Table II. Kinetics of the Chloride-Catalyzed Aquation of $Cr(NH_3)_5ONO^{2+}$ [a]

$10^2[H^+]$, M	$10^2[Cl^-]$, M	10^3k_{obsd}, sec^{-1} [b]	k_{Cl},[e] M^{-2} sec^{-1}
2.26	2.10	3.13 ± 0.15[c]	3.31
2.26	6.29	6.14 ± 0.13	3.22
2.26	10.5	8.83 ± 0.31[d]	3.06
1.36	6.29	3.59 ± 0.19	3.10
4.52	6.29	11.7 ± 0.1	3.02
9.04	6.29	23.4 ± 1.4	3.02

[a] At 10°, $\mu = 1.00$ M ($LiClO_4$), $[Cr(III)] \sim 3 \times 10^{-4} M$. [b] Average of three measurements, unless indicated otherwise. [c] Average of five measurements. [d] Average of six measurements. [e] $k_{Cl} \equiv (k_{obsd} - k_H[H^+])/[H^+][Cl^-]$.

Table III. Kinetics of the Bromide-Catalyzed Aquation of $Cr(NH_3)_5ONO^{2+}$ [a]

$10^2[H^+]$, M	$10^2[Br^-]$, M	10^3k_{obsd}, sec^{-1} [b]	k_{Br},[d] M^{-2} sec^{-1}
0.452	6.36	7.88 ± 0.25	26.3
0.452	10.6	13.4 ± 1.2	27.3
1.36	2.12	9.40 ±0.18	29.4
1.36	6.36	24.8 ± 1.1	27.6
1.36	10.6	37.2 ± 2.8	25.1
2.26	2.12	15.7 ± 0.4	29.5
2.26	6.36	41.7 ± 1.4	27.9
2.26	10.6	72.2 ± 3.1[c]	30.1

[a] At 10°, $\mu = 1.00$ M ($LiClO_4$), $[Cr(III)] \sim 3 \times 10^{-4} M$. [b] Average of three measurements, unless indicated otherwise. [c] Average of four measurements. [d] $k_{Br} \equiv (k_{obsd} - k_H[H^+])/[H^+][Br^-]$.

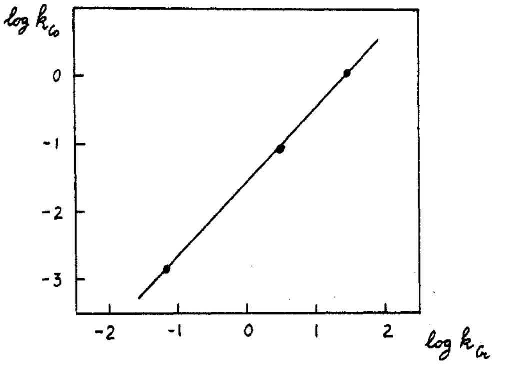

Figure 1.

the mechanisms of the two sets of reactions are identical, namely, rapid equilibrium protonation of the adjacent oxygen atom, followed by unassisted loss of NO^+ in the k_H pathway (eq 1) or assisted removal of NO^+ by Cl^- or Br^- in the k_{Cl} and k_{Br} pathways (eq 2).

Registry No. $Cr(NH_3)_5ONO^{2+}$, 22269-22-3; Cl^-, 16887-00-6; Br^-, 24959-67-9.

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A New Zerovalent Nickel Complex. Bis[1,2-bis(difluorophosphino)cyclohexane]nickel(0)

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We have recently reported the photoreaction of tetrafluorodiphosphine with various olefins.[1-3] Our investigation of the reaction of the resulting bidentate ligand 1,2-bis(difluorophosphino)cyclohexane with tetracarbonylnickel(0) has resulted in the high-yield preparation of a new zerovalent nickel complex under relatively mild conditions.

Experimental Section

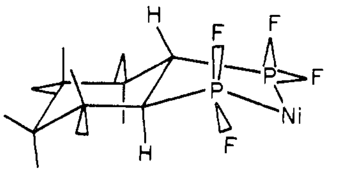
Into a 50-ml heavy-walled Pyrex vessel equipped with a Teflon stopcock, 1.71 mmol of $Ni(CO)_4$ (Strem Chemicals) and 4.90 mmol of $P_2F_4C_6H_{10}$[3] were condensed using standard vacuum techniques. Dry, air-free tetrahydrofuran (ca. 30 ml) was condensed into the reaction vessel, and the mixture was allowed to warm slowly to room temperature. Liberated CO was removed while holding the mixture at −196°. Upon warming, the vessel was placed in an oil bath with occasional shaking at 60° to ensure complete reaction. After 48 hr, the volatile material was pumped off and the remaining white solid was collected and sublimed. The reaction appeared to be essentially complete within 20 hr due to the absence of CO emerging from the solution. Recovery of 4.0 equiv of CO/equiv of $Ni(CO)_4$ substantiated the occurrence of complete substitution. Decomposition occurs upon melting at 169° (uncorrected). Anal. Calcd for $NiP_4F_8C_{12}H_{20}$: Ni, 11.77; C, 28.91; H, 4.01. Found: Ni, 11.61; C, 28.83, H, 4.16. (Galbraith Laboratories, Knoxville, Tenn.). NMR spectra were recorded on a Varian XL-100 spectrometer operating in the CW mode. Infrared spectra were recorded on a Beckman IR-20A spectrometer as KBr pellets. Mass spectra were recorded at 70 eV on a Hitachi Perkin-Elmer RMU-6E spectrometer.

Results and Discussion

Bis[1,2-bis(difluorophosphino)cyclohexane]nickel(0) was obtained as a dry, white powder which was stable in air for long periods of time with no apparent decomposition, in contrast to the rapid decomposition of the ligand in air.

The 40.5-MHz phosphorus-31 NMR spectrum of $Ni(P_2F_4C_6H_{10})_2$ in dry THF gives a broad triplet centered at −244.0 ppm (85% H_3PO_4 external reference) with $J_{F-P} = 1115$ Hz resulting from the two fluorine nuclei directly attached to the phosphorus. The free ligand shows two triplets, a large one (trans, diequatorial conformation) at −234.1 ppm and a small triplet (trans, diaxial), which disappears at low temperatures, at −241.1 ppm, with $J_{F-P} = 1218$ and 1203 Hz, respectively.[3] The absence of the second triplet in the complex is attributable to the absence of the trans, diaxial ligand configuration; models show the latter configuration to be nonamenable to bidentate bonding to metals. The downfield coordination shift δ_P(complex) − δ_P(ligand) = −9.9 ppm is in agreement with the observations reported in the literature for tetrakis(fluorophosphine)nickel(0) complexes.[4]

The ^{19}F NMR spectrum (94.1 MHz) of $Ni(P_2F_4C_6H_{10})_2$ in dry benzene suggests the presence of a mixture of isomers. A large doublet centered at 71 ppm (CCl_3F external standard) and two small doublets centered at approximately 65 and 63 ppm were observed with $J_{P-F} \simeq 1150$ Hz for each doublet. All are shifted downfield from the uncoordinated ligand which displays a complex doublet at 81.3 ppm with $J_{P-F} \simeq 1174$ Hz. These shifts are consistent with other fluorophosphine–metal complexes.[5] Though the peaks were quite broad and noisy, the three sets of doublets were clearly observed with area ratio of ~5:1 (combined area of smaller doublets). The small doublets were in a 1:1 area ratio. The doublets appear to result from the presence of coordinated trans and cis difluorophosphino groups in the ligand. The large doublet is assigned to the dominant,[3] coordinated trans ligand isomer, structure **1**. Inspection of models indicates that, in structure **1**, the four fluorine nuclei will interact equivalently with the ring protons, especially given rapid ring inversion on the NMR time scale, giving a single chemical shift for all four nuclei. The two small doublets are assigned to the coordinated cis ligand isomer, structure **2**. In this case, rapid ring inversion leads always to two sets of two fluorine nuclei (labeled a and b) which interact differently with the ring protons. It is noteworthy that no evidence for a cis–trans isomer mixture was observed in the NMR spectra (either ^{19}F or ^{31}P) of the uncoordinated ligand.[3] A complex multiplet was observed in the ^{19}F spectrum of the ligand which showed no temperature dependence and which was entirely consistent with the presence of a single isomer. The free ligand spectrum consisted of a mirror image about the center point, each half containing nine resolved lines in a pattern completely reminiscent of the spectra of other F_2PMPF_2 species.[6] Further unambiguous resolution of the eight expected doublets[6] was not achieved due, likely, to coupling with the ring protons. On this basis, it appears either that some ring isomerization occurred during the reaction or that whatever minor component of cis isomer may have been present in the ligand (<10%) was preferentially coordinated. The latter interpretation seems suspect in that more steric crowding is apparent in the cis ligand complex, **2**, than in the trans ligand complex. The spectra do not allow analysis of the isomer mixture of complexes, i.e., bis[*cis*-, bis[*trans*-, and bis[*cis*,*trans*-1,2-bis(difluorophosphino)cyclohexane]nickel(0).



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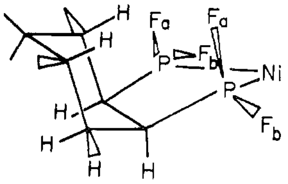

2

The 100.1-MHz proton NMR spectrum of bis[1,2-bis(difluorophosphino)cyclohexane]nickel(0) gives a complex multiplet at δ 2.12 with benzene as the internal reference (free ligand, δ 1.97, broad peak).

The solid-phase infrared spectrum of the complex consists of the following bands (cm^{-1}) with some tentative assignments as shown: 2895 vs (ν_{CH}), 2835 vs (ν_{CH}), 1435 s (δ_{CH_2}), 1326 w, 1301 w, 1267 w, 1179 w, 1164 w, 1063 m, 1040 w, 988 w, 865 m, sh, 779 vs, br (ν_{PF}), 710 vs (ν_{PF}), 604 w, 506 m, 483 w, 373 w. Absorptions in the CO region were not observed. The coordinated ligand P–F stretch is seen at 779 cm^{-1} as compared to the free ligand P–F stretch at 799 cm^{-1} suggesting,[5] as expected, a significant $d\pi$–$d\pi$ bonding interaction between phosphorus and nickel.

The mass spectrum contains two intense fragments, one which corresponds to the parent ion at m/e 498 [$(NiP_4F_8C_{12}H_{20})^+$, 100%] and one at m/e 278 [$(NiP_2F_4C_6H_{10})^+$, 35%] which represents the loss of one bis(difluorophosphino)cyclohexane moiety from the molecule. In both cases, the nickel isotope envelope was present and consistent. Only two other peaks of relative intensity greater than 5% were observed: m/e 138 ($P_2F_4^+$ and $NiC_6H_8^+$, 10%) and 82 ($C_6H_{10}^+$, 6%). The formulation as a coordination monomer was confirmed by vapor pressure osmometry.

The mild conditions required for the complete displacement of CO from $Ni(CO)_4$ are in contrast to those required for displacement by PF_3[7] and illustrate the effective combination of π-acceptor and chelating character in this ligand.

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Registry No. $Ni(P_2F_4C_6H_{10})_2$, 56488-42-7; $Ni(CO)_4$, 13463-39-3.

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Facile Separation of the Cis Isomers of Dicyclohexyl-18-crown-6[1]

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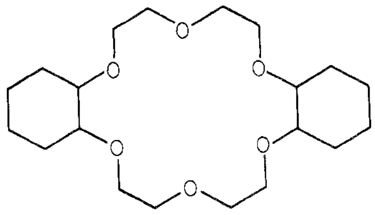
Since crown ethers were first reported by Pedersen,[3] they have been used extensively as cation complexing agents.[4,5] Owing to its ready availability and favorable solubility characteristics, dicyclohexyl-18-crown-6 (I)[3] has found the most use in recent years.[5] When compound I is produced from the catalytic hydrogenation of dibenzo-18-crown-6, two of the possible five isomers of dicyclohexyl-18-crown-6 are produced and have been identified structurally as the cis-syn-cis[7,8] (Ia) and cis-anti-cis[8,9] (Ib) isomers. We have found that the two isomers of I have markedly different ligating properties toward mono- and divalent cations in aqueous and polar, nonaqueous solvents.[10,11] For a given cation, Ia usually has a larger equilibrium constant of formation than does Ib. As expected, Ag^+ reacts in water both with Ia (log K = 2.3)[12] and with Ib (log K = 1.6);[10] however, the reaction with Ia is almost entirely due to favorable entropy effects, $\Delta S = +11$ eu,[11] while the reaction with Ib is almost entirely due to favorable enthalpy effects, $\Delta H = -2.1$ kcal/mol.[10]



Ia, cis-syn-cis isomer
Ib, cis-anti-cis isomer

The two cis isomers of dicyclohexyl-18-crown-6 have been separated by column chromatography on Woelm alumina (activity grade I) using *n*-hexane–diethyl ether solvent mixtures as eluents.[10,11] This separation is costly and very time consuming and yields about 20–30% of each isomer. We have developed a new separation technique which takes advantage of the great solubility differences between the $Pb(ClO_4)_2$ and OH_3ClO_4 complexes of Ia and Ib

$$\mathrm{Ia + Ib + Pb(ClO_4)_2 \xrightarrow{H_2O} [PbIb][ClO_4]_2 \cdot H_2O(s) + [PbIa]^{2+}}$$

$$\mathrm{Ia + Ib + HClO_4 \xrightarrow{H_2O} [OH_3Ia][ClO_4](s) + [OH_3Ib]^+}$$

Nearly all of Ib precipitates from solution as the lead perchlorate complex with essentially no contamination by Ia. Similarly, nearly all of Ia precipitates from solution as the