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Synthesis and Crystal Structure of the Nickel(II) Phosphoranide Complex *trans*-$(PMe_3)_2[(C_4H_6O_3)_2P\text{-}P]NiCl$

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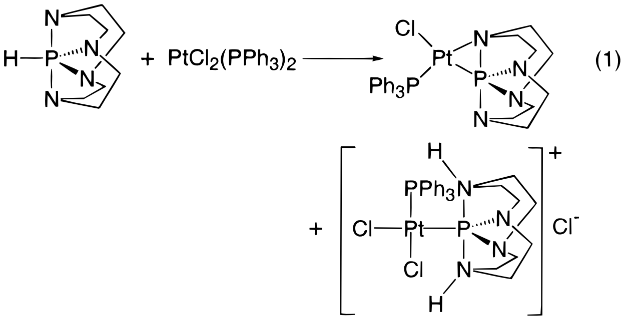
Introduction

The first transition metal phosphoranide or metallophosphorane was prepared in 1981 by Riess.[1] Since then a number of other such compounds have been synthesized primarily by three routes: oxidative addition to the phosphorus of a metal phosphide;[2] nucleophilic substitution of a transition metal carbonyl anion on a chlorophosphorane;[3] deprotonation of a phosphorane.[4] This last method has proved the most fruitful but has employed mainly one specific phosphorane as in eq 1.[4]



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In this work, we propose a variation on the deprotonation method which may provide the most general route to metal phosphoranides yet.

Experimental Section

General Methods. All manipulations were performed under prepurified nitrogen in a Vacuum Atmospheres HE 553-2 glovebox equipped with a MO-40 2H purifier or in standard Schlenk type glassware.

Solvents were dried by refluxing first over calcium hydride and then over sodium benzophenone followed by distillation under Ar. Deuterated benzene was purchased from Aldrich Chemicals and dried over 4 Å molecular sieves and vacuum transferred prior to use.

$HP(OCMe_2COO)_2$ was prepared by the literature method[5] as was $NiCl_2(PMe_3)_2$.[6]

^1H NMR spectra were recorded on a Bruker WH-400 (400 MHz) or a Varian XL-300 (300 MHz). ^{31}P NMR were recorded on a Varian XL-300 (121.42 MHz) and were referenced to external $P(OMe)_3$, set to +141.0 ppm relative to 85% H_3PO_4.

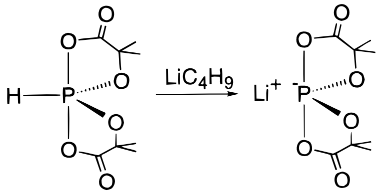
***trans*-$(PMe_3)_2[(C_4H_6O_3)_2P\text{-}P]NiCl$, 1.** To a solution of $HP(OCMe_2COO)_2$ (0.105 g; 0.445 mmol) in THF (10 mL) was added a 1.6 M solution of *n*-butyllithium in hexane (0.3 mL; 0.48 mmol). Then a solution of $[NiCl_2(PMe_3)_2]$ (0.120 g; 0.426 mmol) in THF (5 mL) was added, and the mixture was left stirring for 48 h. The mixture was filtered through Celite, and the solvent was pumped off, yielding a brown powder which was recrystallized from toluene and collected. Yield: 0.135 g (66%). ^1H NMR (C_6D_6): 1.23 (virt. t, ^2J(H,P) = 4.2 Hz), 1.30 (s), 1.32 (s). $^{31}P\{^1H\}$ NMR (C_6D_6, ppm): −11.9 (d), 0.5 (t), ^2J(P,P) = 150 Hz.

X-ray Crystallographic Analysis of 1. Selected crystallographic data appear in Table 1. Data were collected on a Rigaku/ADSC CCD diffractometer. The final unit-cell parameters were based on 16 113 reflections with $2\theta = 4.0-60.3°$. The data were processed[7] and corrected for Lorentz and polarization effects and absorption (empirical, based on a three-dimensional analysis of symmetry-equivalent data using 4th order spherical harmonics).

The structure was solved by the Patterson method. The structure analysis was initiated in the noncentrosymmetric space group $Pna2_1$ on the basis of the *E*-statistics, this choice being validated by subsequent calculations. The binuclear molecule is situated at a crystallographic inversion center. The non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms were fixed in calculated positions with C−H = 0.99 Å and $B_H = 1.2B_{\text{bonded atom}}$. No correction for secondary extinction was necessary. Neutral atom scattering factors for all atoms[8a] and anomalous dispersion corrections for the non-hydrogen atoms[8b] were taken from the *International Tables for X-ray Crystallography*. The polarity was established by parallel refinement of the mirror image, which generated considerably higher residuals (*R* and R_w factor ratios: 1.42 and 1.58, respectively). Selected bond lengths and bond angles appear in Table 2. Complete tables of crystallographic data, atomic coordinates and equivalent isotropic thermal parameters, hydrogen atom parameters, anisotropic thermal parameters, bond lengths, bond angles, torsion angles, intermolecular contacts, and least-squares planes are included as Supporting Information.

Discussion

Synthetic Route. This synthesis of metallophosphoranes involves the deprotonation of a hydro spirobicyclic phosphorane using LiC_4H_9 as shown in eqs 2 and 3 followed by the reaction



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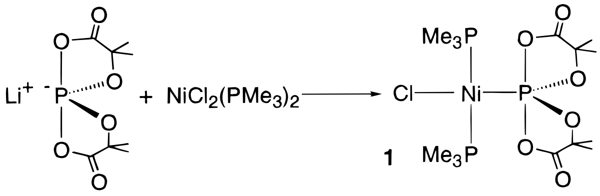

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Table 1. Crystallographic Data

compd	**1**
formula	$C_{14}H_{30}ClNiO_6P_3$
fw	481.46
cryst system	orthorhombic
space group (No.)	$Pna2_1$ (33)
a, Å	17.8221(7)
b, Å	9.3525(10)
c, Å	13.3040(4)
V, Å^3	2217.5(3)
Z	4
ρ_{calc}, g/cm^3	1.442
T, °C	−93
radiation	Mo
λ, Å	0.710 69
μ, cm^{-1}	12.36
transm factors (relative)	0.82−1.00
$R(F)^a$	0.031
R_w (F^2)	0.072

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$ (for reflections with $I \geq 3\sigma(I)$); $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ (based on all data).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *trans*-$(PMe_3)_2[(C_4H_6O_3)_2P$-$P]NiCl$, **1**

Ni(1)−Cl(1)	2.2034(7)	Ni(1)−P(1)	2.1456(7)
Ni(1)−P(2)	2.2506(7)	Ni(1)−P(3)	2.2437(8)
P(1)−O(1)	1.811(2)	P(1)−O(3)	1.618(2)
P(1)−O(4)	1.784(2)	P(1)−O(6)	1.618(2)
P(2)−C(9)	1.820(3)	P(2)−C(10)	1.825(3)
P(2)−C(11)	1.815(3)	P(3)−C(12)	1.823(3)
P(3)−C(13)	1.821(3)	P(3)−C(14)	1.812(3)
Cl(1)−Ni(1)−P(1)	177.61(3)	Cl(1)−Ni(1)−P(2)	85.38(3)
Cl(1)−Ni(1)−P(3)	85.46(3)	P(1)−Ni(1)−P(2)	94.84(3)
P(1)−Ni(1)−P(3)	94.32(3)	P(2)−Ni(1)−P(3)	170.84(3)
Ni(1)−P(1)−O(1)	91.00(6)	Ni(1)−P(1)−O(3)	124.90(7)
Ni(1)−P(1)−O(4)	93.81(7)	Ni(1)−P(1)−O(6)	126.09(7)
O(1)−P(1)−O(3)	88.79(9)	O(1)−P(1)−O(4)	175.18(9)
O(1)−P(1)−O(6)	87.59(9)	O(3)−P(1)−O(4)	88.32(10)
O(3)−P(1)−O(6)	108.96(10)	O(4)−P(1)−O(6)	89.70(9)
Ni(1)−P(2)−C(9)	125.94(10)	Ni(1)−P(2)−C(10)	108.47(11)
Ni(1)−P(2)−C(11)	112.94(10)	C(9)−P(2)−C(10)	101.2(2)
C(9)−P(2)−C(11)	100.91(13)	C(10)−P(2)−C(11)	105.2(2)
Ni(1)−P(3)−C(12)	125.99(10)	Ni(1)−P(3)−C(13)	111.72(11)
Ni(1)−P(3)−C(14)	109.57(11)	C(12)−P(3)−C(13)	101.86(14)
C(12)−P(3)−C(14)	100.4(2)	C(13)−P(3)−C(14)	105.2(2)

of the lithiated species with $NiCl_2(PMe_3)_2$. While deprotonations of hydrophosphoranes have been reported previously,[9] such a reaction has not yet been employed in the synthesis of metallophosphoranes. This route to metallophosphoranes is presented as potentially the most general route yet as both the spirobicyclic phosphorane and metal chloride starting materials can be readily varied.

***trans*-$(PMe_3)_2[(C_4H_6O_3)_2P$-$P]NiCl$, 1.** The above synthesis yielded the brown crystalline compound *trans*-$(PMe_3)_2$-$[(C_4H_6O_3)_2P$-$P]NiCl$, **1**, which was characterized by ^1H and $^{31}P\{^1H\}$ NMR.

In the ^1H NMR spectrum only three signals were observed; there was no signal due to the P−H proton of the starting phosphorane confirming that the depronoration had occurred. A virtual triplet at 1.23 ppm was assigned to the methyls of the PMe_3 ligands while the inequivalent diastereotopic methyls of the phosphoranide ligand gave rise to two singlets at 1.32 and 1.30 ppm. The virtual triplet was suggestive of trans-disposed phosphines, and this was confirmed by the ^{31}P NMR.

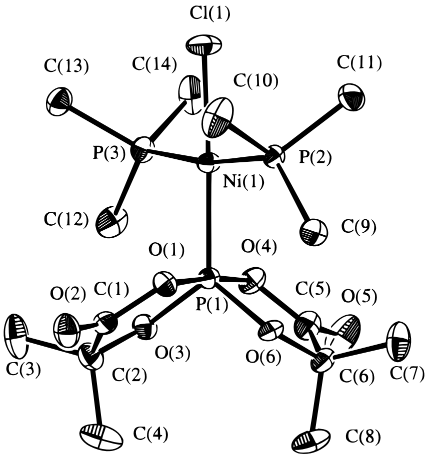

Figure 1. ORTEP view of *trans*-$(PMe_3)_2[(C_4H_6O_3)_2P$-$P]NiCl$, with 50% probability thermal ellipsoids shown for the non-hydrogen atoms.

Rather than the expected doublet and triplet in the ^{31}P NMR, further splitting of the two signals was observed. NMR simulation[10] however showed that this was the beginning of second-order effects in an AB_2 system with $\delta(P_A) = 0.53$ ppm for the phosphoranide signal, $\delta(P_B) = -11.85$ ppm for the phosphine signal, and $^2J(P_A,P_B) = 150$ Hz. (We could then return to the ^1H NMR and likewise simulate the PMe_3 virtual triplet as part of an $A_9XX'A'_9$ system with $^2J(H,P) = 4.2$ Hz and $^2J(P,P') = 150$ Hz.) The AB_2 spin system in the ^{31}P NMR spectrum confirmed the stereochemistry about the nickel as square-planar with trans-disposed phosphines as opposed to an ABC system with cis-disposed phosphines.

Crystal Structure of 1. The structure of compound **1** is shown in Figure 1. The geometry about the nickel atom is square planar with trans PMe_3 ligands, which is consistent with the solution structure as determined by the NMR studies. However there is some angular distortion within the square plane presumably due to the large steric demands of the phosphoranide ligand. The phosphorus atoms on the two phosphine ligands are bent up toward the chloride ligand and away from the phosphorus of the phosphoranide ligand; the Cl−Ni−P(phosphine) angles are 85.38(3) and 85.46(3)°, while the P(phosphoranide)−Ni−P(phosphine) angles are 94.32(3) and 94.84(3)°. The Ni−phosphoranide bond length of 2.1456(7) Å is the shortest metal−P(V) bond length yet recorded.[11] Other bond lengths and angles are included in Table 2.

Also of interest in phosphorane structures is the geometry about the five-coordinate phosphorus. In compound **1** the geometry is that of a distorted trigonal bipyramid (TBP) with the metal in an equatorial position which is consistent with all structurally characterized metalated phosphoranes.[11] In this case the distortion from TBP toward SP is 18.9% as measured by the method of Holmes,[12,13] which is a rather small value by comparison to most other metalated phosphoranes.[11]

Typically with nonmetalated phosphoranes this distortion is toward a square pyramidal geometry (SP) and follows closely the Berry pseudorotation mechanism.[12] We have previously noted[11] that this is not always true in the case of metalated

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phosphoranes. Likewise with compound **1** the distortion does not follow the Berry coordinate as indicated by the fact that the percentage distortions from TBP to SP (18.9%) and from SP to TBP (117.3%) add up to a value significantly greater than 100%. Furthermore the equatorial O(3)−P(1)−O(6) angle has closed down to 108.96° rather than opened up further as it would be expected to in the Berry pseudorotation mechanism. At the same time the four angles between the nickel and each of the other substituents about the phosphorus has opened up to a value greater than 90 or 120°. Therefore it would appear that the distortion about the phosphorus, like that in the square-planar geometry of the nickel, represents an attempt to lessen the steric interactions between the Ni moiety and the other substituents on the phosphorus.

Conclusions

We report the first nickel phosphoranide complex, *trans*-$(PMe_3)_2[(C_4H_6O_3)_2P\text{-}P]NiCl$. The structure of the phosphorane moiety displays distortion from a trigonal bipyramid that does not follow the Berry pseudorotation coordinate. This complex was prepared using a new route: the deprotonation of a hydridophosphorane using *n*-butyllithium, followed by metathesis with a metal chloride. We believe that this route has potential for a general route for the preparation of metal phosphoranide complexes.

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Supporting Information Available: One X-ray crystallographic file, in CIF format, is available on the Internet only. Access information is given on any current masthead page.

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