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Synthesis and Structure of the Solvent-Free Sodium Aryl $(NaC_6H_3\text{-}2,6\text{-}Mes_2)_2$

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Summary: The synthesis and first structural characterization of a solvent-free sodium aryl derivative, $(NaC_6H_3\text{-}2,6\text{-}Mes_2)_2$, are described. Molecules of $(NaC_6H_3\text{-}2,6\text{-}Mes_2)_2$ are metal-bridged dimers in which the Na^+ cations are primarily coordinated to ipso phenyl and ipso mesityl carbons.

Although the simplest sodium aryl, phenylsodium,[1] has been known for some time, its solid-state structure has not been determined. This circumstance is partly a result of its lack of solubility in nondonor solvents, which hampers normal crystal growing techniques. Its reactivity is problematical even in normal donor solvents such as ethers or amines, which are readily cleaved by the more reactive sodium alkyls or aryls. Nevertheless, relatively stable complexes can be isolated by working at lower temperatures and by using chelating ligands such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) or *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMEDTA). This approach has resulted in the structural characterization of the dimeric $\{NaPh(PMEDTA)\}_2$[2] and the mixed-metal species $[\{Na(TMEDA)\}_3LiPh_4]$.[3] More recently, the structure of the intramolecularly solvated trimer $\{NaC_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2\}_3$[4] has been determined. Hydrocarbon solubility and consequent ease of crystal growth may be increased by using lipophilic terphenyl substituents. These sterically encumbering groups recently have allowed the structural characterization of the solvent-free, σ-bonded lithium aryls $(LiC_6H_3\text{-}2,6\text{-}Mes_2)_2$[5] (**1**), $(LiC_6H_3\text{-}2,6\text{-}Dipp_2)_2$[6] (Dipp = 2,6-*i*-$Pr_2$-$C_6H_3$−), and $(LiC_6H_3\text{-}3,5\text{-}t\text{-}Bu_2)_6$.[7] In this paper the bulky, lipophilic terphenyl substituent 2,6-Mes_2-C_6H_3− is used to effect the first structural characterization of a solvent-free sodium aryl, $(NaC_6H_3\text{-}2,6\text{-}Mes_2)_2$ (**2**).

The synthesis of compound **2** was first attempted by a transmetalation that involved the reaction of sodium with the mercury diaryl $Hg(C_6H_3\text{-}2,6\text{-}Mes_2)_2$ (**3**). For this purpose **3** was synthesized[8a] by the reaction of $HgBr_2$ with 2 equiv of $LiC_6H_3\text{-}2,6\text{-}Mes_2$.[5] The X-ray structure[9] of **3** reveals no unusual features (Figure 1). The C−Hg−C angle of 178.6(3)° is practically linear, and a torsion angle of 88.7° is observed between the two metal-substituted aryl moieties. The Hg−C bond lengths of 2.069(7) and 2.076(7) Å are very similar to the values in the crowded species $Hg(C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3)_2$ (2.077(6) and 2.083(6) Å),[10a] but they are shorter than those in $Hg\{C_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}_2$ (2.15(2) Å).[10b] Experiments on an NMR-tube scale showed that the sterically crowded compound **3** does not react with sodium or potassium metal in C_6D_6 at ambient temperature. Even under

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[1] See for example: Houben-Weyl. *Methoden der Organischen Chemie*; Thieme: Stuttgart, Germany, 1970; Vol. XIII 1. The synthesis of halide-free NaPh was first described in: Thirase, G.; Weiss, E. *J. Organomet. Chem.* **1974**, *81,* C1.

[2] Schümann, U.; Behrens, U.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1989**, *28,* 476.

[3] Schümann, U.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1988**, *27,* 584.

[4] den Besten, R.; Brandsma, L.; Spek, A. L.; Kanters, J. A.; Veldman, N. *J. Organomet. Chem.* **1995**, *498,* C6.

[5] Ruhlandt-Senge, K.; Ellison, J.; Wehmschulte, R. J.; Pauer, F.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115,* 11353.

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

[7] Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119,* 2847.

[8] All manipulations were carried out under anaerobic and anhydrous conditions. (a) Anhydrous $HgBr_2$ (0.24 g, 0.67 mmol) was added to a solution of $LiC_6H_3\text{-}2,6\text{-}Mes_2$ (0.43 g, 1.35 mmol) in toluene (15 mL), and the mixture was stirred overnight. After removal of the solvent under reduced pressure, the residue was extracted with hexane. The resulting solution was filtered, and the volume of the filtrate was reduced to incipient crystallization. Cooling in a −20 °C freezer afforded colorless crystals (0.39 g, 70%) of **3**. Crystals of **3**·0.5C_6H_6 suitable for X-ray crystallographic studies were grown from benzene. Mp: 295−298 °C. ^1H NMR (C_6D_6): δ 1.78 (*o*-CH_3), 2.21 (*p*-CH_3), 6.85 (*m*-Mes), 6.97 (d, *m*-C_6H_3), 7.10 (t, *p*-C_6H_3). ^{13}C NMR (C_6D_6): δ 21.2 (*o*-CH_3), 21.2 (*p*-CH_3), 127.0 (*m*-C_6H_3), 128.2 (*p*-C_6H_3), 128.6 (*m*-Mes), 136.1 (*o*+*p*-Mes), 142.2 (*i*-Mes), 148.8 (*o*-C_6H_3), 172.8 (*i*-C_6H_3). IR (Nujol, cm^{-1}): 1722 vw, 1612 s, 1560 m, 1480 sh, 1245 w, 1169 vw, 1097 vw, 1087 w, 1026 m, 1009 w, 846 vs, 802 s, 781 w, 739 s, 573 w, 545 sh, 492 w, 333 w, 270 w. (b) Spectroscopic data for **4** are as follows: ^1H NMR (C_6D_6): δ 2.07 (*o*-CH_3), 2.21 (*p*-CH_3), 6.76 (*i*-C_6H_3), 6.86 (*m*-Mes), 6.99 (d, *m*-C_6H_3), 7.25 (t, *p*-C_6H_3). ^{13}C NMR (C_6D_6): δ 21.0 (*o*-CH_3), 21.1 (*p*-CH_3), 127.7 (*m*-C_6H_3), 128.5 (*m*-Mes), 128.8 (*p*-C_6H_3), 130.7 (*i*-C_6H_3), 135.7 (*o*-Mes), 136.4 (*p*-Mes), 139.4 (*i*-Mes), 141.9 (*o*-C_6H_3). (c) NaO-*t*-Bu (0.20 g, 2.08 mmol) was added at *ca.* 5 °C to a solution of $LiC_6H_3\text{-}2,6\text{-}Mes_2$ (0.64 g, 2.00 mmol) in *ca.* 20 mL of benzene, and the mixture was stirred for 1 h. After removal of the solvent under reduced pressure, the residue was extracted three times with small portions of cold hexane. The remaining white solid was dried at 0.05 Torr to give 0.28 g (42%) of pure **2**. Crystals suitable for X-ray crystallographic studies were obtained at *ca.* 0 °C from a 20:1 mixture of *n*-hexane and benzene. Mp: between 115 and 300 °C, crystals change color from yellow through red to black; no melting was observed. ^1H NMR (C_6D_6): δ 1.90 (*o*-CH_3), 2.14 (*p*-CH_3), 6.78 (*m*-Mes), 6.94 (d, *m*-C_6H_3), 7.28 (t, *p*-C_6H_3). ^{13}C NMR (C_6D_6): δ 21.0 (*o*-CH_3), 21.1 (*p*-CH_3), 122.4 (*m*-C_6H_3), 124.6 (*p*-C_6H_3), 129.2 (*m*-Mes), 135.4 (*o*-Mes), 135.4 (*p*-Mes), 147.7 (*i*-Mes), 152.0 (*o*-C_6H_3), 188.6 (*i*-C_6H_3). IR (Nujol, cm^{-1}): 1731 w, 1602 ms, 1580 m, 1209 ms, 1156 w, 1085 m, 1062 ms, 1030 m, 1008 m, 973 vw, 950 vw, 884 vw, 851 vs, 794 s, 775 w, 747 sh, 740 m, 722 s, 630 m, 567 w, 541 vw, 301 m, 263 m.

[9] (a) Crystal data for **3**·0.5 C_6H_6 at 130 K with Mo Kα ($\lambda = 0.710\,73$ Å) radiation: $C_{51}H_{53}Hg$, fw 866.5, $a = 10.398(2)$ Å, $b = 10.794(2)$ Å, $c = 20.469(4)$ Å, $\alpha = 86.70(2)°$, $\beta = 80.88(2)°$, $\gamma = 67.02(2)°$, $V = 2088.3(7)$ Å^3, triclinic, space group $P\bar{1}$, $Z = 2$, $R_1 = 0.057$ for 7665 ($I > 2\sigma(I)$) reflections. (b) Crystal data for **2** at 130 K with Cu Kα ($\lambda = 1.541\,78$ Å) radiation: **2**, $C_{48}H_{50}Na_2$, fw 672.8, $a = 18.085(4)$ Å, $b = 15.374(2)$ Å, $c = 16.317(3)$ Å, $\beta = 121.034(12)°$, $V = 3887.4(12)$ Å^3, monoclinic, space group $C2/c$, $Z = 4$, $R_1 = 0.045$ for 2232 ($I > 2\sigma(I)$) reflections; (c) Crystal data for **4** at 130 K with Cu Kα ($\lambda = 1.541\,78$ Å) radiation: $C_{48}H_{52}$, fw 628.9, $a = 9.049(3)$ Å, $b = 11.757(4)$ Å, $c = 18.524(5)$ Å, $\alpha = 98.28(3)°$, $\beta = 95.71(3)°$, $\gamma = 106.50(3)°$, $V = 1849.3(10)$ Å^3, triclinic, space group $P\bar{1}$, $Z = 2$ (two independent molecules), $R_1 = 0.057$ for 3809 ($I > 2\sigma(I)$) reflections. Important distances (Å) and angles (deg) for one of the two independent molecules: C(1)−C(2) = 1.388(4), C(1)−C(6) = 1.396(4), C(2)−C(3) = 1.393(4), C(3)−C(4) = 1.391(4), C(4)−C(5) = 1.371(4); C(2)−C(1)−C(6) = 121.9(3), C(1)−C(2)−C(3) = 118.9(2), C(1)−C(2)−C(7) = 120.7(2), C(1)−C(6)−C(5) = 117.8(2), C(1)−C(6)−C(16) = 121.7(2). Compounds **2**−**4** were refined on F^2 with SHELXL-93 (G. M. Sheldrick, Göttingen, Germany, 1993).

[10] (a) Huffman, J. C.; Nugent, W. A.; Kochi, J. K. *Inorg. Chem.* **1980**, *19,* 2749. (b) Brooker, S.; Bertel, N.; Stalke, D.; Noltemeyer, M.; Roesky, H. W.; Sheldrick, G. M.; Edelmann, F. T. *Organometallics* **1992**, *11,* 192.

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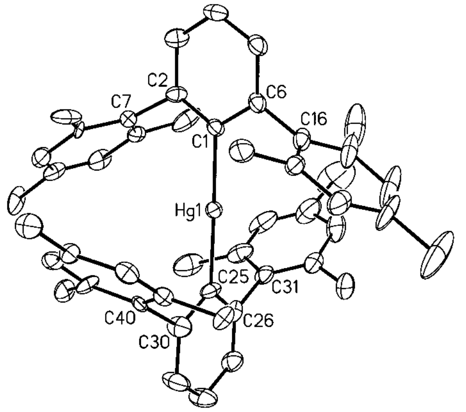

Figure 1. Thermal ellipsoidal plot (30%) of **3**. H atoms are not shown. Important distances (Å) and angles (deg): Hg(1)−C(1) = 2.069(7), Hg(1)−C(25) = 2.076(7); C(1)−Hg(1)−C(25) = 178.6(3).

more rigorous conditions (75 °C, 14 h), more than 96% of the starting material **3** remains unreacted. With cesium metal no reaction was observed at room temperature, but warming to 60 °C for 3 h leads to the formation of 1,3-Mes_2-C_6H_4 (**4**) in 30% yield. Complete consumption of **3** was achieved after 16 h at 75 °C. Apparently, under these reaction conditions the cesium aryl formed reacts immediately with the solvent to give the arene **4**.[8b]

An alternative synthetic approach to heavier alkali-metal aryls and alkyls is the well-known metal alkoxide exchange route.[11] Thus, the reaction of LiC_6H_3-2,6-Mes_2 with a slight excess of NaO-*t*-Bu affords NaC_6H_3-2,6-Mes_2[8c] in a moderate purified 42% yield. When the reaction is monitored by ^1H NMR, the signals of an intermediate species can be detected after 5 min. The observed chemical shifts[12] lie between the values for **1** and **2** and suggest the formation of the mixed-metal compound $LiNa(C_6H_3\text{-}2,6\text{-}Mes_2)_2$. After 1 h, complete conversion of the lithium aryl **1** to the sodium derivative **2** is observed. The more soluble byproduct LiO-*t*-Bu, and the decomposition product **4**, can be removed by repeated extraction with *n*-hexane. Colorless crystals of compound **2** can be stored at −20 °C for several weeks. In benzene solution it slowly metalates the solvent, and 50% conversion is observed at 20 °C over a period of *ca.* 30 h. Unfortunately, the potassium analogue of **2** is much less stable. When C_6D_6 is added to **1** and KO-*t*-Bu in an NMR tube, the mixture immediately assumes an orange color and a microcrystalline off-white solid precipitates. Only 1,3-Mes_2-C_6H_4 can be detected by ^1H NMR spectroscopy of the supernatant liquid. When the same reaction is carried out in *n*-hexane at 0 °C, the formation of a fine orange precipitate is observed. Apparently a highly associated metalated compound, probably involving a benzylic moiety, is formed.

Colorless crystals of **2**, suitable for X-ray crystallographic studies,[9b] were grown from a *n*-hexane/benzene mixture at 0 °C. It crystallizes as dimers in the space group *C*2/*c* with half of the molecule comprising the asymmetric unit (Figure 2). The remaining half is generated by a C_2 symmetry operation around the axis of the two sodiums. There is a torsion angle of 53.6° between the metalated aryl rings. The sodiums interact almost equally strongly with the the *ipso* carbons of the central phenyl ring (Na(1)−C(1) = 2.572(2) Å and Na(2)−C(1) = 2.609(2) Å) and with the *ipso* carbons of the mesityl groups (Na(1)−C(7) = 2.595(2) Å and Na(2)−C(16) = 2.663(2) Å). These distances may be compared to those found in the solvated sodium aryls $\{NaPh(PMEDTA)\}_2$[2] (2.658(4), 2.682(6) Å), $[\{Na(TMEDA)\}_3][LiPh_4]$[3] (2.566(8)−2.756(9) Å), and $\{NaC_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2\}_3$[4] (2.495(5)−2.554(5) Å), in the solvent-free sodium alkyls $\{NaCH(SiMe_3)_2\}_x$[13] (2.555(10) Å) and $NaC(SiMe_2Ph)_3$[14] (2.754(14), 2.983(14) Å), and in the unique sodate species $[Na(TMEDA)_2(OEt_2)][Na\{C(SiMe_3)_3\}_2]$[14] (2.479(6) Å). In addition, Na(1) and Na(2) have secondary contacts (2.864(2)−3.020(2) Å) to the *ortho* carbons (C(2), C(6), C(8), C(12), C(17)) of the phenyl ring and the mesityl substituents. The relatively high quality of the data sets for compounds **2** and **4** also permits comparison of the bond parameters within the phenyl rings. The metalation leads to a slight lengthening of the average C(*ipso*)−C (*ortho*) bond length, from 1.391(6) Å in **4** to 1.420(3) Å in **2**. In addition, the C−C−C angle at the *ipso* carbon is decreased from 121.9(3)° in **4** to 113.3(2)° in **2**, whereas the average C(*ipso*)−C(*ortho*)−C(*meta*) angle increases from 118.4(3)° (**4**) to 123.6(2)° (**2**).

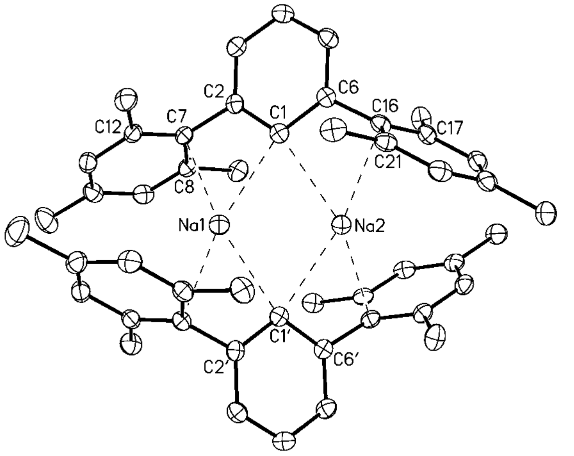

Figure 2. Thermal ellipsoid plot (30%) of **2**. H atoms are not shown. Important distances (Å) and angles (deg): Na(1)−C(1) = 2.572(2), Na(1)−C(7) = 2.595(2), Na(2)−C(1) = 2.609(2), Na(2)−C(16) = 2.663(2), Na(1)···Na(2) = 2.874(2), C(1)−C(2) = 1.421(3), C(1)−C(6) = 1.418(3), C(2)−C(7) = 1.508(3), C(6)−C(16) = 1.505(3); C(1)−Na(1)−C(1)′ = 113.82(10), C(1)−Na(2)−C(1)′ = 111.40(10), C(6)−C(1)−C(2) = 113.3(2).

The dimeric structure of **2** differs from that of the corresponding lithium species $(LiC_6H_3\text{-}2,6\text{-}Mes_2)_2$ (**1**)[5] in that the lithiums in **1** interact primarily with the *ipso* carbons of the phenyl groups (Li−C = *ca.* 2.17 Å) and display significantly weaker interactions with the mesityl *ipso* carbons (Li−C = *ca.* 2.55 Å). In contrast, the Na^+ ions in **2** interact almost equally strongly with the same carbons as outlined above. Interestingly, the dispositions of the organic ligands in **1**−**3** resemble each other, even though the structure of **3** contains just one

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[11] Lochmann, L.; Pospísil, J.; Lím, D. *Tetrahedron Lett.* **1966**, 257.

[12] ^1H NMR (C_6D_6): δ 1.85 (*o*-CH_3), 2.15 (*p*-CH_3), 6.80 (*m*-Mes), 6.87 (d, *m*-C_6H_3), 7.24 (t, *p*-C_6H_3). ^1H NMR for **1** in C_6D_6 (see also ref 5): δ 1.81 (*o*-CH_3), 2.17 (*p*-CH_3), 6.83 (*m*-Mes), 6.83 (d, *m*-C_6H_3), 7.23 (t, *p*-C_6H_3).

[13] Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P.; Diansheng, L.; Shun, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1386.

[14] Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; Izod, K.; Mallien, M.; Smith, J. D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1268.

metal. For example, the separations of the *ipso* phenyl carbons in **2** and **3** are *ca*. 4.31(1) and 4.14(1) Å, respectively, and the torsion angles between the planes of the phenyl rings 88.7(4)° in **2** *vs* 53.6(4)° in **3**.

The solubility of **2** in benzene-d_6 enables its ready characterization by ^{1}H NMR and ^{13}C NMR spectroscopy. The phenyl *ipso* carbons afford a relatively sharp resonance at 188.6 ppm, whereas the corresponding signal for the lithium analogue **1** is observed at 173.5 ppm.[5] This low-field shift is in agreement with the increasing polarity of the carbon−metal bond as one proceeds from lithium to the heavier alkali metals. The stronger interaction of the sodium ion with the mesityl *ipso* carbons, in comparison with that of the lithium derivative, also results in a low-field shift from 143.1 ppm in **1** to 147.7 ppm in **2**.

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Supporting Information Available: For **2**, **3**·$0.5C_6H_6$, and **4**, tables of crystal data, data collection, solution, and refinement parameters, atomic coordinates, bond distances and angles, anisotropic displacement coefficients, and hydrogen atom coordinates (41 pages). Ordering information is given on any current masthead page.

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