Synthesis and Characterization of the Very Bulky Phenols Ar*OH and Ar′OH ($Ar^* = C_6H_3$-2,6-$Trip_2$, Trip = C_6H_2-2,4,6-$i$$Pr_3$; Ar′ = C_6H_3-2,6-$Dipp_2$, Dipp = C_6H_3-2,6-$i$$Pr_2$) and Their Lithium and Sodium Derivatives $(LiOAr')_2$ and $(NaOAr^*)_2$

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Dedicated to the memory of Ron Snaith, a pioneer in alkali metal chemistry

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The very bulky phenols Ar*OH (**1**) and Ar′OH (**2**), where Ar* = C_6H_3-2,6-$Trip_2$ (Trip = C_6H_2-2,4,6-$i$$Pr_3$) and Ar′ = C_6H_3-2,6-$Dipp_2$ (Dipp = C_6H_3-2,6-$i$$Pr_2$), as well as their lithium and sodium derivatives $(LiOAr^*)_2$ (**3**), $(LiOAr')_2$ (**4**) and $(NaOAr^*)_2$ (**5**) have been synthesized and characterized. The terphenols **1** and **2** were obtained by the reaction of the aryllithium reagents with nitrobenzene and were isolated in *ca.* 70% yield. The lithium or sodium salts **3**–**5** were isolated by the reaction of **1** or **2** with nBuLi or sodium metal. All compounds were characterized spectroscopically, and by X-ray crystallography in the case of **1**, **2**, **4** and **5**. The large terphenyl substituents prevent hydrogen-bonded association of the phenols **1** and **2**. Instead, the O–H hydrogens interact with the π-electron cloud on one of the flanking Trip or Dipp rings. The dimeric structures of **4** and **5** are relatively rare examples of structurally characterized alkali metal phenoxides that are unsolvated by internal electron pair donors or classical Lewis bases such as ethers or amines.

Introduction

The continuing interest in sterically encumbered phenols is mainly due to use of their deprotonated derivatives (aryloxides) as protecting ligands for a large variety of metallic and non-metallic reactive centers.[1] Such ligands have been extensively used to stabilize low coordinate compounds,[1,2] persistent odd-electron species[3] and heavier main group compounds with multiple bonds.[4] Aryloxides have been used as supporting ligands in metal catalysts as exemplified by the employment of Zn^{II} and Cd^{II} aryloxide derivatives in the copolymerization of epoxides and carbon dioxide.[5] In addition, aryloxide ligands have been employed to synthesize bowl-shaped Lewis acid host molecules as in $Al\{OC_6H_3\text{-}2,6\text{-}Ph_2\}_3$ which can encapsulate Lewis base guests and protect and accelerate chemical reactions with various substrates.[6] The most common, currently used, sterically hindered aryloxides are those that employ either tBu or Ph substituents at the ortho positions of the phenoxide aryl ring. Some members of these ligand classes are commercially available as illustrated by the examples 1-HOC_6H_2-2,4,6-$t$$Bu_3$ and 1-HOC_6H_3-2,6-Ph_2. In both of these ligands, however, the ortho tBu or Ph groups are susceptible to activation either to form oxametallacycle rings, or dehydrogenation can occur in the alkyl-substituted species. For the phenyl-substituted -OC_6H_3-2,6-Ph_2 activation of the ortho phenyls by close approach of the phenyl CH groups to the reactive center can occur by rotation of the ortho phenyl ring so that it is almost coplanar with the central phenoxide moiety. Recent work by Rothwell and coworkers has shown that when large meta substituents are also present at the central ring, as in -OC_6H-2,6-Ph_2-3,5-$t$$Bu_2$,[7] resistance or immunity to the cyclometallation reaction is induced because the ortho phenyl rings cannot become coplanar with the central ring due to the steric effects of the tBu substituents. In related work we have pursued the use of very bulky terphenyl ligands in the stabilization of several new compound classes.[8] In these ligands, bulky substituents have been introduced on the flanking aryl rings [e.g., iPr groups in -C_6H_3-2,6-$i$$Pr_2$(Dipp) or -$C_6H_2$-2,4,6-$i$$Pr_3$(Trip)] to prevent them from becoming coplanar with the central phenyl ring. In this way an approximately perpendicular orientation of the flanking rings is maintained which protects the wedge shaped cavity containing the reactive center. In much of this work the terphenyl ligand has been attached directly to the reactive center. However, we have also shown that several derivatives of terphenyl ligands (or their precursors) can be synthesized by attachment of

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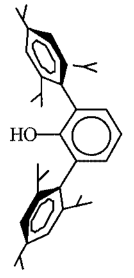
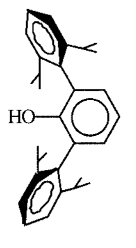
-NH_2,[9] PH_2,[9] AsH_2,[9] SbH_2,[9] -SH,[10] or SeH[10] groups to the central phenyl ring at the C-1 position to give very bulky terphenylamines, phosphanes, thiols, etc. A notable omission from this list are the corresponding phenol derivatives. Their absence can be partially explained on the basis of synthetic difficulties due to steric hindrance and solubility effects. In seeking a route to such compounds we have examined several synthetic routes to the two bulky terphenols and show that they can be synthesized in good yield and that they readily form alkali metal salts in essentially quantitative yields.



1-HOC_6H_3-2,6-$Trip_2$, Ar*OH

1



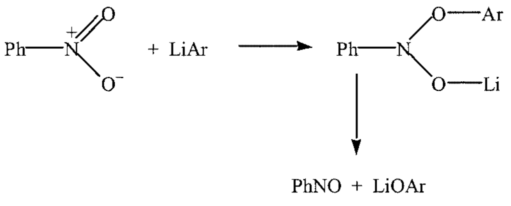
1-HOC_6H_3-2,6-$Dipp_2$, Ar'OH

2

Results and Discussion

Synthesis

There exist several methods for the synthesis of phenols on a laboratory scale.[11] Among the most prominent of these are the diazotization of arylamines followed by hydrolysis, conversion of halides to phenols in the presence of concentrated KOH or NaOH, and the sulfonation-alkaline melting process. The synthesis of the bulky phenols **1** and **2** was attempted by each of these methods. None afforded yields that were useful. It seems likely that the steric effects of the flanking aryl rings and the low solubility of the aryl halide precursors in aqueous phases prevent efficient reactions in these cases. There are other routes to terphenols in the literature[12,13] but since we already had terphenyllithium reagents to hand, we were drawn to the, apparently little used, anhydrous route,[14] which involves the reaction between nitrobenzene and an aryllithium derivative and afforded as products the nitrosobenzene and the lithium aryloxide salt as depicted below.



It may be noted that the addition of the bulky aryl group, Ar, to nitrogen is disfavored for steric reasons, although it seems likely that products in which the Ar group is bound to nitrogen will be obtained under appropriate reaction conditions. Quenching of the reaction with a methanol/water mixture affords ArOH in ca. 70% yield for both of the very bulky aryl substituents Ar = Ar* and Ar′. The above route was discovered in 1966−67[14] during the investigation of the reactions of various substituted benzenes with organolithium compounds. The reaction of *o*-nitrobromobenzene with phenyllithium readily afforded the expected *o*-nitrophenyllithium.[15] However, it was found that for pure nitrobenzene the nitro group rather than the aryl ring was attacked. Investigations showed that the addition of one equivalent of phenyllithium to nitrobenzene in THF, with cooling to ca. −95 °C, afforded nitrosobenzene and lithium phenoxide in good yield. We found that a similar reaction result is obtained upon treatment of nitrobenzene with the very bulky lithium reagents LiAr*[11] or LiAr′[12] which afford nitrosobenzene and LiOAr* or LiOAr′ which can then be hydrolysed to give the terphenols **1** and **2**. The terphenols may then be readily converted into their lithium or sodium salts by reaction with *n*BuLi or sodium metal.

Structures

The main feature of the structures of **1** (Figure 1) and **2** (Figure 2) is that they are monomers and contain no inter-

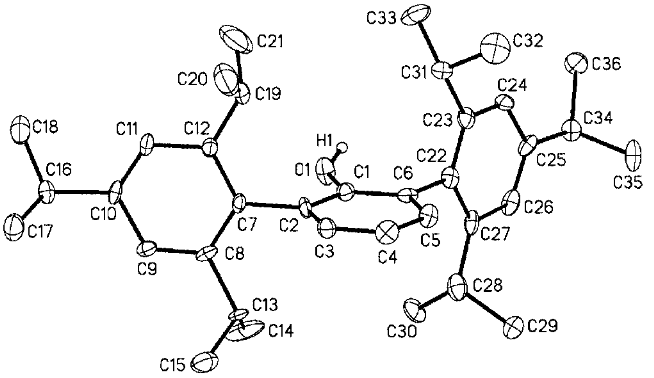


Figure 1. Thermal ellipsoid (35%) plot of **1**. H atoms (except O−H) are not shown; selected bond lengths and angles are given in Table 2

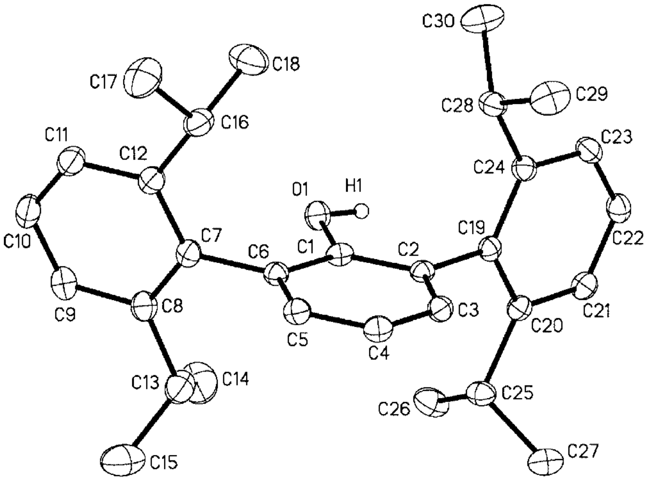


Figure 2. Thermal ellipsoid (35%) plot of **2**. H atoms (except O−H) are not shown; selected bond lengths and angles are given in Table 2

molecular hydrogen bonding. Although alcohols and phenols are prone to intermolecular hydrogen bonding, this is prevented in **1** and **2** by the steric effects of the ortho Trip or Dipp substituents. Instead, the structures of **1** and **2** show evidence of interaction between the O−H hydrogens and the π-electrons of an ortho phenyl ring. The coordination planes of the O(1) atom and the central aryl ring plane are essentially coincident in each molecule. In **1** the H(1)···C(22) distance is 2.64 Å and in **2** the corresponding H(2)···C(19) separation is 2.39 Å. In addition there is a long H(2) to Dipp(centroid) contact of 3.30 Å to a Dipp ring in an adjacent molecule in **2**, although an interaction of this length may not be significant. The intramolecular O−H···Ar distances resemble those found in the structure of 2,6-diphenylphenol [2.40(4) and 2.43 Å].[16] The O−H stretching frequencies observed in **1** and **2** (3520 and 3530 cm^{-1}) also support the existence of an O−H···π interaction since they are red shifted by 70−80 cm^{-1} in comparison to the O−H stretching frequency observed for phenol in dilute CCl_4 solution.[17] However, there is no clear pattern in the angles and distances surrounding the O(1), C(1), C(2) and C(6) atoms in the molecules that suggests that the O−H···π interaction has any systematic effect on the geometry in the remainder of the molecule. A previous publication has noted that the O−C(1)−C(ortho) angle on the side of the hydroxyl group is wider.[16] While this is true for **2** [120.8(1) vs. 117.1(1)°], the opposite is the case for **1** [116.9(5) vs. 120.7(5)°]. The internal angle at the ipso−C(1) atom exceeds the idealized 120° value by ca. 2° and this is consistent with previous structures of phenols,[16,18,19] and the fact that the very electronegative oxygen substituent removes electron density from C(1) toward itself, thereby permitting a widening of the C(2)−C(1)−C(6) angle. The C−O bond lengths in **1** and **2** are similar to those observed in other sterically encumbered phenols.[14,16,17] As in most structures with bulky terphenyl ligands[8] the flanking aryl rings subtend almost vertical angles (83.1−85.7°) with the central ring and this is maintained in solution, as evidenced by the observation of two sets of methyl doublets for the *i*Pr groups.

Both **1** and **2** react immediately with *n*BuLi to form the lithium salts LiOAr* (**4**) or LiOAr′ (**5**). However, only crystals of the LiOAr′ species were suitable for X-ray crystallography. These proved to exist as dimers, as shown in Figure 3. This structure is a relatively rare example of an alkali metal aryloxide unsolvated[20−24] by internal Lewis base donors or molecules such as Et_2O, THF or pyridine. It consists of centrosymmetric dimers in which the lithiums bridge two OAr′ groups. The lower degree of aggregation in **5** may be contrasted with the trimer structure observed for $(LiOC_6H\text{-}2,6\text{-}Ph_2\text{-}3,5\text{-}t\text{Bu}_2)_3$ [24] which has the less crowded phenyl substituents in the ortho positions. The planar Li_2O_2 rhombic core features two different Li−O distances of 1.807(3) and 1.979(3) Å and LiOLi and OLiO angles of 81.2(1)° and 98.8(1)°. These distances lie near the lower and upper extremities of the known Li−O range for dimeric solvated and unsolvated LiOR species.[18−25] Each lithium further interacts with the ipso (Li−C = 2.39 Å) and ortho carbons (Li−C = 2.54 and 2.65 Å) of a flanking Dipp ring. The Ar′ groups are tilted toward the side which interacts with the lithiums as indicated by the ca. 22° difference between the LiOC angles. The oxygen atoms have almost stanar coordination. The O−C bond length of 1.335(2) is 0.05−0.07 Å shorter than the corresponding distances in **1** and **2** probably as a result of the increased ionic contribution to the O−C bond strength when hydrogen is replaced by lithium. The flanking aryl rings subtend angles of 88.3° (C7 ring) and 82.8° (C19 ring) with respect to the central ring. A notable difference between the structure of $(LiOAr')_2$ and **1** and **2** concerns the internal angle at the ipso carbon of the central aryl ring of the terphenyl substituent. The much more negative character of the oxygen in the lithium salt means that, relatively speaking, it is less electronegative than the oxygens in **1** and **2**. This is reflected in the C(2)−C(1)−C(6) angle, which, at 117.55(14)°, is ca. 4.5° narrower than the corresponding angle in **2**.

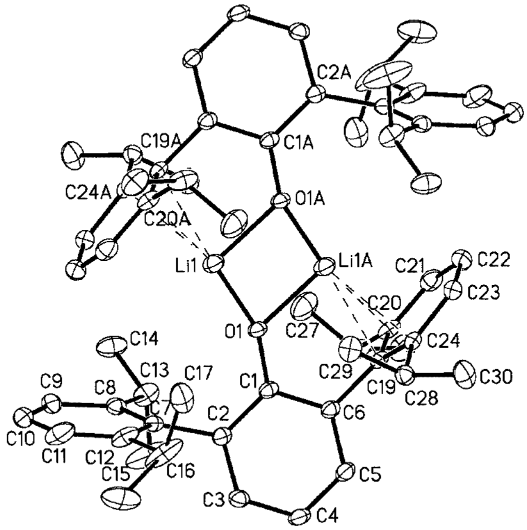


Figure 3. Thermal ellipsoid (35%) plot of **5**. H atoms are not shown; selected bond lengths and angles are given in Table 2

The structure of NaOAr* (**4**; Figure 4) is a relatively rare example of a structurally characterized unsolvated (by internal or external Lewis base donors) sodium phenolate. It crystallizes as two slightly different sodium-bridged dimeric units. One dimer incorporates a twofold rotational axis along the Na···Na [Na(1) and Na(2)] vector, whereas the other involves a twofold rotational axis along the O···O [O(2) and O(3)] vector. The planar Na_2O_2 cores are very similar in each molecule, having Na−O−Na angles near 94.5° and O−Na−O angles near 85.5°. The Na−O bonds are in the narrow range 2.221(2)−2.237(2) Å. The sodiums also display close interactions to the ipso carbons of the flanking Trip rings in the range 2.995(3)−3.076(3) Å. The Na−O−C(ipso) angles are symmetric and lie within the narrow limits 132.1(2)−132.78(6)°.

The unassociated dimeric structural motif in **4** provides a good illustration of the disruption of the stacking of dimeric units[26] in the polymeric structures of $(NaOPh)_n$ [22,23] or $(NaOC_6H_4\text{-}4\text{-}Me)_n$.[20] The Na−O bond lengths in

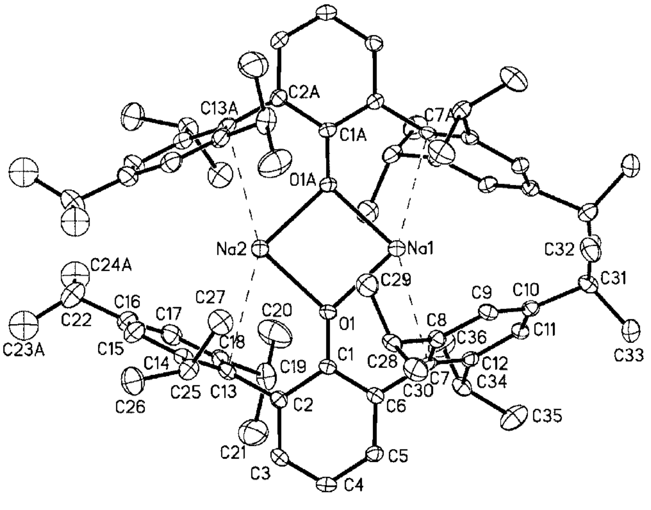


Figure 4. Thermal ellipsoid (35%) plot of one of the molecules in the asymmetric unit of **4**. H atoms are not shown; selected bond lengths and angles are given in Table 2

4 are at the shorter end of the range previously observed in species such as $(NaOC_6H_4\text{-}4\text{-}Me)_n$,[20] $[(MeOCH_2CH_2OMe)NaOC_6H_4\text{-}4\text{-}Me]_4$ [18] or $(NaOPh)_n$.[22,23] The Na···C interactions are similar to the average Na−C(arene) distance of 2.94(11) Å observed in $(NaOC_6H_4\text{-}4\text{-}Me)_n$ [20] and 3.05(8) Å in $(NaOPh)_n$.[23] The basic structural motif in **4** resembles that observed for the dimer $(NaSAr^*)_2$.[10] However, in the latter species the sodium displays unequal and weaker interactions with the aryl rings. Apparently, the Na^+ ions are a better fit for the cavity generated by the flanking aryl rings in the case of **4**. As in the structure of **5**, and for the same reasons, the internal angles at the ipso carbons of the central aryl rings [117.6(3) and 117.7(4)°] are less than the idealized 120° and the flanking aryl rings subtend high angles with respect to the central aryl ring.

Conclusions

The reaction of LiAr* or LiAr′ with nitrobenzene at low temperature, followed by hydrolysis, is an effective, high-yield route to very bulky terphenols from their lithium terphenyl precursors. The latter are available in essentially quantitative yield from the reaction of terphenyl iodide with *n*BuLi thereby permitting the terphenols to be isolated in *ca*. 70% from the terphenyl iodide starting material.

Experimental Section

General Procedures: All manipulations were carried out (except where otherwise noted) by using modified Schlenk techniques under an atmosphere of Ar or N_2 or in Vacuum Atmospheres HE-43 or NEXUS dryboxes. All solvents were distilled from molten Na/K alloy and degassed prior to use. Nitrobenzene was distilled off P_2O_5 and stored over molecular sieves. The lithium compounds $Et_2O{\cdot}LiC_6H_3\text{-}2,6\text{-}Trip_2$ (LiAr*)[27] and $LiC_6H_3\text{-}2,6\text{-}Dipp_2$ (LiAr′)[28] were prepared as described previously. The ^1H and ^{13}C NMR spectra were recorded on a Varian 300 or 400 MHz spectrometer and referenced to known standards. Melting points were recorded in glass capillaries under N_2 and are uncorrected. Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin−Elmer-1430 spectrometer.

1-HOC$_6$H$_3$-2,6-Trip$_2$ (Ar*OH, 1): $Et_2O{\cdot}LiAr^*$ (1.7 g, 3.0 mmol) was dissolved in diethyl ether (20 mL) with rapid stirring. This solution was cooled in a CH_2Cl_2/liquid N_2 slush bath, and nitrobenzene (1.5 mL, ca. 15 mmol) was added dropwise by syringe. A red solution was formed immediately upon the addition of nitrobenzene, and after stirring for ca. 5 min, methanol (20 mL) was added with a syringe. The resulting amber colored mixture was warmed to room temperature and water (25 mL) was added to afford a solution with two layers. The upper layer was separated and the aqueous alcohol layer was acidified with concentrated HCl (1.0 mL), extracted with 2 × 20 mL portions of diethyl ether and combined with the upper layer. The combined organic layers were washed with 2 × 100 mL portions of water and 2 × 100 mL saturated $NaCl/H_2O$ solution. The ethereal layer was separated, dried over $MgSO_4$, filtered and concentrated to ca. 10 mL. Column chromatography on silica gel with use of pentane eluent afforded, upon concentration to ca. 10 mL, large orange-yellow crystals of the crude product upon standing overnight. These were purified by recrystallization from diethyl ether to afford colorless crystals of **1**. Yield: 1.12 g, 2.25 mmol, (75%), m.p. 148−150 °C. The crystals proved suitable for X-ray crystallographic studies. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 1.21 [d, $^3J_{H,H}$ = 7.50 Hz, 12 H, *o*-CH(*CH*$_3$)$_2$], 1.24 [d, $^3J_{H,H}$ = 6.60 Hz, 12 H, *o*-CH(*CH*$_3$)$_2$], 1.27 [d, $^3J_{H,H}$ = 6.90 Hz, 12 H, *p*-CH(*CH*$_3$)$_2$], 2.82 [sept, $^3J_{H,H}$ = 6.90 Hz, 2 H, *p*-*CH*(CH$_3$)$_2$], 3.02 [sept, $^3J_{H,H}$ = 6.90 Hz, 4 H, *o*-*CH*(CH$_3$)$_2$], 4.57 [s, 1 H, −OH], 6.89 [t, $^3J_{H,H}$ = 7.50 Hz, 1 H, *p*-Ph], 7.06 [d, $^3J_{H,H}$ = 7.50 Hz, 2 H, *m*-Ph], 7.23 [s, 4 H, *m*-Trip] ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 24.36 [*o*-CH(*CH*$_3$)$_2$], 24.43 [*o*-CH(*CH*$_3$)$_2$], 24.69 [*p*-CH(*CH*$_3$)$_2$], 31.04 [*o*-*CH*(CH$_3$)$_2$], 34.65 [*p*-*CH*(CH$_3$)$_2$], 120.07 (*p*-Ph), 121.29 (m-Trip), 126.64 (i-Trip), 130.23 (*o*-Ph), 131.02 (p-Trip), 147.79 (*m*-Ph), 148.83 (o-Trip), 150.96 (i-Ph) ppm. IR (Nujol): $\tilde{\nu}$ = 3520 cm^{-1} (ν_{OH}, sharp).

1-HOC$_6$H$_3$-2,6-Dipp$_2$ (Ar′OH, 2): In a similar manner to that described for **1**, nitrobenzene (3.5 mL, ca. 35 mmol) was syringed into a rapidly stirred solution of LiAr′ (2.93 g, 7.0 mmol) dissolved in diethyl ether (20 mL) with cooling to ca. −95 °C. Quenching with MeOH (20 mL), followed by warming to room temperature, and water addition, afforded two layers, which were worked up as described for **1**, to yield colorless crystals of **2**. Yield: 2.0 g, 4.83 mmol (69%); m.p. 164−166 °C. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.08 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, *o*-CH(*CH*$_3$)$_2$], 1.13 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, *o*-CH(*CH*$_3$)$_2$], 2.72 [sept, $^3J_{H,H}$ = 6.9 Hz, 4 H, *o*-*CH*(CH$_3$)$_2$], 4.46 [s, 1 H, −O*H*], 7.03−7.09 [m, 2 H, *p*-Ph and *p*-Dipp], 7.25 [d, $^3J_{H,H}$ = 7.5 Hz, 4 H, *m*-Dipp], 7.37 [d, $^3J_{H,H}$ = 7.8 Hz, 2 H, *m*-Ph] ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 24.14 [*o*-CH(*CH*$_3$)$_2$], 24.50 [*o*-CH(*CH*$_3$)$_2$], 30.86 [*o*-*CH*(CH$_3$)$_2$], 120.08 (*p*-Ph), 123.10 (m-Dipp), 126.36 (i-Dipp), 128.76 (p-Dipp), 129.91 (*m*-Ph), 133.36 (0-Ph), 147.97 (o-Dipp), 150.86 (i-Ph) ppm. IR (Nujol): $\tilde{\nu}$ = 3530 cm^{-1} (ν_{OH}, sharp).

LiOAr* (3): MeLi (1.1 mmol, 0.65 mL, 1.6 M in ether) was added from a syringe to a well-stirred solution of **1** (0.5 g, *ca*. 1 mmol) in diethyl ether (20 mL) at room temperature. After 10 minutes, the solution became a pale red and the reaction was stirred for another 4 h. The diethyl ether was pumped off and hexane (20 mL) was added. The volume of the clear red solution was reduced to ca. 10 mL under reduced pressure and the flask was placed in a ca. −20 °C freezer overnight. Colorless crystals (stable up to 260 °C) had formed after 24 h, but they were found to be unsuitable for X-ray crystallography. Several efforts were made to grow crystals from other solvents without success. The isolated yield of **3** was 0.465 g, 0.92 mmol (92%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.92 [d, $^3J_{H,H}$ = 11.1 Hz, 12 H, *o*-CH(CH_3)$_2$], 1.10 [d, $^3J_{H,H}$ = 11.1 Hz, *o*-CH(CH_3)$_2$], 1.40 [d, $^3J_{H,H}$ = 11.1 Hz, 12 H, *p*-CH(CH_3)$_2$], 3.00 [m, 6 H, o+*p*-*CH*(CH_3)$_2$], 6.61 [t, J_{ortho} = 8.1 Hz, 1 H, *p*-Ph], 6.73 [d, J_{ortho} = 10.5 Hz, 2 H, *m*-Ph], 7.16 (s, 4 H, *m*-Tripp) ppm. ^{13}C NMR (300 MHz, C_6D_6, 25 °C): δ = 24.10 [*o*-CH(CH_3)$_2$], 24.40 [*o*-CH(CH_3)$_2$], 24.85 [*p*-*CH*(CH_3)$_2$], 31.02 [*o*-*CH*(CH_3)$_2$], 34.41 [*p*-*CH*(CH_3)$_2$], 115.05 (*p*-Ph), 121.91 (m-Trip), 126.51 (i-Trip), 131.04 (p-Trip), 137.38 (*o*-Ph), 147.11 (*m*-Ph), 147.25 (o-Trip), 161.41 (i-Ph) ppm.

NaOAr* (4): A solution of Ar*OH (**1**; 0.5 g, 1 mmol) in toluene was added via cannula to sodium metal 0.050 g (ca. 2 mmol) suspended in toluene (5 mL). The mixture was refluxed overnight. The red solution obtained was pumped to dryness and the residue was extracted in diethyl ether (15 mL) and the resultant solution allowed to settle. The clear, red supernatant solution was decanted off, and pumped down to ca. 5 mL, and stored in a ca. −20 °C freezer. After three weeks, colorless crystals of **4** were formed which were suitable for X-ray analysis. Yield: 0.45 g, 0.86 mmol (86%). m.p. 230−232 °C. ^{1}H NMR (300 MHz, C_6D_6, CD_3, 25 °C): δ = 1.01 [d, $^3J_{H,H}$ = 6.0 Hz, 12 H, *o*-CH(CH_3)$_2$], 1.20 [d, $^3J_{H,H}$ = 6.0 Hz, 12 H, *o*-CH(CH_3)$_2$], 1.47 [d, $^3J_{H,H}$ = 6.0 Hz, 12 H, *p*-CH(CH_3)$_2$], 3.17 [s broad, 6 H, o+*p*-*CH*(CH_3)$_2$], 6.61 [s, 1 H, *p*-Ph], 6.83 [s, 2 H, *m*-Ph], 7.19 [s, 4 H, *m*-Trip] ppm. ^{13}C NMR (300 MHz, [D$_8$]toluene, 25 °C): δ = 23.87 [*o*-CH(CH_3)$_2$], 24.14 [*o*-CH(CH_3)$_2$], 24.75 [*p*-CH(CH_3)$_2$], 30.56 [*o*-*CH*(CH_3)$_2$], 33.96 [*p*-*CH*(CH_3)$_2$], 111.97 (*p*-Ph), 120.92 (m-Trip), 128.55 (i-Trip), 130.26 (p-Trip), 138.67 (*o*-Ph), 146.53 (o-Trip), 147.27 (*m*-Ph), 166.02 (i-Ph) ppm.

LiOAr′ (5): Ar′OH (**2**; 0.36 g, 0.86 mmol) was dissolved in diethyl ether (15 mL) and the resulting solution was cooled to 0 °C. *n*-Butyllithium (0.6 mL, 0.96 mmol, 12% excess of a 1.6 M solution in hexane) was slowly added with a syringe. Evolution of gas (*n*BuH) was seen during addition. The solution was stirred at room temperature for an additional 2 h, the diethyl ether was pumped off, and hexane (*ca.* 20 mL) was added. The resulting yellow solution was concentrated to about 10 mL and let stand in a ca. −20 °C freezer. After three days small, colorless crystals were obtained. They were suitable for X-ray analysis. Yield: 0.334 g, 0.79 mmol (92%). M.p. 198−200 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 0.92 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, *o*-CH(CH_3)$_2$], 1.02 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, *o*-CH(CH_3)$_2$], 2.89 [sept, $^3J_{H,H}$ = 6.9 Hz, 4 H, *o*-*CH*(CH_3)$_2$], 6.67 [t, $^3J_{H,H}$ = 6.3 Hz, 1 H, *p*-Ph], 6.84 [d, $^3J_{H,H}$ = 7.5 Hz, 2 H, *m*-Ph], 7.03 [d, $^3J_{H,H}$ = 7.5 Hz, 4 H, *m*-Dipp], 7.14 [t, $^3J_{H,H}$ = 6.3 Hz, 2 H, *p*-Dipp] ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): δ = 24.54 [*o*-CH(CH_3)$_2$], 24.62 [*o*-CH(CH_3)$_2$], 30.71 [*o*-*CH*(CH_3)$_2$], 114.76 (*p*-Ph), 124.30 (*m*-Dipp), 128.57 (*p*-Dipp), 129.17 (i-Dipp), 130.26 (*m*-Ph), 139.17 (*o*-Ph), 146.71 (*o*-Dipp), 161.13 (i-Ph) ppm.

X-ray Crystallographic Studies: Sample preparation consisted of removing the crystal from the Schlenk tube under a rapid flow of Argon and immediately submerging it in hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, mounted on a copper pin and rapidly placed in the cold stream of N_2 of the diffractometer for data collection.[29] Data were collected at 293 K (**1**), 130 K (**2**) or 90 K (**4**) and (**5**) with Mo-K_α (λ = 0.71073Å) radiation (**1**, **4** and **5**) or Cu-K_α (λ = 1.54178Å) (**2**) on a Bruker SMART 1000 (**1**, **4** and **5**) or Siemens P4 (**2**) diffractometers. Data collection and processing were performed using the Bruker programs SMART and SAINT (**1**, **4** and **5**) or Siemens P3-PC (**2**). Empirical absorption corrections were applied using SADABS,[30a] XABS.[30b] The crystal structures were solved using either direct methods or the Patterson option in SHELXS program and refined by the full-matrix least-squares procedure in the SHELXL program.[31] All non-hydrogen atoms were refined anisotropically while hydrogen atoms (with the exception of those attached to oxygen in **1** and **2** which were located) were placed at calculated positions and included in refinement using a riding model. Some details of the data collection and refinement are given in Table 1. Further details can be found in the supporting information.

CCDC-218873 (**1**), -218874 (**2**) -218875 (**4**) and -218876 (**5**) contain the supplementary crystallographic data for this paper. These data

Table 1. Selected crystallographic data for compounds **1**, **2**, **4**, and **5**

Compound	**1**	**2**	**4**	**5**
Formula	$C_{36}H_{50}O$	$C_{30}H_{38}O$	$C_{36}H_{49}NaO$	$C_{60}H_{78}Li_2O_2$
Mol. wt.	498.76	414.60	520.74	845.1
Color, habit	colorless, block	colorless, plate	colorless, plate	colorless, block
Cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$Pna2_1$	$P2_1/n$	$P2/c$	$P2_1/n$
a, Å	8.6426(8)	10.8581(10)	19.1061(18)	10.9610(4)
b, Å	14.3044(16)	20.8313(15)	17.2110(16)	19.8181(7)
c, Å	25.501(3)	11.1785(8)	19.6114(18)	11.3802(4)
α, °				
β, °		94.474(7)	90.100(2)	91.352(1)
γ, °				
V, A^3	3152.7(6)	2520.7(3)	6448.9(10)	2471.39(15)
Z	4	4	8	2
Cryst dims, mm	0.10 × 0.07 × 0.05	0.60 × 0.28 × 0.08	0.37 × 0.29 × 0.09	0.31 × 0.31 × 0.17
D calc, g cm^{-3}	1.051	1.092	1.073	1.136
μ, mm^{-1}	0.061	0.480	0.074	0.065
No. of rflns	9958	3307	11638	4868
No. of obsd rflns	5236	2871	7600	3746
R, obsd rflns	0.0499	0.0383	0.0579	0.0529
wR_2, all rflns	0.1197	0.0954	0.1479	0.1560

Table 2. Selected bond lengths (Å) and angles (°) for **1**, **2**, **4**, and **5**

1 (Ar*OH)		**2** (Ar′OH)	
O(1)−C(1)	1.381(2)	O(1)−C(1)	1.407(2)
O(1)−H(1)	0.83(3)	O(1)−H(1)	0.85(1)
C(1)−C(2)	1.398(7)	C(1)−C(2)	1.394(2)
C(1)−C(6)	1.396(7)	C(1)−C(6)	1.396(2)
C(2)−C(7)	1.514(6)	C(2)−C(19)	1.502(2)
C(6)−C(22)	1.479(6)	C(6)−C(7)	1.499(2)
C(1)−O(1)−H(1)	129(2)	C(1)−O(1)−H(1)	107(2)
C(2)−C(1)−C(6)	122.4(1)	C(2)−C(1)−C(6)	122.1(1)
C(2)−C(1)−O(1)	120.7(5)	C(2)−C(1)−O(1)	120.8(1)
C(6)−C(1)−O(1)	116.9(5)	C(6)−C(1)−O(1)	117.1(1)
C(1)−C(2)−C(7)	117.8(4)	C(1)−C(2)−C(19)	121.0(1)
C(1)−C(6)−C(22)	121.8(4)	C(1)−C(6)−C(7)	119.8(1)

4 (NaOAr*)$_2$		**5** (LiOAr′)$_2$	
Na(1)−O(1)	2.237(2)	Li(1)−O(1)	1.807(3)
Na(2)−O(1)	2.225(2)	Li(1)−O(1A)	1.979(3)
Na(3)−O(3)	2.221(2)	O(1)−C(1)	1.335(2)
Na(3)−O(2)	2.226(2)	C(1)−C(2)	1.415(2)
O(1)−C(1)	1.320(4)	C(1)−C(6)	1.420(2)
C(1)−C(2)	1.420(4)	C(2)−C(7)	1.502(2)
C(1)−C(6)	1.408(4)	C(6)−C(19)	1.494(2)
C(2)−C(13)	1.497(5)	Li(1)−C(19)	2.390(3)
C(6)−C(7)	1.495(5)	Li(1)−C(20)	2.647(3)
O(2)−C(37)	1.313(5)	Li(1)−C(24)	2.543(3)
O(3)−C(56)	1.308(5)	Li(1)···Li(1A)	2.468(6)
C(37)−C(38)	1.415(4)	O(1)−C(1)−C(2)	123.43(14)
C(56)−C(57)	1.424(4)	O(1)−C(1)−C(6)	119.01(14)
C(57)−C(60)	1.497(5)	C(2)−C(1)−C(6)	117.55(14)
C(38)−C(41)	1.499(5)	C(1)−C(2)−C(7)	124.63(14)
Na(1)−C(7)	2.995(3)	C(1)−C(6)−C(19)	117.44(14)
Na(2)−C(13)	3.074(3)	Li−O(1)−Li(1A)	81.22(14)
Na(3)−C(14)	3.015(3)	O(1)−Li−O(1A)	98.78(14)
Na(3)−C(46)	3.043(3)	Li(1)−O(1)−C(1)	155.11(14)
Na(3)−C(60)	3.076(3)	Li(1A)−O(1)−C(1)	122.91(13)
Na(1)···Na(2)	3.269(2)		
Na(3)···Na(3A)	3.268(2)		
O(1)−Na(1)−O(1A)	85.49(12)		
O(1)−Na(2)−O(1A)	86.07(12)		
Na(1)−O(1)−Na(2)	94.22(9)		
Na(1)−O(1)−C(1)	132.1(2)		
Na(2)−O(1)−C(1)	132.7(2)		
O(1)−C(1)−C(2)	121.2(3)		
O(1)−C(1)−C(6)	121.2(3)		
C(1)−C(2)−C(6)	117.6(3)		
C(1)−C(2)−C(13)	119.6(3)		
C(1)−C(6)−C(7)	120.0(3)		
Na(3)−O(2)−C(37)	132.78(6)		
Na(3)−O(3)−C(56)	132.64(6)		
Na(3)−O(2)−Na(3A)	94.44(12)		
Na(3)−O(3)−Na(3A)	94.72(12)		
O(2)−Na(3)−O(3)	85.42(8)		
Na(3)−O(2)−C(37)	132.78(6)		
Na(3)−O(3)−C(56)	132.64(6)		
C(38)−C(37)−C(38A)	117.7(4)		
O(2)−C(37)−C(38)	121.14(3)		
C(38)−C(37)−(38A)	117.7(4)		
O(3)−C(56)−C(57)	121.37(19)		
C(57)−C(56)−C(57A)	117.3(4)		

can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] D. C. Bradley, R. C. Mehrotra, I. P. Rothwell, A. Singh. *Alkoxo and Aryloxo Derivatives of Metals*, Academic, San Diego, 2001.

[2] B. Cetinkaya, I. Gumrukcu, M. F. Lappert, J. L. Atwood, R. D. Rogers, M. J. Zawarotko, *J. Am. Chem. Soc.* **1980**, *102*, 2088.

[3] B. Cetinkaya, A. Hudson, M. F. Lappert, P. P. Power, H. Goldwhite, *J. Chem. Soc., Chem. Commun.* **1982**, 609.

[4] P. P. Power, *Chem. Rev.* **1999**, *99*, 3463.

[5] D. J. Darensbourg, M. W. Holtcamp, G. E. Struck, M. S. Zimmer, S. A. Niezgoda, P. Rainey, J. B. Robertson, J. D. Draper, J. H. Reibenspies, *J. Am. Chem. Soc.* **1999**, *121*, 107.

[6] T. Ooi, Y. Kondo, K. Maruoka, *Angew. Chem. Int. Ed.* **1998**, *37*, 3039.

[7] J. S. Vilardo, M. A. Lockwood, L. G. Hanson, J. R. Clark, B. C. Parker, P. E. Fanwick, I. P. Rothwell, *J. Chem. Soc., Dalton Trans.* **1997**, 3353.

[8] B. Twamley, S. T. Haubrich, P. P. Power, *Adv. Organomet. Chem.* **1999**, *44*, 1.

[9] B. Twamley, C.-S. Hwang, N. J. Hardman, P. P. Power, *J. Organomet. Chem.* **2000**, *609*, 152.

[10] M. Niemeyer, P. P. Power, *Inorg. Chem.* **1996**, *35*, 7264.

[11] M. B. Smith, J. March. *March's Advanced Organic Chemistry*, 5th ed.; Wiley, New York, 2001, p. 874, 1685.

[12] S. Ueji, *J. Org. Chem.* **1985**, *50*, 2711.

[13] S. Saito, T. Kano, K. Hatanaka, H. Yamamoto, *J. Org. Chem.* **1997**, *62*, 5651.

[14] P. Buck, G. Köbrich, *Tetrahedron Lett.* **1967**, 1563.

[15] G. Köbrich, P. Buck, *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 1044.

[16] K. Nakatsu, H. Yoshioka, K. Kunimoto, T. Kinugasa, S. Ueji, *Acta Crystallgr.* **1978**, *B34*, 2357.

[17] S. Ueji, N. Ueda, T. Kinugasa, *J. Chem. Soc., Perkin Trans. 2* **1976**, 178.

[18] Y. Iimure, T. Sakurai, Y. Ohno, K. Asahi, K. Isono, *Acta Crystallogr., Sect. C* **1983**, *39*, 778.

[19] K. Bekkouch, M. Perrin, A. Thozet, *Acta Crystallogr., Sect. C* **1988**, *44*, 2161.

[20] W. J. Evans, R. E. Golden, J. W. Ziller, *Inorg. Chem.* **1993**, *32*, 3041.

[21] F. Pauer, P. P. Power, *Lithium Chemistry* (Eds.: A.-M. Sapse, P. v. R. Schleyer), J. Wiley, New York, 1995, Chapter 9.

[22] R. E. Dinnebier, M. Pink, J. Sieler, P. W. Stephens, *Inorg. Chem.* **1997**, *36*.

[23] M. Kunert, E. Dinjus, M. Nauck, J. Sieler, *Chem. Ber./Receuil* **1997**, *130*, 1461.

[24] J. S. Vilardo, P. E. Fanwick, I. P. Rothwell, *Polyhedron* **1998**, *17*, 769.

[25] M. B. Dinger, M. J. Scott, *Inorg. Chem.* **2000**, *39*, 1238.

[26] K. Gregory, P. v. R. Schleyer, R. Snaith, *Adv. Inorg. Chem.* **1991**, *37*, 47.

[27] B. Schiemenz, P. P. Power, *Organometallics* **1996**, *15*, 958.

[28] B. Schiemenz, P. P. Power, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2150.

[29] H. Hope, *Prog. Inorg. Chem.* **1995**, *41*, 1.

[30] [30a] SADABS: Area Detector Absorption Connections: Bruker AXS Inc: Madison, WI, 1996. [30b] XABS 2 an empirical absorption correction program: S. R. Parkin, B. Moezzi, H. Hope, *J. Applied Crystallogr.* **1995**, *28*, 53.

[31] SHELXL Version 5.1: Bruker AXS Inc: Madison, WI, 1997.

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