# Reaction of $NaP_5$ with Half-Sandwich Complexes of Nickel: The First Example of an Ni-Promoted Transformation of the $P_5^-$ Anion

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The reaction of sodium pentaphosphacyclopentadienide, $NaP_5$, with [Cp*NiBr($PPh_3$)] (Cp* = $\eta^5$-$C_5Me_5$) gave only decomposition products. However, with [($\eta^3$-$C_3Ph_3$)NiBr($PMe_2Ph$)] sodium 1,2-diphosphacyclopentadienide was formed, which is the product of an unusual Ni-promoted degradation of the pentaphosphacyclopentadienide anion.

## Introduction

Compounds that contain “naked” oligophosphorus fragments $P_x$ without substituents on the phosphorus atoms are highly interesting, as they can be considered as possible intermediates formed by cleavage of white phosphorus by electrophilic and/or nucleophilic reagents. The investigation of their structure and chemical behavior is one possible method for understanding the pathways of the cleavage of white phosphorus and thus to control this process.[1,2] In addition, $P_x$ fragments are very interesting ligands or building blocks for the construction of various organometallic complexes and clusters, such as unusual one- and two-dimensional polymeric compounds[3] and a unique fullerene-like molecule,[4] which were obtained from pentamethylpentaphosphaferrocene and copper(I) halides. Furthermore, these compounds are very important for understanding the diagonal and isolobal relationship between carbon and phosphorus.[5]

In this respect the pentaphosphacyclopentadienide anion is especially interesting, as this compound is one of the few examples of phosphorus anions for which the organometallic chemistry of the carbon analogue, the cyclopentadienide anion, is well known and thus allows the reactivity of the two compounds to be compared.

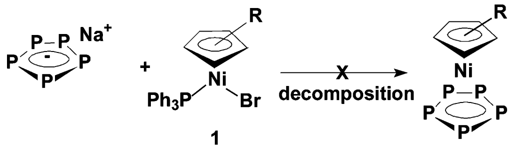
We have previously studied the chemical behavior of $NaP_5$ toward half-sandwich complexes of iron[6,7] and found that the stability of the resulting pentaphosphaferrocenes is highly dependent on the number and nature of the substituents on the cyclopentadienyl ring. Thus, only pentaphosphaferrocenes in which the cyclopentadienyl ring has at least four methyl or two *tert*-butyl or trimethylsilyl groups are stable.

In addition to the steric factor there is also an electronic factor that determines the stability of sandwich complexes with $P_5$ ligands. Thus, most of the transition metal complexes with $P_5$ ligands have 18 valence electrons, an exception being [Ti{$\eta^5$-(*cyclo*-$P_5$)}$_2$]$^{2-}$.[8,9]

We now report on our attempts to extend this chemistry to nickelocene derivatives with 18 or 20 valence electrons.

## Results and Discussion

It is known that the reaction of half-sandwich complexes of nickel with lithium cyclopentadienide, CpLi, gives 20-valence-electron nickelocenes.[10] However, we found that $NaP_5$ reacts with [Cp*NiBr($PPh_3$)] (Cp* = $\eta^5$-$C_5Me_5$)[10] (**1**) to give only decomposition products under various conditions (eq 1).



**(1)**

In all cases a black precipitate formed, which was insoluble in common solvents (hexane, toluene, thf, $CH_2Cl_2$, dmf, dmso). In the $^{31}P$ NMR spectrum of the reaction mixture no signal was detected for $NaP_5$ (at

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(1) Ehses, M.; Romerosa, A.; Peruzzini, M. *Top. Curr. Chem.* **2002**, *220*, 107−140.

(2) Scherer, O. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 1029−1030.

(3) Bai, J.; Virovets, A. V.; Scheer, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1737−1740.

(4) Bai, J.; Virovets, A. V.; Scheer, M. *Science* **2003**, *300*, 781−783.

(5) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy: From Organophosphorus to Phospha-organic Chemistry*; Wiley-VCH: Weinheim, 1998.

(6) Miluykov, V. A.; Sinyashin, O. G.; Scherer, O. J.; Hey-Hawkins, E. *Mendeleev Commun.* **2002**, 1−2.

(7) Miluykov, V. A.; Sinyashin, O. G.; Lönnecke, P.; Hey-Hawkins, E. *Mendeleev Commun.* **2003**, 212−213.

(8) Urnezius, E.; Brennessel, W. W.; Cramer, C. J.; Ellis, J. E.; von Ragué Schleyer, P. *Science* **2002**, *295*, 832−834.

(9) Lein, M.; Frunzke, J.; Frenking, G. *Inorg. Chem.* **2003**, *42*, 2504−2511.

(10) Mise, T.; Yamazaki, H. *J. Organomet. Chem.* **1978**, *164*, 391−400.

10.1021/om050078u CCC: $30.25

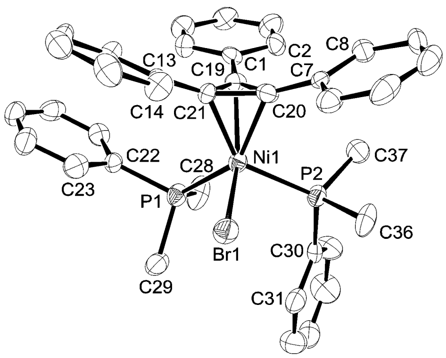
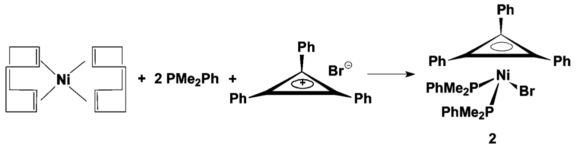


**Figure 1.** Molecular structure of **2**. Hydrogen atoms omitted for clarity; thermal ellipsoids drawn at 50% probability.

+470 ppm). The fact that $PPh_3$ can be isolated from the solution also indicates that a reaction between **1** and $NaP_5$ has taken place. However, the proposed 20-electron complex $[Cp^*NiP_5]$ is apparently unstable.

Thus, replacement of the Cp* ligand by a cyclopropenyl ligand should result in stable 18-valence-electron nickel sandwich complexes with a $P_5$ fragment. A similar reaction of the carbon analogue of $NaP_5$, the $Cp^-$ anion, with $[(\eta^3\text{-}Ph_3C_3)NiCl(py)_2]$ to give $[CpNi(\eta^3\text{-}Ph_3C_3)]$ was already described.[11]

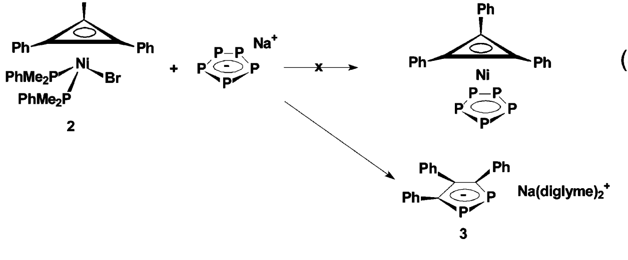
The starting material **2** can be prepared by a known procedure[12] from $[Ni(cod)_2]$, triphenylcyclopropenyl bromide, and 2 equiv of $PMe_2Ph$ (eq 2). Complex **2** was characterized by NMR spectroscopy and X-ray analysis (Figure 1).



(2)

The cyclopropenylium ring has an $\eta^3$ coordination mode, and the C−C (1.425(8) to 1.432(8) Å) and Ni−C (1.970(6) to 2.016(6) Å) bond lengths differ only slightly (Table 2). The shortest distance of Ni(1) to the C(19)−C(20)−C(21) plane is 1.815(2) Å.

Complex **2** was treated with $NaP_5$ at room temperature (eq 3). After 6 h two signals were observed in the $^{31}P$ NMR spectrum of the reaction mixture, of which that at −9 ppm was assigned to $[Ni(PMe_2Ph)_4]$,[13] while the singlet at 190 ppm is in the range characteristic for metal sandwich complexes with $P_5$ fragments.



(3)

However, an X-ray structure determination carried out on crystals obtained from toluene at −30 °C showed that this signal is due to the 1,2-diphospha-3,4,5-triphenylcyclopentadienide anion, obtained as the sodium salt, which is the first structurally characterized 1,2-diphosphacyclopentadienide anion (Figure 2, Table 3).

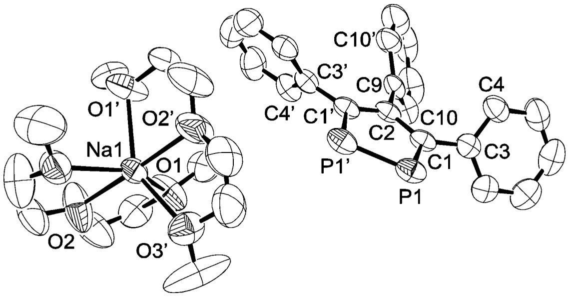


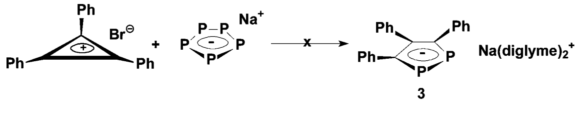
**Figure 2.** Molecular structure of the cation and the 1,2-diphospha-3,4,5-triphenylcyclopentadienide anion in **3**. Hydrogen atoms omitted for clarity; thermal ellipsoids drawn at 50% probability.

The formation of a 1,2-diphosphacyclopentadienide anion, which was, however, only characterized by $^{31}P$ NMR spectroscopy and mass spectrometry, was previously reported by F. Mathey and co-workers.[14]

The anion and the cation are located on a crystallographic $C_2$ axis, which passes through Na(1) and C(2). The three carbon and two phosphorus atoms are coplanar. The P−P distance of 2.111(3) Å is similar to those in $[Cp^*FeP_5]$[15] and $[Li(dme)_3][cyclo\text{-}(1,2,4\text{-}P_3C_2Bu^t_2)]$.[16] The phenyl rings have a propeller-like orientation with dihedral angles of ca. 127°. The sodium cation is solvated by two diglyme molecules in a "meridional-like" fashion, and no cation−anion interaction is observed, which is in contrast to the potassium salt of 1,3-diphosphacyclopentadienide,[17] in which the anion interacts with the potassium cation ($\eta^5$ coordination).

In **3**, the solvated sodium cations and the 1,2-diphosphacyclopentadienide rings are oriented in columns along the *b* axis, and the $C_3P_2$ planes have a parallel arrangement (Figure 3).

Even though it is unclear how the diphosphacyclopentadienide anion is formed, nickel(II) plays an important part in this reaction. Thus, no reaction is observed between triphenylcyclopropenyl bromide and $NaP_5$ in diglyme at room temperature or at 90 °C (eq 4).



(4)

In summary, an unusual Ni-promoted reaction of $NaP_5$ with a cyclopropenyl ring to give the structurally characterized 1,2-diphosphacyclopentadienide anion was observed.

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(11) Rausch, M. D.; Tuggle, R. M.; Weaver, D. L. *J. Am. Chem. Soc.* **1970**, *92*, 4981−4982.

(12) Cecconi, F.; Ghilardi, C. A.; Mindollini, S.; Monet, S.; Orlandini, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 833−834.

(13) Tolman, C. A.; Reutter, D. W.; Seidel, W. C. *J. Organomet. Chem.* **1976**, *117*, C30−C33.

(14) Maigrot, N.; Avarvari, N.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 590−592.

(15) Scherer, O. J.; Bruck, T.; Wolmershäuser, G. *Chem. Ber.* **1988**, *121*, 935−938.

(16) Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Weeber, U.; Westerhausen, M. *Nova Acta Leopoldina* **1985**, *59*, 55−67.

(17) Cloke, F. G. N.; Hitchcock, P. B.; Nixon, J. F.; Wilson, D. J. *Organometallics* **2000**, *19*, 219−220.

**Table 1. Crystallographic Data for [($\eta^3$-$C_3Ph_3$)NiBr($PMe_2Ph$)] (2) and [Na(diglyme)$_2$][*cyclo*-(1,2-$P_2C_3Ph_3$)] (3)**

| | 2 | 3 |
|---|---|---|
| empirical formula | $C_{37}H_{37}BrNiP_2$ | $C_{33}H_{43}NaO_6P_2$ |
| fw | 682.23 | 620.60 |
| cryst color/habit | red/prism | pale pink/thin plate |
| cryst size/mm | 0.20 × 0.05 × 0.05 | 0.40 × 0.10 × 0.01 |
| temperature/K | 210(2) | 210(2) |
| wavelength $\lambda$/pm | 71.073 | 71.073 |
| cryst syst | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2/n$ |
| unit cell dimens | | |
| $a$/pm | 1232.3(3) | 1290.5(4) |
| $b$/pm | 1748.7(5) | 1097.8(3) |
| $c$/pm | 1506.8(4) | 1319.2(4) |
| $\beta$/deg | 99.24(1) | 111.30(1) |
| $V$/nm$^3$ | 3.2049(15) | 1.7413(8) |
| $Z$ | 4 | 2 |
| density (calcd)/Mg·m$^{-3}$ | 1.414 | 1.184 |
| absorption coeff/mm$^{-1}$ | 1.977 | 0.177 |
| $F$(000) | 1408 | 660 |
| $\theta$ range for data collection | 1.80 to 23.28° | 1.85 to 23.27° |
| index ranges | $-13 \leq h \leq 13$<br>$-19 \leq k \leq 19$<br>$-16 \leq l \leq 16$ | $-14 \leq h \leq 14$<br>$-11 \leq k \leq 12$<br>$-14 \leq l \leq 13$ |
| reflns collected | 17 862 | 7363 |
| indep reflns | 4616 [$R$(int) = 0.1310] | 2508 [$R$(int) = 0.0705] |
| restraints/params | 0/374 | 0/192 |
| goodness of fit on $F^2$ | 0.994 | 1.073 |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0609<br>wR2 = 0.0795 | R1 = 0.0770<br>wR2 = 0.1687 |
| $R$ indices (all data) | R1 = 0.1261<br>wR2 = 0.0956 | R1 = 0.1250<br>wR2 = 0.1898 |
| largest diff peak/hole/e·Å$^{-3}$ | 0.436/−0.380 | 0.291/−0.240 |

**Table 2. Selected Bond Lengths (Å) and Angles (deg) in 2 (Ct = center of the cyclopropenyl ring)**

| | | | |
|---|---|---|---|
| C(19)−C(21) | 1.425(8) | Ni(1)−C(21) | 1.996(6) |
| C(19)−C(20) | 1.429(8) | Ni(1)−C(19) | 2.016(6) |
| C(20)−C(21) | 1.432(8) | Ni(1)−Ct | 1.816 |
| Ni(1)−Br(1) | 2.495(1) | Ct−Ni(1)−P(2) | 117.06 |
| Ni(1)−P(1) | 2.254(2) | Ct−Ni(1)−P(1) | 120.34 |
| Ni(1)−P(2) | 2.276(2) | Ct−Ni(1)−Br(1) | 114.97 |
| Ni(1)−C(20) | 1.970(6) | P(1)−Ni(1)−P(2) | 104.69(7) |

**Table 3. Selected Bond Lengths (Å) and Angles (deg) in the 1,2-Diphospha-3,4,5-triphenylcyclopentadienide Anion in 3**

| | |
|---|---|
| P(1)−C(1) | 1.771(4) |
| P(1)−P(1) | 2.111(3) |
| C(1)−C(2) | 1.408(5) |
| C(1)−C(3) | 1.477(6) |
| C(2)−C(9) | 1.499(9) |
| C(1)−P(1)−P(1) | 94.9(2) |
| C(2)−C(1)−P(1) | 116.0(4) |
| C(1)−C(2)−C(1) | 118.1(6) |

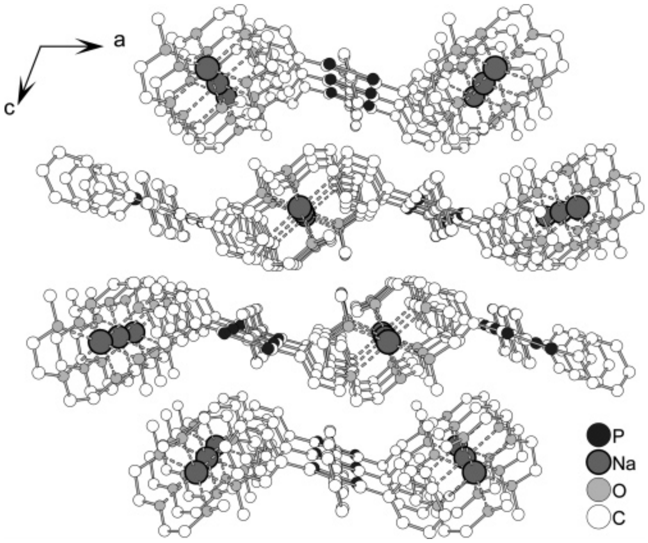

**Figure 3.** Three-dimensional packing of sodium bis(diglyme)-1,2-diphospha-3,4,5-triphenylcyclopentadienide (**3**). Hydrogen atoms omitted for clarity; thermal ellipsoids drawn at 50% probability.

## Experimental Section

**Equipment.** All reactions and manipulations were carried out under dry pure nitrogen in standard Schlenk apparatus. All solvents were distilled from sodium/benzophenone and stored under nitrogen before use. The NMR spectra were recorded on a Bruker AVANCE DRX 400 or an MSL-400 ($^1$H 400 MHz, $^{31}$P 121.7 MHz, $^{13}$C 100.6 MHz). $SiMe_4$ was used as internal reference for $^1$H and $^{13}$C NMR chemical shifts, and 85% $H_3PO_4$ as external reference for $^{31}$P.

**X-ray Analyses.** Data were collected with a Siemens CCD (SMART) diffractometer ($\omega$-scans). Data reduction was performed with SAINT. Empirical absorption correction was performed using the program SADABS. The structures were solved by direct methods, and non-hydrogen atoms were refined anisotropically (SHELX97). All H atoms were calculated on idealized positions and refined isotropically. Pictures were generated with ORTEP3 for Windows.[18] CCDC 261784 (**2**) and 261783 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[18] (a) *SMART*: Area-Detector Software Package; Siemens Industrial Automation, Inc.: Madison, WI, 1993. (b) *SAINT*: Area-Detector Integration Software. Version 6.01; Siemens Industrial Automation, Inc.: Madison, WI, 1999. (c) Sheldrick, G. M. *SADABS*, Program for Scaling and Correction of Area-detector Data; Göttingen, 1997. (d) SHELX97 [Includes SHELXS97, SHELXL97]: Sheldrick, G. M. *SHELX97*. Programs for Crystal Structure Analysis (Release 97-2); University of Göttingen: Germany, 1997. (e) ORTEP3 for Windows: Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

**Synthesis.** $PMe_2Ph$,[19] [Cp*NiBr($PPh_3$)],[10] [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene),[20] and ($Ph_3C_3$)Br[21] were prepared according to literature procedures.

**Sodium Pentaphosphacyclopentadienide, $NaP_5$.**[22] A mixture of white phosphorus (2.04 g, 16 mmol), sodium (0.76 g, 33 mmol), and dibenzo-18-crown-6 (20 mg, 0.055 mmol) in diglyme (40 mL) was refluxed for 6 h. After cooling, the precipitate was filtered off and the solution was used for further reactions without additional purification. The $NaP_5$ concentration of this solution was determined by $^{31}P$ NMR spectroscopy by comparing the intensity of the signal of $NaP_5$ with that of an internal standard (1.0 M solution of $Ph_4PCl$ in THF). $^{31}P$ NMR ($C_6D_6$): $\delta$ 469 (s).

**Bis(dimethylphenylphosphine)triphenylcyclopropenylnickel(II) Bromide (2).** A solution of $PMe_2Ph$ (0.56 mL, 0.54 g, 3.92 mmol) in THF (10 mL) was added at −70 °C to a solution of [Ni(cod)$_2$] (0.54 g, 1.96 mmol) in THF (50 mL). After stirring for 1 h at −70 °C ($Ph_3C_3$)Br (0.71 g, 2.00 mmol) was added and the reaction mixture was stirred for 12 h at room temperature. The mixture was filtered, the solvent evaporated, and the residue dissolved in toluene (10 mL). Hexane (50 mL) was added, and the resulting red precipitate was isolated by filtration, washed three times with cold hexane, and dried in vacuo. Yield: 0.93 g (69.5%) of **2** as red-brown powder. Mp: 157 °C (dec). Crystals suitable for X-ray analysis were grown from toluene at −30 °C. $^1H$ NMR ($C_6D_6$): $\delta$ 1.3 (d, 12 H, $^2J_{PH}$ = 5.7 Hz, Me), 6.8−7.2 (m, 25 H, Ph). $^{13}C$ NMR (thf-$d_8$): $\delta$ 22.03 (d, $^1J_{PC}$ = 12.0 Hz, PMe), 124.91 (s, *m*-C in Ph), 126.50 (s, *m*-C in Ph), 127.67 (s, *p*-C in Ph), 127.78 (s, *p*-C in Ph), 127.91 (d, $^1J_{PC}$ = 11.6 Hz, *ipso*-C in PPh), 128.22 (s, *ipso*-C in Ph), 129.01 (s, *o*-C in Ph), 130.19 (s, *o*-C in Ph), 133.66 (s, C in *C*$_3$Ph$_3$). $^{31}P$ NMR ($C_6D_6$): $\delta$ −6.0 (s). Anal. Calcd for $C_{37}H_{37}BrNiP_2$ (682.23): C, 65.14; H, 5.47; P, 9.08. Found: C, 65.51; H, 5.41; P, 9.27.

**Sodium Bis(diglyme)-1,2-diphospha-3,4,5-triphenylcyclopentadienide (3).** A solution of **2** (1.36 g, 1.99 mmol) in THF (20 mL) was added to a solution of $NaP_5$ in diglyme ($5 \times 10^{-2}$ M, 40 mL). The reaction mixture was stirred for 6 h at room temperature. The solvent was evaporated and the residue extracted three times with 50 mL of toluene. The toluene solution was concentrated (10 mL), and then hexane (50 mL) was added. The resulting precipitate was isolated by filtration and washed with hexane. Yield: 0.72 g (59%) of **3** as light brown powder. Mp: 125 °C (dec). Crystals suitable for X-ray analysis were grown from toluene at −30 °C. $^1H$ NMR (thf-$d_8$): $\delta$ 3.15 (s, 12H, MeO), 3.30 (t, 8H, $^3J_{HH}$ = 5.1 Hz, $OCH_2$), 3.38 (t, 8H, $^3J_{HH}$ = 5.1 Hz, $OCH_2$), 6.63 (t, 2H, $^3J_{HH}$ = 7.3 Hz, *p*-CH in Ph), 6.75 (br s, 9H, Ph), 6.93 (br d, 4H, $^3J_{HH}$ = 7.3 Hz, *o*-CH in Ph). $^{13}C$ NMR (thf-$d_8$): $\delta$ 58.07 (s, MeO), 69.69 (s, $OCH_2$), 71.39 (s, $OCH_2$), 121.77 (s, *m*-C in Ph), 122.96 (s, *m*-C in Ph), 125.91 (s, *p*-C in Ph), 126.20 (s, *p*-C in Ph), 129.73 (t, $^2J_{PC}$ = 4.9 Hz, *ipso*-C in Ph), 131.93 (s, *ipso*-C in Ph), 143.88 (s, *o*-C in Ph), 144.27 (s, *o*-C in Ph), 147.02 (t, $^2J_{PC}$ = 8.9 Hz, *C*-Ph), 161.61 (t, $^1J_{PC}$ = 28.5 Hz, *C*-Ph). $^{31}P$ NMR (thf-$d_8$): $\delta$ 190.0 (s). Anal. Calcd for $C_{33}H_{43}NaO_6P_2$ (620.60): C, 63.86; H, 6.98; P, 9.98. Found: C, 64.1; H, 7.04; P, 9.57.

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**Supporting Information Available:** Crystallographic details, including lists of positional parameters, thermal displacement parameters, bond lengths, and bond angles, for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Bartlett, P. D.; Meguerian, G. *J. Am. Chem. Soc.* **1956**, *78*, 3710−3715.

(20) Krysan, D. J.; Mackenzie, P. B. *J. Org. Chem.* **1990**, *55*, 4229−4230.

(21) Breslow, R.; Won Chang, H. *J. Am. Chem. Soc.* **1961**, *83*, 2367−2375.

(22) Miluykov, V. A.; Sinyashin, O. G. Russian Patent N 2178385, 2002.