4(4)
O(2)−C(7)−C(6)	113.5(5)	P−C(2)−C(3)	113.5(3)
2, $C_{28}H_{64}Cl_2NiO_8P_4$			
Ni−Cl(1)	2.479(3)	Ni−P(3)	2.222(3)
Ni−P(1)	2.213(3)	Ni−P(4)	2.237(3)
Ni−P(2)	2.215(4)		
Cl(1)−Ni−P(1)	90.7(1)	P(1)−Ni−P(3)	168.1(1)
Cl(1)−Ni−P(2)	95.0(1)	P(1)−Ni−P(4)	93.7(1)
Cl(1)−Ni−P(3)	101.1(1)	P(2)−Ni−P(3)	93.8(1)
Cl(1)−Ni−P(4)	95.9(1)	P(2)−Ni−P(4)	169.1(1)
P(1)−Ni−P(2)	85.3(1)	P(3)−Ni−P(4)	84.9(1)
3, $C_{28}H_{64}ClO_8P_4Rh$			
Rh(1)−P(1)	2.296(2)	Rh(2)−P(5)	2.280(2)
Rh(1)−P(2)	2.292(2)	Rh(2)−P(6)	2.286(2)
Rh(1)−P(3)	2.278(2)	Rh(2)−P(7)	2.292(2)
Rh(1)−P(4)	2.283(2)	Rh(2)−P(8)	2.297(2)
P(1)−Rh(1)−P(2)	83.24(7)	P(5)−Rh(2)−P(6)	85.02(7)
P(1)−Rh(1)−P(3)	175.65(8)	P(5)−Rh(2)−P(7)	169.79(8)
P(1)−Rh(1)−P(4)	96.01(8)	P(5)−Rh(2)−P(8)	96.33(8)
P(2)−Rh(1)−P(3)	96.13(8)	P(6)−Rh(2)−P(7)	96.53(8)
P(2)−Rh(1)−P(4)	176.97(8)	P(6)−Rh(2)−P(8)	170.04(7)
P(3)−Rh(1)−P(4)	84.84(8)	P(7)−Rh(2)−P(8)	83.89(8)
4, $C_{36}H_{80}Cl_3O_8P_4Ru$			
Ru−Cl(1)	2.336(2)	Ru−P(2)	2.400(2)
Ru−P(1)	2.400(2)		
Cl(1)−Ru−P(1)	86.98(5)	P(1)−Ru−P(2)	82.02(6)
Cl(1)−Ru−P(2)	89.86(6)		

[a] Symmetry code: (i) $1 - x, -y, -z$.

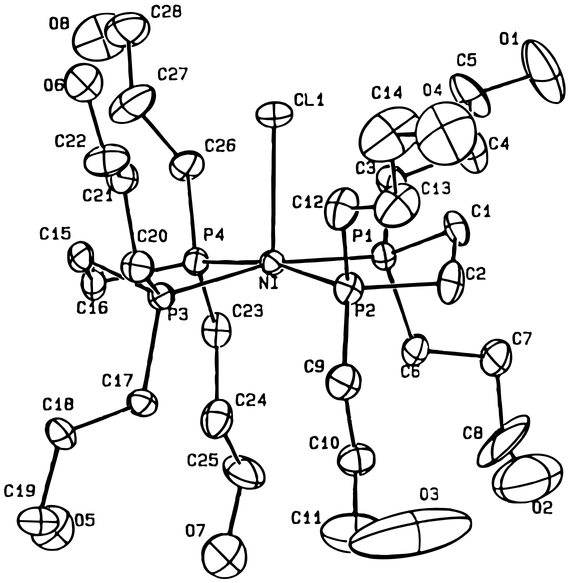

Figure 2. Molecular structure of the $[Ni(DHPrPE)_2Cl]^+$ cation (**2**). The hydrogen atoms have been omitted for clarity.

Table 5. Atomic Coordinates and Thermal Parameters ($Å^2$) for **2**[a]

atom	*x*	*y*	*z*	B_{eq}
Ni	0.53799(7)	0.5070	0.24419(6)	2.81(6)
Cl(1)	0.6421(2)	0.3501(3)	0.2267(2)	4.8(2)
Cl(2)	0.5000	0.8889(6)	0	11.3(5)
Cl(3)	0.5000	0.0041(14)	0.5000	27(1)
P(1)	0.4345(2)	0.3885(3)	0.2149(2)	3.3(1)
P(2)	0.5093(2)	0.4528(3)	0.3434(2)	4.0(2)
P(3)	0.6208(2)	0.6529(3)	0.2759(2)	3.2(1)
P(4)	0.5476(2)	0.5869(3)	0.1467(2)	3.2(1)
O(1)	0.3576(10)	0.0389(11)	0.0588(6)	13(1)
O(2)	0.1588(11)	0.4736(21)	0.2473(9)	19(2)
O(3)	0.3500(17)	0.6396(30)	0.4930(9)	35(3)
O(4)	0.6453(9)	0.1819(18)	0.5187(8)	15(1)
O(5)	0.5123(10)	1.0068(22)	0.2428(8)	8.9(4)[b]
O(5A)	0.5058(17)	1.0019(34)	0.3541(13)	9.1(7)[b]
O(6)	0.9032(7)	0.5015(15)	0.3699(6)	6.6(3)[b]
O(6A)	0.7887(18)	0.5069(38)	0.4380(15)	7.2(7)[b]
O(7)	0.2869(11)	0.8688(19)	0.1313(9)	9.0(5)[b]
O(7A)	0.2723(14)	0.6580(24)	0.1013(11)	6.8(6)[b]
O(8)	0.6983(7)	0.4539(13)	−0.0365(5)	10.6(9)
C(1)	0.4284(7)	0.2809(11)	0.2775(6)	4.4(6)
C(2)	0.4267(7)	0.3411(14)	0.3413(6)	5.3(7)
C(3)	0.4452(7)	0.3046(11)	0.1407(5)	4.2(6)
C(4)	0.3963(10)	0.1902(15)	0.1317(7)	7(1)
C(5)	0.4042(11)	0.1377(13)	0.0675(7)	8(1)
C(6)	0.3332(6)	0.4547(11)	0.2120(5)	4.0(6)
C(7)	0.2559(8)	0.3801(15)	0.2065(8)	7.5(9)
C(8)	0.1745(9)	0.4612(28)	0.1881(13)	16(2)
C(9)	0.4753(8)	0.5530(12)	0.4048(6)	5.4(7)
C(10)	0.3947(8)	0.6224(13)	0.3882(6)	5.3(7)
C(11)	0.3676(14)	0.6990(22)	0.4397(9)	12(1)
C(12)	0.5982(7)	0.3738(15)	0.3813(6)	6.0(8)
C(13)	0.5871(9)	0.3113(17)	0.4403(8)	8(1)
C(14)	0.6603(12)	0.2434(25)	0.4608(8)	12(2)
C(15)	0.6798(6)	0.6949(11)	0.2074(5)	3.9(6)
C(16)	0.6176(7)	0.7123(11)	0.1516(5)	4.2(6)
C(17)	0.5652(7)	0.7831(11)	0.2965(5)	4.1(6)
C(18)	0.6119(8)	0.8959(12)	0.3043(7)	5.9(7)
C(19)	0.5653(9)	1.0105(17)	0.3092(9)	9(1)
C(20)	0.6990(7)	0.6425(12)	0.3397(5)	4.5(6)
C(21)	0.7746(7)	0.5645(12)	0.3277(6)	4.9(7)
C(22)	0.8335(8)	0.5590(13)	0.3876(6)	6.2(8)
C(23)	0.4553(7)	0.6404(12)	0.1066(5)	4.1(6)
C(24)	0.4043(8)	0.7317(13)	0.1402(6)	5.4(8)
C(25)	0.3212(9)	0.7623(14)	0.1047(8)	8(1)
C(26)	0.5945(7)	0.4983(14)	0.0827(5)	4.9(6)
C(27)	0.6843(8)	0.4886(19)	0.0777(7)	8(1)
C(28)	0.7170(10)	0.4184(16)	0.0249(8)	8(1)

[a] $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$. [b] Site occupancy factors: O(5), 0.62; O(5A), 0.38; O(6), 0.70; O(6A), 0.30; O(7), 0.60; O(7A), 0.40; all refined isotropically.

the environment in the coordination pocket is more hydrophobic than in $Ni(DHMPE)Cl_2$, which has shorter alkyl chains. Thus, Cl^- is less likely to dissociate in the former complex. (In support of this hypothesis, it is noted that *both* Cl^- ligands are coordinated in $Fe(DHBuPE)_2Cl_2$. This ligand will form an even more hydrophobic pocket than does DHPrPE.)

As expected from the structure, $Ni(DHPrPE)Cl_2$ is highly water soluble (>0.5 M). Additional Ni compounds were generated in situ by reacting the DHBuPE and DHPePE ligands with $NiCl_2$ in a 2:1 ratio in water to form orange solutions. The ^{31}P NMR of each solution showed a single singlet, suggesting the formation of a single complex. Both complexes are highly water soluble (>0.5 M). The solubility of these complexes was determined by monitoring the solubility of the ligand in the presence of $NiCl_2$. For example, the solubility of the DHPePE ligand is ≈0.002 M in water, whereas the solubility in the presence of 0.5 equiv of $NiCl_2$ increases the solubility of the ligand to >0.5 M. The solubility of the metal complexes in water can be attributed to the hydrophilic hydroxyl groups, which surround the outside of the complexes, and to the charges on the molecules.

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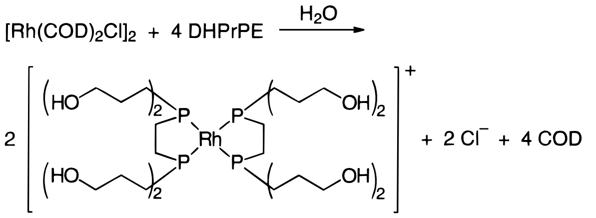
(16) Nieckarz, G. F.; Weakley, T. J. R.; Miller, W. K.; Miller, B. E.; Lyon, D. K.; Tyler, D. R. *Inorg. Chem.* **1996**, *35,* 1721−1724.

Table 6. Atomic Coordinates and Thermal Parameters (Å^2) for **3**^{a}

atom	*x*	*y*	*z*	B_{eq}	atom	*x*	*y*	*z*
Rh(1)	0.19658(4)	0.38985(4)	0.74260(3)	2.29(3)	C(14)	0.0580(8)	0.0923(7)	0.9532(6)
Rh(2)	0.30752(4)	0.11626(4)	0.24378(3)	2.25(3)	C(15)	0.2217(6)	0.3501(5)	0.5549(4)
Cl(1)	0.7460(2)	0.3779(2)	0.5781(2)	6.0(2)	C(16)	0.2896(6)	0.4242(5)	0.5520(4)
Cl(2)	0.8146(3)	0.0838(2)	0.1904(2)	11.0(3)	C(17)	0.4417(6)	0.3708(5)	0.6288(4)
P(1)	0.2546(2)	0.4449(2)	0.8379(1)	2.9(1)	C(18)	0.4357(6)	0.2731(5)	0.6261(5)
P(2)	0.0765(2)	0.3393(2)	0.8438(1)	3.0(1)	C(19)	0.5307(7)	0.2186(6)	0.6243(5)
P(3)	0.1305(2)	0.3443(1)	0.6491(1)	2.8(1)	C(20)	0.3590(6)	0.5461(5)	0.6362(4)
P(4)	0.3220(2)	0.4344(2)	0.6432(1)	3.2(1)	C(21)	0.2742(7)	0.6157(5)	0.6404(5)
P(5)	0.4459(2)	0.1307(2)	0.1450(1)	3.1(1)	C(22)	0.3065(11)	0.7086(6)	0.6442(7)
P(6)	0.2277(2)	0.1003(1)	0.1498(1)	2.8(1)	C(23)	0.0198(6)	0.4071(5)	0.6326(4)
P(7)	0.1799(2)	0.0766(2)	0.3445(1)	2.9(1)	C(24)	0.0265(6)	0.5052(5)	0.6247(5)
P(8)	0.3764(2)	0.1571(2)	0.3386(1)	3.1(1)	C(25)	−0.0754(8)	0.5509(5)	0.6223(7)
O(1)	0.5845(4)	0.2530(4)	0.8368(4)	5.9(4)	C(26)	0.0918(6)	0.2336(5)	0.6513(4)
O(2)	0.1377(7)	0.7414(5)	0.8905(6)	11.4(8)	C(27)	0.1711(6)	0.1606(5)	0.6565(4)
O(3)	0.2597(6)	0.5151(5)	0.8452(5)	10.9(7)	C(28)	0.1289(7)	0.0708(5)	0.6666(5)
O(4)	0.1541(6)	0.0526(5)	0.9433(4)	8.1(6)	C(29)	0.4186(6)	0.1048(5)	0.0545(4)
O(5)	0.6075(5)	0.2347(5)	0.5556(4)	8.0(6)	C(30)	0.3089(6)	0.1310(5)	0.0566(4)
O(6)	0.3323(7)	0.7222(5)	0.7134(5)	10.0(8)	C(31)	0.5542(5)	0.0547(5)	0.1465(4)
O(7)	−0.0736(8)	0.6369(7)	0.6060(6)	7.5(3)^a	C(32)	0.5278(6)	−0.0375(5)	0.1732(5)
O(7A)	−0.1032(15)	0.5424(12)	0.5664(11)	6.3(4)^a	C(33)	0.6164(8)	−0.0965(6)	0.1839(6)
O(8)	0.0573(4)	0.0597(4)	0.7361(3)	5.5(4)	C(34)	0.5058(6)	0.2325(5)	0.1220(4)
O(9)	0.6559(5)	−0.0662(5)	0.2424(4)	8.0(6)	C(35)	0.4394(7)	0.3037(6)	0.0930(5)
O(10)	0.4297(6)	0.4480(4)	0.0425(4)	9.5(6)	C(36)	0.4903(9)	0.3849(7)	0.0716(7)
O(11)	0.3138(5)	−0.2199(4)	0.0518(4)	6.8(5)	C(37)	0.1851(5)	−0.0038(5)	0.1279(4)
O(12)	0.0177(6)	0.3504(5)	0.1205(4)	9.0(6)	C(38)	0.2698(6)	−0.0724(5)	0.0981(4)
O(13)	−0.0675(6)	0.2663(5)	0.4868(5)	10.1(7)	C(39)	0.2316(7)	−0.1563(6)	0.0818(5)
O(14)	0.2552(5)	−0.2569(4)	0.2844(3)	6.4(5)	C(40)	0.1163(6)	0.1743(5)	0.1566(4)
O(15)	0.6540(7)	0.0732(6)	0.4859(5)	5.6(2)^a	C(41)	0.1280(6)	0.2659(5)	0.1806(5)
O(15A)	0.6273(13)	−0.0303(11)	0.4061(9)	5.8(4)^a	C(42)	0.0339(8)	0.3272(6)	0.1941(6)
O(16)	0.3275(8)	0.4894(7)	0.2906(6)	6.8(2)^a	C(43)	0.2239(6)	0.0729(5)	0.4319(4)
O(16A)	0.4030(13)	0.4614(11)	0.3564(9)	5.2(4)^a	C(44)	0.2833(6)	0.1498(6)	0.4309(4)
C(1)	0.1888(6)	0.3998(5)	0.9313(4)	4.0(5)	C(45)	0.0641(6)	0.1472(5)	0.3691(4)
C(2)	0.0798(6)	0.3950(5)	0.9309(4)	3.9(5)	C(46)	−0.0172(6)	0.1246(5)	0.4382(5)
C(3)	0.3849(6)	0.4344(5)	0.8417(4)	3.5(5)	C(47)	−0.1015(7)	0.1928(7)	0.4578(6)
C(4)	0.4315(6)	0.3416(5)	0.8420(4)	3.9(5)	C(48)	0.1372(5)	−0.0329(5)	0.3441(4)
C(5)	0.5415(6)	0.3398(6)	0.8363(5)	5.4(6)	C(49)	0.2194(6)	−0.1042(5)	0.3208(4)
C(6)	0.2220(6)	0.5626(5)	0.8463(4)	3.9(5)	C(50)	0.1800(7)	−0.1889(5)	0.3090(5)
C(7)	0.2244(8)	0.6072(6)	0.9191(5)	6.1(7)	C(51)	0.4864(6)	0.0918(5)	0.3528(4)
C(8)	0.2215(8)	0.7057(6)	0.9108(7)	7.4(9)	C(52)	0.5210(6)	0.1061(5)	0.4236(4)
C(9)	−0.0569(6)	0.3445(5)	0.8499(4)	4.0(5)	C(53)	0.6265(6)	0.0622(5)	0.4163(5)
C(10)	−0.1056(7)	0.4354(5)	0.8459(5)	4.8(6)	C(54)	0.4122(6)	0.2695(5)	0.3372(5)
C(11)	−0.2168(7)	0.4310(6)	0.8510(7)	8(1)	C(55)	0.3399(6)	0.3387(5)	0.3182(5)
C(12)	0.1018(6)	0.2228(5)	0.8662(4)	4.5(6)	C(56)	0.3870(8)	0.4257(6)	0.3053(7)
C(13)	0.0546(7)	0.1899(6)	0.9457(5)	5.9(7)				

^{a} $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$. ^{b} Refined isotropically. Site occupancy factors: O(7, 15, 16), 0.65; O(7A, 15A, 16A), 0.35.

The water-soluble [Rh^{I}(DHPrPE)$_2$][Cl] complex (**3**) was prepared in high yield by reacting [Rh(COD)Cl]$_2$ with DHPrPE in water or polar organic solvents (eq 3). Orange, cubic crystalsof [Rh^{I}(DHPrPE)$_2$][Cl] suitable for an X-ray diffraction study were grown from ethanol/THF (Figure 3; Tables 4 and 6). The asymmetric unit contains two [Rh(C$_{14}$H$_{32}$P$_4$O$_8$)$_2$]$^+$ cations and two Cl$^-$ anions. No solvent of crystallization is present. The cations exhibit square-planar coordination with some tetrahedral distortion, particularly around Rh(2); the distances of phosphorus atoms from the RhP$_4$ mean planes are −0.082, 0.063, −0.081, −0.060(2) Å for the Rh(1) cation and 0.209, −0.195, 0.194, −0.206(2) Å for Rh(2). The −(CH$_2$)$_3$-OH side chains around Rh(1) are all extended roughly normal



(3)

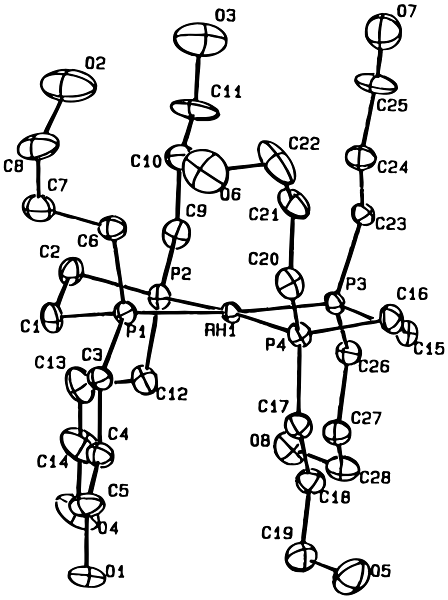


Figure 3. Molecular structure of the [Rh(DHPrPE)$_2$]$^+$ cation (**3**). The hydrogen atoms have been omitted for clarity.

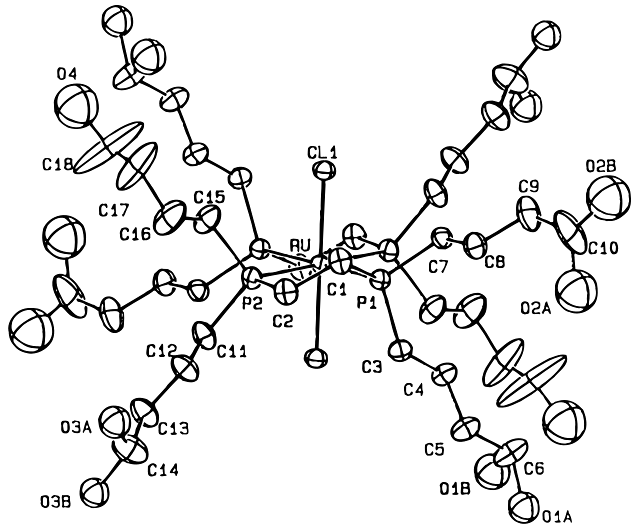
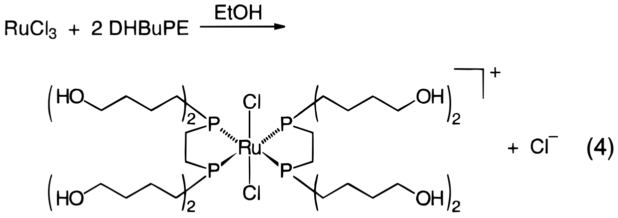


Figure 4. Molecular structure of the $[Ru(DHBuPE)_2Cl_2]^+$ cation (**4**). The hydrogen atoms have been omitted for clarity.

to the RhP_4 plane, four on each side, and block access to the Rh atom, while three of the side chains around Rh(2) are extended normal to the RhP_4 plane on each side and two are roughly parallel to it. An extensive system of hydrogen bonds involving all hydroxyl groups is inferred from the shorter O••Cl distances [3.04−3.38(1) Å] and interanion O••O distances [2.69−2.78(1) Å].

In a similar reaction, $[Ru^{III}(DHBuPE)_2Cl_2][Cl]$ (**4**) was prepared by reacting DHBuPE with $RuCl_3$ in ethanol. X-ray



(4)

crystallographic analysis shows that the complex cation lies on a crystallographic inversion center and has *trans*-octahedral geometry (Figure 4; Tables 4 and 7).

In conclusion, the 1,2-bis(bis(hydroxyalkyl)phosphino)ethane ligands, where alkyl = butyl and pentyl, are easily prepared by free-radical addition of the olefin alcohol to 1,2-bis(phosphino)ethane. These ligands form highly water-soluble transition metal complexes with Ni(II), Ru(III), and Rh(I). Further work with these ligands is in progress and will be reported in future papers.

Table 7. Atomic Coordinates and Thermal Parameters ($Å^2$) for **4**[a]

atom	*x*	*y*	*z*	B_{eq}
Ru	0.50000	0.50000	0.50000	3.14(3)
Cl(1)	0.57271(11)	0.50897(8)	0.37632(10)	4.52(7)
Cl(2)	0	0.4548(3)	0.25000	16.3(5)
P(1)	0.35126(10)	0.50340(9)	0.40123(10)	3.74(7)
P(2)	0.48113(12)	0.39099(8)	0.47397(11)	4.02(7)
O(1A)	−0.0097(10)	0.5962(7)	0.5779(9)	9.2(3)[b,c]
O(1B)	0.1234(12)	0.6170(8)	0.6299(11)	11.9(5)[b,c]
O(2A)	0.0449(16)	0.6121(12)	0.1929(14)	17.6(8)[b,c]
O(2B)	0.1280(18)	0.6714(13)	0.0976(17)	19.0(8)[b,c]
O(3A)	0.3426(10)	0.1614(7)	0.5661(10)	10.0(4)[b,c]
O(3B)	0.3525(9)	0.1689(6)	0.7200(8)	8.2(3)[b,c]
O(4)	0.7969(9)	0.2457(6)	0.3526(7)	18.6(4)[b]
C(1)	0.3477(5)	0.4324(3)	0.3366(4)	4.8(3)
C(2)	0.3694(5)	0.3783(3)	0.3996(4)	4.9(3)
C(3)	0.2423(4)	0.4976(3)	0.4475(4)	4.6(3)
C(4)	0.2115(5)	0.5563(4)	0.4891(5)	5.4(4)
C(5)	0.1122(5)	0.5506(4)	0.5110(6)	6.6(4)
C(6)	0.0795(6)	0.6085(5)	0.5499(7)	9.0(6)
C(7)	0.3300(4)	0.5653(3)	0.3199(4)	4.4(3)
C(8)	0.2382(5)	0.5609(4)	0.2538(5)	5.9(4)
C(9)	0.2234(7)	0.6174(4)	0.1949(6)	8.4(5)
C(10)	0.1205(10)	0.6241(7)	0.1443(8)	13.5(9)
C(11)	0.4763(6)	0.3419(3)	0.5691(5)	6.0(4)
C(12)	0.4119(6)	0.2877(4)	0.5606(5)	6.6(4)
C(13)	0.4173(6)	0.2497(4)	0.6427(6)	7.1(4)
C(14)	0.3473(7)	0.2003(5)	0.6384(7)	9.5(6)
C(15)	0.5719(5)	0.3539(4)	0.4218(6)	6.9(4)
C(16)	0.5625(7)	0.2908(5)	0.3887(8)	10.1(6)
C(17)	0.6413(10)	0.2668(8)	0.3448(13)	17(1)
C(18)	0.7170(14)	0.2631(15)	0.3725(21)	34(3)

[a] $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j$. [b] Isotropic. [c] Site occupancy factor 0.5.

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Supporting Information Available: Tables of crystallographic information, bond lengths and bond angles, nonbonded contact distances, calculated coordinates and thermal parameters for hydrogen atoms, anisotropic thermal parameters, torsion angles, and least-squares planes for complexes **1**−**4** (28 pages). Ordering information is given on any current masthead page.

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