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Articles

Alkali Metal Bis(*o*-anisyl)phosphides: Characterization of $\mathrm{MP(C_6H_4OMe\text{-}}o)_2$ (M = Li, Na) and Crystal Structure of a Sodium Secondary Organophosphide

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Lithium bis(*o*-anisyl)phosphide **(1)** may be prepared by reaction of *n*-BuLi with bis(*o*-anisyl)phosphine in THF or toluene; sodium bis(*o*-anisyl)phosphide **(2)** is prepared by reaction of sodium with tris(*o*-anisyl)phosphine in liquid ammonia/THF; both compounds are isolated as unsolvated solids. **1** decomposes quantitatively in THF to give tetrakis(*o*-anisyl)diphosphine **(4)**; **2** decomposes in THF to give a mixture containing **4** and bis(*o*-anisyl)phosphine. Addition of diglyme to **2** gives $[\mathrm{Na}\{\mu\text{-}\mathrm{P(C_6H_4OMe\text{-}}o)_2\}(\mathrm{MeO(CH_2CH_2O)_2Me})]_2$ **(2a)**, which has been characterized by single-crystal X-ray diffraction. Each Na atom in **2a** is 6-coordinate, being bonded to two P atoms, three diglyme O atoms, and one O atom from an *o*-anisyl group. Crystal data: monoclinic, $P2_1/n$, a = 14.549(4) Å, b = 18.555(6) Å, c = 15.846(4) Å, β = 91.07(2)°, Z = 4, final R = 0.041, R_w = 0.053.

Introduction

The chemistry of metal complexes of tertiary phenylphosphines can be profoundly altered by the presence of a potentially chelating *o*-methoxy substituent on one or more of the phenyl rings; for example (*o*-methoxyphenyl)phosphine complexes of Ir(I) show enhanced reactivity toward oxidative addition.[1] Recent investigations of the reactions of tris(2,4,6-trimethoxyphenyl)phosphine with $[\mathrm{Rh_2(MeCO_2)_4(MeOH)}]$ demonstrated chelation *via* *o*-methoxy groups as well as C−O bond cleavage in methoxy groups;[2] C−O bond cleavage of anisylphosphines has also been observed on reaction with Li in THF.[3] Our interest in *o*-anisylphosphines began when we showed that the ambidentate bis(*o*-anisyl)phosphide ligand forms complexes with the lanthanides, a group of metals for which complexes with phosphorus donors are extremely rare.[4]

In this paper we report on lithium and sodium bis(*o*-anisyl)phosphides, which are valuable phosphide transfer agents for the synthesis of metal complexes and organophosphine ligands. Detailed structural studies of lithium dialkyl- and diphenylphosphides have shown a remarkable diversity in structures depending on the steric bulk of the alkyl/aryl groups and the presence or absence of coordinating solvents.[5] Reactivity is profoundly affected by the degree of association of the complexes in solution; solvation leads to lower degrees of association and hence to higher reactivity. However, structural data on sodium organophosphides are extremely sparse[6] and we are aware of no published data on sodium salts of *simple* secondary phosphines. The presence of potentially chelating *o*-methoxy groups may be expected to lead to lesser degrees of association and/or solvation in these compounds.

Results and Discussion

Lithium bis(*o*-anisyl)phosphide is most easily prepared by reaction of *n*-BuLi with bis(*o*-anisyl)phosphine at 0 °C.

$$\mathrm{BuLi} + \mathrm{HP(C_6H_4OMe\text{-}}o)_2 \rightarrow \mathrm{LiP(C_6H_4OMe\text{-}}o)_2 + \mathrm{BuH}$$

If the reaction is carried out in toluene, a clear, bright yellow solution is initially formed; a yellow microcrystalline solid **1**, which may be redissolved on gentle heating, is precipitated after a few hours. If the reaction is carried out in THF, the product **(1a)** is precipitated immediately as a bright yellow microcrystalline solid which cannot easily be redissolved even in a large quantity of hot THF. Rapid precipitation of a yellow solid is also effected by addition of THF to a toluene solution of **1**; however after brief vacuum-drying (*ca.* 0.01 mmHg, 20 °C), elemental analysis of **1** and **1a** showed these materials to be the same, unsolvated compound.

Sodium bis(*o*-anisyl)phosphide **(2)** is prepared by cleavage of tris(*o*-anisyl)phosphine with Na in liquid NH_3 and can be isolated as a bright orange-red crystalline product from THF at −10 °C; the *o*-anisylsodium byproduct is destroyed by careful addition of NH_4Cl.

$$\mathrm{P(C_6H_4OMe\text{-}}o)_3 + 2\mathrm{Na} \xrightarrow{\mathrm{NH_3(l)}} \mathrm{NaP(C_6H_4OMe\text{-}}o)_2 + \mathrm{Na(C_6H_4OMe\text{-}}o)$$

The reactions to prepare both **1** and **2** are clean and quantita-

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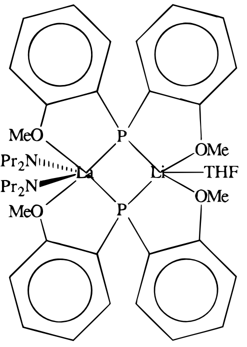
Table 1. NMR Data (ppm)

compound	solvent	$^{31}P\{^1H\}^a$	$^7Li^b$	$^{23}Na^c$
$HP(C_6H_4OMe\text{-}o)_2$	C_6D_6	−74.1		
$[P(C_6H_4OMe\text{-}o)_2]_2$	C_6D_6	−44.1		
$LiP(C_6H_4OMe\text{-}o)_2$	C_7H_8/C_6D_6	−89.3 (br)	5.5 (br)	
$LiP(C_6H_4OMe\text{-}o)_2$	THF/C_6D_6	−70.6 (br)		
$NaP(C_6H_4OMe\text{-}o)_2$	THF/C_6D_6	−64.9 to −71.9, depending on concn		6.4 (broad)
$NaP(C_6H_4OMe\text{-}o)_2$	0.04 M, THF/C_6D_6	−68.7		
	0.075 M, THF/C_6D_6	−70.7		5.1 (br s)
	0.15 M, THF/C_6D_6	−71.8		6.2 (br s)
$[NaP(C_6H_4OMe\text{-}o)_2(diglyme)]_2$	THF/C_6D_6	−61.4		

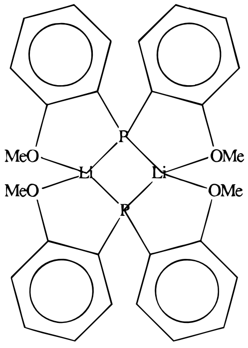
[a] Relative to 85% H_3PO_4 as external reference. [b] Relative to 1 M LiCl in D_2O as external reference. [c] Relative to 1 M NaCl in D_2O as external reference.

tive: ^{31}P NMR spectra of the crude reaction mixtures show no other phosphorus-containing products.

The ^{31}P NMR chemical shifts for **1** are dependent on the solvent (see Table 1); in THF it is likely that a solvate is present, whereas in toluene the complex must be unsolvated. Surprisingly, the THF solvate must be only slightly soluble as, in the presence of THF, a solid is precipitated. Elemental analysis, however, shows that the THF is only weakly coordinated and is rapidly lost under reduced pressure. We have already found that the bis(*o*-anisyl)phosphide ligand in $[La(NPr^i{}_2)_2\{\mu\text{-}P(C_6H_4OMe\text{-}o)_2\}_2Li(THF)]$ **(3)** can chelate through OMe groups to both La and Li as shown below,[4] and a nonpolar dimeric structure may be envisaged for **1** in a noncoordinating solvent. This structure would satisfy the steric requirements of the small Li atom: a coordination number of 4 is observed for Li in $[Li(PPh_2)(THF)_2]_\infty$[5c] and $[Li(PPh_2)(TMEDA)]_2$.[7] We were unable to resolve any Li−P coupling in the ^{31}P or ^7Li NMR spectra of **1** at room temperature, and due to poor solubility, we were unable to record spectra at low temperature.



3



Proposed structure for unsolvated **1**

2 is very soluble in THF and diglyme but is insoluble in toluene, petroleum ether, or diethyl ether; it may be crystallized at −10 °C from concentrated THF solutions. Microanalysis of the vacuum-dried crystals from THF shows them, like **1a**, to be unsolvated, though from the concentration dependence of the ^{31}P NMR chemical shift it is probable that a THF solvate is formed in solution. The unsolvated complex is probably polymeric in order to satisfy the steric requirements of the large Na atom. Addition of 1 equiv of diglyme to a THF solution of **2** resulted a significant change in ^{31}P NMR chemical shift, indicating the formation of a new complex **(2a)**, and deep red-orange crystals analyzing as $[Na\{P(C_6H_4OMe\text{-}o)_2\}(diglyme)]$ could be isolated from THF/petroleum ether at −10 °C.

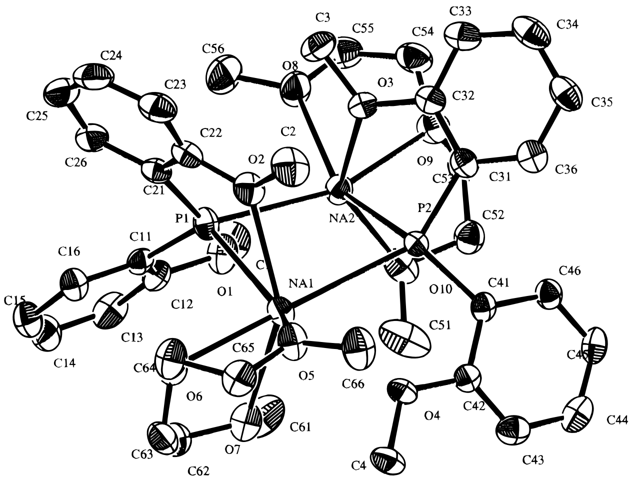


Figure 1. ORTEP plot of **2a**.

1 is rather unstable in solution: after 7 days at room temperature a THF solution shows clean and complete decomposition to tetrakis(*o*-anisyl)diphosphine **(4)**, identified by ^{31}P NMR and mass spectrometry. The mechanism of this reaction is unclear: $[P(C_6H_4OMe\text{-}o)_2]^-$ has been oxidatively coupled, but the identity of the oxidant is unknown. Clean oxidative coupling of $[PPh_2]^-$ has been reported in the presence of mild 1-electron oxidants such as $Cr(OBu^t)_4$[8] or $Ti(NR_2)_3Cl$.[9] Ph_2PPPh_2 has also been reported as a minor byproduct (5%) in the preparation of $LiPPh_2$ from $HPPh_2$ and *n*-BuLi in THF,[10] but no mechanism for its formation was suggested; we have found that $LiPPh_2$ shows some decomposition in THF solution at room temperature, but nowhere nearly as much as **1**. In toluene solution, **1** is rather more stable, and ^{31}P NMR spectroscopy shows partial decomposition to both **4** and secondary phosphine after several days at room temperature. **2** also decomposes in THF over the course of several days at room temperature but forms a small quantity of secondary phosphine as well as **4**.

Crystal Structure of 2a. An ORTEP plot of **2a** is shown in Figure 1; fractional atomic coordinates and selected bond distances and angles are given in Tables 2 and 3, respectively. The molecule consists of two Na atoms bridged by two $P(C_6H_4OMe\text{-}o)_2$ ligands. Each Na is 6-coordinate, being bonded to two P atoms, the three O atoms of a facially coordinated diglyme ligand, and one O atom from an *o*-anisyl group. The average Na−O(diglyme) distance of 2.48 Å is slightly larger than the values of 2.38 Å in $[Na(diglyme)_2]_2[perylene]$[11] and 2.40 Å in $[Na(diglyme)_2][Cp_2Lu(C_{14}H_{10})]$,[12] where the diglyme ligands are meridional, and the O(diglyme)−Na−O(diglyme) bite angles are correspondingly less. The Na(1)−O(4) and Na(2)−O(1) distances are 2.796(2) and 3.068(3) Å, respectively, and thus are too long to be considered as bonded. In contrast to the planar Na_2P_2 ring found in $[Na\{P(C_6H_{11})H\}(pmdeta)]_2$, the Na_2P_2 ring of **2a** is nonplanar, with a P(1)−Na(1)−P(2)−Na(2) torsion angle of −15.91(4)°. The Na−P−Na angles are

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Table 2. Fractional Atomic Coordinates for **2a**

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
P(1)	0.55127(5)	0.24754(5)	0.92591(5)	C(24)	0.6722(3)	0.4507(2)	0.7975(2)
P(2)	0.26428(5)	0.24842(5)	0.87650(5)	C(25)	0.7256(3)	0.4134(2)	0.8539(2)
Na(1)	0.43040(7)	0.19677(6)	0.79093(7)	C(26)	0.6933(2)	0.3514(2)	0.8918(2)
Na(2)	0.39311(8)	0.25622(7)	1.03001(7)	C(31)	0.2037(2)	0.3302(2)	0.9070(2)
O(1)	0.5591(1)	0.1633(1)	1.0821(1)	C(32)	0.2536(2)	0.3871(2)	0.9446(2)
O(2)	0.4691(1)	0.3315(1)	0.7928(1)	C(33)	0.2129(2)	0.4520(2)	0.9662(2)
O(3)	0.3461(1)	0.3737(1)	0.9605(1)	C(34)	0.1193(3)	0.4632(2)	0.9502(2)
O(4)	0.2715(1)	0.1120(1)	0.7897(1)	C(35)	0.0682(2)	0.4093(2)	0.9111(2)
O(5)	0.3890(1)	0.2112(1)	0.6458(1)	C(36)	0.1107(2)	0.3454(2)	0.8903(2)
O(6)	0.5591(1)	0.1615(1)	0.6942(1)	C(41)	0.1787(2)	0.1782(2)	0.8833(2)
O(7)	0.4832(1)	0.0670(1)	0.8070(1)	C(42)	0.1942(2)	0.1126(2)	0.8396(2)
O(8)	0.4675(1)	0.3319(1)	1.1372(1)	C(43)	0.1368(2)	0.0535(2)	0.8478(2)
O(9)	0.2859(1)	0.2931(1)	1.1385(1)	C(44)	0.0612(2)	0.0564(2)	0.8992(2)
O(10)	0.3269(2)	0.1483(1)	1.1049(1)	C(45)	0.0442(2)	0.1189(2)	0.9438(2)
C(1)	0.5630(3)	0.1484(2)	1.1707(2)	C(46)	0.1013(2)	0.1777(2)	0.9351(2)
C(2)	0.4052(2)	0.3734(2)	0.7450(2)	C(51)	0.3156(3)	0.0825(2)	1.0600(3)
C(3)	0.4058(2)	0.4334(2)	0.9739(2)	C(52)	0.2417(2)	0.1721(2)	1.1369(2)
C(4)	0.2826(2)	0.0529(2)	0.7338(2)	C(53)	0.2583(2)	0.2356(2)	1.1917(2)
C(11)	0.6463(2)	0.1918(2)	0.9623(2)	C(54)	0.3174(3)	0.3551(2)	1.1832(2)
C(12)	0.6387(2)	0.1519(2)	1.0370(2)	C(55)	0.4169(3)	0.3499(2)	1.2099(2)
C(13)	0.7060(2)	0.1034(2)	1.0628(2)	C(56)	0.5638(3)	0.3421(2)	1.1478(3)
C(14)	0.7832(2)	0.0922(2)	1.0148(2)	C(61)	0.4766(3)	0.0456(2)	0.8926(2)
C(15)	0.7930(2)	0.1310(2)	0.9409(2)	C(62)	0.5721(2)	0.0556(2)	0.7748(2)
C(16)	0.7260(2)	0.1795(2)	0.9157(2)	C(63)	0.5720(2)	0.0858(2)	0.6870(2)
C(21)	0.6060(2)	0.3226(2)	0.8733(2)	C(64)	0.5457(2)	0.1977(2)	0.6157(2)
C(22)	0.5536(2)	0.3619(2)	0.8131(2)	C(65)	0.4494(2)	0.1895(2)	0.5814(2)
C(23)	0.5847(3)	0.4249(2)	0.7770(2)	C(66)	0.2963(2)	0.2151(2)	0.6167(2)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2a**

Bond Lengths			
P(1)−Na(1)	2.901(2)	Na(1)−O(6)	2.529(2)
P(1)−Na(2)	2.861(2)	Na(1)−O(7)	2.538(3)
P(2)−Na(1)	2.953(2)	Na(2)−O(3)	2.531(3)
P(2)−Na(2)	3.047(2)	Na(2)−O(8)	2.441(3)
Na(1)−O(2)	2.563(3)	Na(2)−O(9)	2.441(2)
Na(1)−O(5)	2.381(2)	Na(2)−O(10)	2.527(3)
Bond Angles			
Na(1)−P(1)−Na(2)	87.73(4)	P(1)−Na(2)−O(10)	122.95(7)
Na(1)−P(2)−Na(2)	83.42(4)	P(2)−Na(2)−O(3)	62.36(6)
P(1)−Na(1)−P(2)	92.64(4)	P(2)−Na(2)−O(8)	147.26(8)
P(1)−Na(1)−O(2)	62.89(5)	P(2)−Na(2)−O(9)	100.60(7)
P(1)−Na(1)−O(5)	144.53(7)	P(2)−Na(2)−O(10)	95.94(7)
P(1)−Na(1)−O(6)	94.91(6)	O(3)−Na(2)−O(8)	85.43(9)
P(1)−Na(1)−O(7)	93.21(6)	O(3)−Na(2)−O(9)	83.91(8)
P(2)−Na(1)−O(2)	81.94(6)	O(3)−Na(2)−O(10)	141.68(8)
P(2)−Na(1)−O(5)	102.29(7)	O(8)−Na(2)−O(9)	68.27(8)
P(2)−Na(1)−O(6)	169.81(7)	O(8)−Na(2)−O(10)	107.25(9)
P(2)−Na(1)−O(7)	120.68(6)	O(9)−Na(2)−O(10)	68.73(8)
O(2)−Na(1)−O(5)	87.34(8)	C(11)−P(1)−C(21)	125.9(1)
O(2)−Na(1)−O(6)	95.43(8)	C(11)−P(1)−Na(1)	119.8(1)
O(2)−Na(1)−O(7)	149.09(8)	C(11)−P(1)−Na(2)	117.8(1)
O(5)−Na(1)−O(6)	67.68(7)	C(21)−P(1)−Na(1)	100.1(1)
O(5)−Na(1)−O(7)	105.89(8)	C(21)−P(1)−Na(2)	100.1(1)
O(6)−Na(1)−O(7)	65.74(7)	C(31)−P(2)−C(41)	104.3(1)
P(1)−Na(2)−P(2)	91.51(4)	C(31)−P(2)−Na(1)	142.7(1)
P(1)−Na(2)−O(3)	90.64(6)	C(31)−P(2)−Na(2)	92.4(1)
P(1)−Na(2)−O(8)	94.73(7)	C(41)−P(2)−Na(1)	111.4(1)
P(1)−Na(2)−O(9)	162.45(7)	C(41)−P(2)−Na(2)	113.7(1)

close to the value of 86.2(2)° found for [Na{P(C_6H_{11})H}-(pmdeta)]$_2$;[6a] other angles around the P atoms are similar to those found in **3**. The P−Na−O(anisyl) bite angles are similar to the P−La−O(anisyl) angle of 60.9(2)° of **3** and significantly smaller than the P−Li−O(anisyl) angle of 74.2°, which is to be expected when one considers the relative radii of the metals. The Na−P bond distances vary over a range of *ca.* 0.19 Å from slightly less to slightly greater than those (2.884(8) and 2.936 Å) found in [Na{P(C_6H_{11})H}(pmdeta)]$_2$.

Experimental Section

All the preparations described below were performed under strictly anaerobic conditions using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone ketyl (nondeuterated) or CaH_2 (deuterated) and stored over 4 Å molecular sieves prior to use. Samples for NMR spectroscopy were sealed under vacuum, and spectra were recorded on a Bruker WM250 or AC200 spectrometer. Elemental analyses were performed in duplicate by Mr. S. Apter of this department. HP(C_6H_4OMe-*o*)$_2$ was prepared as previously reported.[4]

Preparation of P(C_6H_4OMe-*o*)$_3$. P(C_6H_4OMe-*o*)$_3$ was prepared by a modification of the published method.[13] To a solution of *n*-BuLi (63.7 cm^3, 184 mmol of a 2.89 M solution in hexanes) and TMEDA (27.8 cm^3, 184 mmol) in Et_2O (100 cm^3) at 0 °C was added anisole (20 cm^3, 184 mmol). The resulting solution was allowed to warm slowly to room temperature and was stirred for 16 h to give a pale yellow solution. This solution was cooled to 0 °C with stirring, and PCl_3 (5.4 cm^3, 61.33 mmol) was added slowly by syringe. A vigorous reaction occurred, and an ivory-colored precipitate formed. The reaction mixture was allowed to warm to room temperature and was then heated to reflux for 1 h. It was then diluted with Et_2O (200 cm^3), and the resultant solution was poured into dilute NaOH (400 cm^3). The mixture was then filtered to remove the ivory-colored precipitate, and the organic phase was separated from the filtrate and evaporated on a rotary evaporator to give a white solid and a small amount of unreacted anisole, which was removed by washing with Et_2O. The white solid was recrystallized from CH_2Cl_2 to give pure product. Yield = 16.1 g (75%). Anal. Calcd for $C_{21}H_{21}P$: C, 71.58; H, 6.01%. Found: C, 69.10; H, 5.87. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −39.0 ppm (s).

Preparation of LiP(C_6H_4OMe-*o*)$_2$ (1). Butyllithium (0.97 cm^3 of a 2.648 M solution in hexanes, 2.60 mmol) was added to a solution of HP(C_6H_4OMe-*o*)$_2$ (0.640 g, 2.60 mmol) in toluene (20 cm^3) at 0 °C. A bright yellow coloration developed immediately, and after approximately 1 h a bright yellow precipitate of **1** had formed. The reaction was shown by ^{31}P NMR spectroscopy to be quantitative. Anal. Calcd for $C_{14}H_{14}LiO_2P$: C, 66.68; H, 5.60. Found: C, 66.50; H, 5.42.

When this reaction was carried out using THF as solvent instead of toluene, a bright yellow solid **(1a)** was precipitated immediately. This was isolated and dried *in vacuo*. Anal. Found: C, 66.69; H, 6.58.

Preparation of NaP(C_6H_4OMe-*o*)$_2$ (2). NaP(C_6H_4OMe-*o*)$_2$ was prepared by a modification of the published method.[14] A dispersion of P(C_6H_4OMe-*o*)$_3$ (6.057 g, 17.19 mmol) in THF (50 cm^3) was added to a solution of Na (1.61 g, 70.00 mmol) in liquid NH_3 (110 cm^3) at −78 °C. The initially deep blue solution was stirred at −78 °C for 4

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h, during which it slowly turned deep red. The reaction mixture was then allowed to warm to room temperature, and the NH_3 was evaporated. A further portion of THF (50 cm^3) was added, and the resulting bright red solution was decanted from unreacted Na. The solution was cooled to −78 °C, and a slurry of freshly sublimed NH_4Cl (0.923 g, 17.25 mmol) in THF (50 cm^3) was added to destroy NaC_6H_4OMe-*o*. On warming of the mixture to room temperature, the bright red solution of $NaP(C_6H_4OMe\text{-}o)_2$ was separated from the precipitated NaCl. The preparation was shown to be quantitative by ^{31}P NMR spectroscopy. Fine orange needle-shaped crystals, unsuitable for X-ray diffraction, could be isolated from cold concentrated THF solutions. Anal. Calcd for $C_{14}H_{14}NaO_2P$: C, 62.69; H, 5.26; P, 11.55. Found: C, 62.39; H, 5.26; P, 11.78.

Preparation of $[NaP(C_6H_4OMe\text{-}o)_2(CH_3(OCH_2CH_2)_2OCH_3)]_2$ (2a). $NaP(C_6H_4OMe\text{-}o)_2$ (0.478 g, 1.78 mmol) was dissolved in diglyme (10 cm^3). Petroleum ether, 40/60 (15 cm^3), was added, and the slightly cloudy deep orange-red solution was cooled to −10 °C. Orange prisms suitable for X-ray diffraction were deposited after a period of several weeks. Anal. Calcd for $C_{20}H_{28}NaO_5P$: C, 59.71; H, 7.02. Found: C, 60.34; H, 7.09.

2a could also be prepared by addition of 1 equiv of diglyme to a THF solution of **2**. Crystallization was effected by addition of petroleum ether and cooling to 0 °C.

X-ray Data Collection and Structure Determination and Refinement for 2a. An air-sensitive orange prism, approximate dimensions 0.5 × 0.2 × 0.65 mm, was mounted on a glass fiber in N_2-saturated Nujol oil and cooled to −120 °C in a stream of N_2 gas. All measurements were made on a Rigaku AFC6S diffractometer. A summary of crystallographic data is given in Table 4. The cell constants were obtained from 25 carefully centered reflections in the range $34.17 < 2\theta < 40.24°$. The intensities of 3 representative reflections which were measured after every 150 reflections remained constant throughout data collection, indicating sample and electronic stability.

The structure was solved using direct methods and refined by full-matrix least-squares methods using the TEXSAN software package.[15] Non-hydrogen atoms were refined anisotropically; hydrogen atoms were either located from difference maps or included in calculated positions ($d_{C-H} = 0.95$ Å) and were not refined. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.36 and −0.26 e/$Å^3$.

Table 4. Crystallographic Data for **2a**

empirical formula	$C_{40}H_{56}O_{10}P_2Na_2$
fw	804.80
crystal system	monoclinic
space group	$P2_1/n$ (No. 14)
lattice params	
a	14.549(4) Å
b	18.555(6) Å
c	15.846(4) Å
β	91.07(2)°
V	4277(2) $Å^3$
Z	4
D_{calc}	1.250 g cm^{-3}
F_{000}	1712
μ(Mo Kα)	1.68 cm^{-1}
radiation	Mo Kα ($\lambda = 0.710\ 69$ Å)
temp	−120 °C
no. of reflns	total: 8070 unique: 7744 ($R_{int} = 0.062$)
no. of observns ($I > 3.00\sigma(I)$)	5047
corrections	Lorentz−polarization
no. of variables	487
refln/param ratio	10.36
R^a	0.041
$R_w{}^b$	0.053
goodness of fit indicator	1.96

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

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Supporting Information Available: Tables of all atomic coordinates, thermal parameters, intramolecular bond lengths and angles, torsion angles, and experimental details of the X-ray structure determination for **2a** (22 pages). Ordering information is given on any current masthead page.

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(15) *TEXSAN-TEXRAY Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985.