

Reaction of NaP₅ with Half-Sandwich Complexes of Nickel: The First Example of an Ni-Promoted Transformation of the P₅[−] Anion

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The reaction of sodium pentaphosphacyclopentadienide, NaP₅, with [Cp^{*}NiBr(PPh₃)] (Cp^{*} = η^5 -C₅Me₅) gave only decomposition products. However, with [η^3 -C₃Ph₃]NiBr(PMe₂Ph)] 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 compounds³ 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 NaP₅ toward half-sandwich complexes of iron^{6,7} and

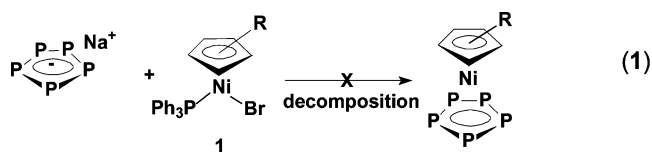
found that the stability of the resulting pentaphosphaferrocenes is highly dependent on the number and nature of the substituents on the cyclopentadienyl ring. Thus, only pentaphosphaferrocenes in which the cyclopentadienyl ring has at least four methyl or two *tert*-butyl or trimethylsilyl groups are stable.

In addition to the steric factor there is also an electronic factor that determines the stability of sandwich complexes with P₅ ligands. Thus, most of the transition metal complexes with P₅ ligands have 18 valence electrons, an exception being [Ti{ η^5 -(cyclo-P₅)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 NaP₅ reacts with [Cp^{*}NiBr(PPh₃)] (Cp^{*} = η^5 -C₅Me₅)¹⁰ (**1**) to give only decomposition products under various conditions (eq 1).



In all cases a black precipitate formed, which was insoluble in common solvents (hexane, toluene, thf, CH₂-Cl₂, dmf, dmsO). In the ³¹P NMR spectrum of the reaction mixture no signal was detected for NaP₅ (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 Phospho-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) Urnezis, 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.

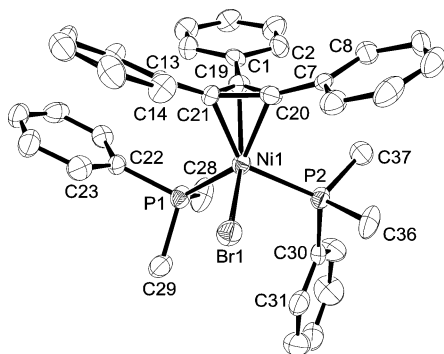
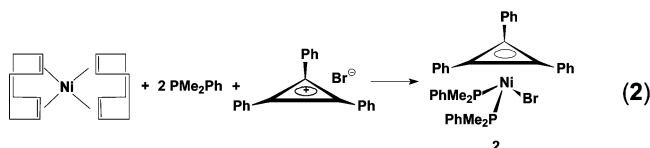


Figure 1. Molecular structure of **2**. Hydrogen atoms omitted for clarity; thermal ellipsoids drawn at 50% probability.

+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 $[\text{Cp}^*\text{NiP}_5]$ 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 $[(\eta^3\text{-Ph}_3\text{C}_3)\text{NiCl}(\text{py})_2]$ to give $[\text{CpNi}(\eta^3\text{-Ph}_3\text{C}_3)]$ was already described.¹¹

The starting material **2** can be prepared by a known procedure¹² from $[\text{Ni}(\text{cod})_2]$, triphenylcyclopropenyl bromide, and 2 equiv of PMe_2Ph (eq 2). Complex **2** was characterized by NMR spectroscopy and X-ray analysis (Figure 1).



The cyclopropenyl ring has an η^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 $[\text{Ni}(\text{PMe}_2\text{Ph})_4]$,¹³ while the singlet at 190 ppm is in the range characteristic for metal sandwich complexes with P_5 fragments.

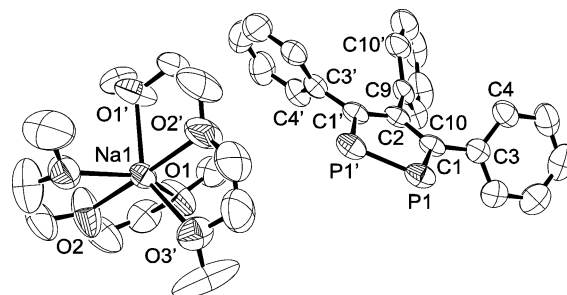
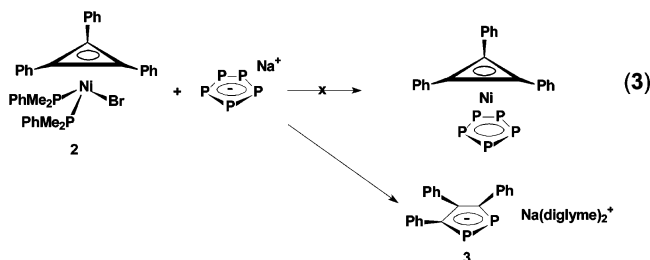


Figure 2. Molecular structure of the cation and the 1,2-diphospha-3,4,5-triphenylcyclopentadienide anion in **3**. Hydrogen atoms omitted for clarity; thermal ellipsoids drawn at 50% probability.

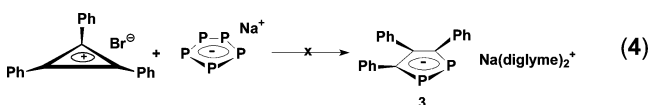
However, an X-ray structure determination carried out on crystals obtained from toluene at -30°C showed that this signal is due to the 1,2-diphospha-3,4,5-triphenylcyclopentadienide anion, obtained as the sodium salt, which is the first structurally characterized 1,2-diphosphacyclopentadienide anion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

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 $[\text{Cp}^*\text{FeP}_5]$ ¹⁵ and $[\text{Li}(\text{dme})_3][\text{cyclo}-(1,2,4\text{-P}_3\text{C}_2\text{Bu}_2)]$.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 (η^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).



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.

(14) Maignot, 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.

(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.

Table 1. Crystallographic Data for [(η^3 -C₃Ph₃)NiBr(PMe₂Ph)] (**2**) and [Na(diglyme)₂][cyclo-(1,2-P₂C₃Ph₃)] (**3**)

	2	3
empirical formula	C ₃₇ H ₃₇ BrNiP ₂	C ₃₃ H ₄₃ NaO ₆ P 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 λ/pm	71.073	71.073
cryst syst	monoclinic	monoclinic
space group	P2 ₁ /n	P2 ₁ /n
unit cell dimens		
<i>a</i> /pm	1232.3(3)	1290.5(4)
<i>b</i> /pm	1748.7(5)	1097.8(3)
<i>c</i> /pm	1506.8(4)	1319.2(4)
β/deg	99.24(1)	111.30(1)
<i>V</i> /nm ³	3.2049(15)	1.7413(8)
<i>Z</i>	4	2
density (calcd)/Mg·m ⁻³	1.414	1.184
absorption coeff/mm ⁻¹	1.977	0.177
<i>F</i> (000)	1408	660
θ range for data collection	1.80 to 23.28°	1.85 to 23.27°
index ranges	−13 ≤ <i>h</i> ≤ 13 −19 ≤ <i>k</i> ≤ 19 −16 ≤ <i>l</i> ≤ 16	−14 ≤ <i>h</i> ≤ 14 −11 ≤ <i>k</i> ≤ 12 −14 ≤ <i>l</i> ≤ 13
reflns collected	17 862	7363
indep reflns	4616 [<i>R</i> (int) = 0.1310]	2508 [<i>R</i> (int) = 0.0705]
restraints/params	0/374	0/192
goodness of fit on <i>F</i> ²	0.994	1.073
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0609 <i>wR</i> 2 = 0.0795	<i>R</i> 1 = 0.0770 <i>wR</i> 2 = 0.1687
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1261 <i>wR</i> 2 = 0.0956	<i>R</i> 1 = 0.1250 <i>wR</i> 2 = 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)

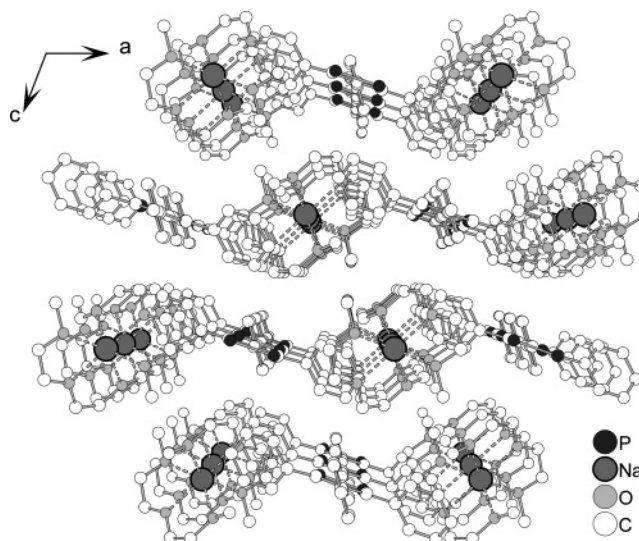
Table 3. Selected Bond Lengths (Å) and Angles (deg) in the 1,2-Diphospha-3,4,5-triphenylcyclopentadienide Anion in **3**

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)

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 (¹H 400 MHz, ³¹P 121.7 MHz, ¹³C 100.6 MHz). SiMe₄ was used as internal reference for ¹H and ¹³C NMR chemical shifts, and 85% H₃PO₄ as external reference for ³¹P.

X-ray Analyses. Data were collected with a Siemens CCD (SMART) diffractometer (ω-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

**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.

(**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).

(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 $[\text{Cp}^*\text{NiBr}(\text{PPh}_3)]$,¹⁰ $[\text{Ni}(\text{cod})_2]$ (cod = 1,5-cyclooctadiene),²⁰ and $(\text{Ph}_3\text{C}_3)\text{Br}$ 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): δ 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 $[\text{Ni}(\text{cod})_2]$ (0.54 g, 1.96 mmol) in THF (50 mL). After stirring for 1 h at -70°C $(\text{Ph}_3\text{C}_3)\text{Br}$ (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): δ 1.3 (d, 12 H, $^2J_{\text{PH}}$ = 5.7 Hz, Me), 6.8–7.2 (m, 25 H, Ph). ^{13}C NMR (thf- d_8): δ 22.03 (d, $^1J_{\text{PC}}$ = 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, $^1J_{\text{PC}}$ = 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_3Ph_3). ^{31}P NMR (C_6D_6): δ -6.0 (s). Anal. Calcd for $\text{C}_{37}\text{H}_{37}\text{BrNiP}_2$ (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 (5×10^{-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): δ 3.15 (s, 12H, MeO), 3.30 (t, 8H, $^3J_{\text{HH}}$ = 5.1 Hz, OCH_2), 3.38 (t, 8H, $^3J_{\text{HH}}$ = 5.1 Hz, OCH_2), 6.63 (t, 2H, $^3J_{\text{HH}}$ = 7.3 Hz, *p*-CH in Ph), 6.75 (br s, 9H, Ph), 6.93 (br d, 4H, $^3J_{\text{HH}}$ = 7.3 Hz, *o*-CH in Ph). ^{13}C NMR (thf- d_8): δ 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, $^2J_{\text{PC}}$ = 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, $^2J_{\text{PC}}$ = 8.9 Hz, C-Ph), 161.61 (t, $^1J_{\text{PC}}$ = 28.5 Hz, C-Ph). ^{31}P NMR (thf- d_8): δ 190.0 (s). Anal. Calcd for $\text{C}_{33}\text{H}_{43}\text{NaO}_6\text{P}_2$ (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.