Inorganic Chemistry

pubs.acs.org/IC

Article

Scrabbling around in Synthetic Nuances Managing Sodium Compounds: Bisphenol/Bisnaphthol Synthesis by Hydroxyl Group Masking

Aleksandra Marszałek-Harych, Danuta Trybuła, Dawid Jędrzkiewicz, and Jolanta Ejfler*

Cite This: https://dx.doi.org/10.1021/acs.inorgchem.0c00310

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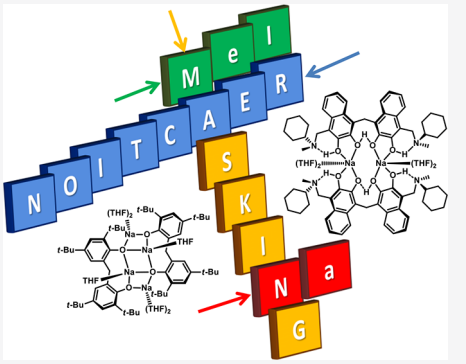
ABSTRACT: A unique method of bisphenol/bisnaphthol synthesis is being proposed, serendipitously discovered in the course of the careful analysis of an aminophenol methylation reaction. The insightful exploration of the synthesis of N- or O-methylated species, originating from functionalized phenols obtained by a conventional strategy, provided the opportunity to discover an unexpected reaction pathway yielding various bisphenols. Sodium complexes were found to be crucial intermediates in the synthetic scenario. Their formation, which is usually an imperceptive step, was substantial for the productive outcome of functional group protection. Thorough exploration revealed an essential structural motif of aminophenolate, necessary for the successful outcome of the reaction, and also enabled establishing the limitations of the new method. The work demonstrated that a slight change in the perspective and close inspection of the synthetic nuances can answer the important question concerning what a specific target-oriented synthesis strategy is lacking.



INTRODUCTION

The masking of a specific part of an organic molecule by using the protective group strategy is a core concept in various fields, including total organic synthesis. The choice of a proper synthetic scenario often plays a decisive role in the case of yielding a target molecule, final efficiency, environmental impact, cost, and safety-related issues. Although there is a vast array of excellently working protection−deprotection protocols in use in sophisticated organic syntheses, the rising complexity of targets requires constant exploration in search for new strategies. Furthermore, in-depth understanding of the chemistry behind well-established protocols allows for their effective development, quite often widening the scope of potential applications.[1−9]

One group of simple organic building blocks that has gained considerable attention is phenolic substrates, presenting structural variety that allows for the modification of their chemical properties and biological activity. The significance of the fundamental organic motif based on appropriately functionalized phenols is evident, as they are building blocks used for the construction of biologically active compounds, both those existing in nature and synthetically tailored toward a specific function. Therefore, an efficient and controllable method of phenolic group protection is quite often a prerequisite in the synthesis or functionalization of a complex organic target molecule designed for a specific chemical or biological application and, also, for use in subsequent transformations as a reactive functionality. In this context, the search for new practical protecting groups for functionalized phenols remains a synthetic problem of high importance.[10−13] Ethers are classical and, quite possibly, one of the most widely used functional groups for phenols. Therefore, studies focused on the mechanistic aspects of the incorporation of the ether group into a phenolic reagent might reveal new details about the masking process, opening new synthetic possibilities. Following the usual organic chemical mode of action, namely, running a typical postreaction workup procedure, often does not make it possible to capture sophisticated and sometimes peculiar transformations that govern the process. Herein, we report on the synthetic nuances that strictly control the hydroxyl group of aminophenol protection, selectively providing a target organic molecule. More importantly, we report on the intermediary sodium complexes of respective compounds that were found to play a crucial role in the mechanisms of the studied organic reactions.

EXPERIMENTAL SECTION

General Materials, Methods, and Procedures. Solvents for synthesis were purified by standard methods: tetrahydrofuran (THF)

Received: January 30, 2020

(high-performance liquid chromatography (HPLC), VWR) was distilled from Na/benzophenone; MeOH (HPLC, VWR) was distilled from CaH_2; dichloromethane (DCM) (99.8% VWR) was distilled from P_2O_5, and *n*-hexane (HPLC, VWR). Solvents for standard workup and chromatography were used as received. Column chromatography was performed on silica gel 60 Å 230−400 mesh (Macherey Nagel) and Macherey Nagel thin-layer chromatography (TLC) plates (silica gel 60 Å, UV 254). All chemicals were obtained from commercial sources and used without further purification: 2,4-*tert*-buthylphenol (99%, Sigma-Aldrich), 2,3-dihydroxynaphthalene (≥98.0%, Sigma-Aldrich), *N*-methyldodecylamine (98%, Alfa Aesar), formaldehyde (37% solution in H_2O, Sigma-Aldrich). *N*-Methylcyclohexylamine (99%, Sigma-Aldrich), dimethylamine (2 M solvent in MeOH, Sigma-Aldrich), dibenzylamine (97%, Sigma-Aldrich), di(2-picolyl)amine (97%, Sigma-Aldrich), 2-methylaminomethyl-1,3-dioxolane (98%, Sigma-Aldrich), iodomethane (99%, Sigma-Aldrich), sodium hydride (95%, Sigma-Aldrich).

The ^1H and ^{13}C NMR spectra were obtained using Bruker Avance 500 MHz spectrometer. The chemical shifts are given in parts per million relative to the residual signals of the solvent ($CDCl_3$, ^1H: 7.26 ppm, ^{13}C: 77.16 ppm and C_6D_6, ^1H: 7.16 ppm, ^{13}C: 128.06 ppm).[14] High-resolution mass spectrometry (HRMS) spectra were recorded using Bruker MicrOTOF-Q spectrometers with electrospray ionization (ESI) ion source and time-of-flight mass analyzer. Microanalyses were conducted with an Elementar CHNS Vario EL III analyzer. All the reactions and operations, which required an inert atmosphere of N_2, were performed by using a glovebox (MBraun) or standard Schlenk apparatus and vacuum line techniques.

Syntheses. Aminophenols were synthesized according to a literature procedure: [L^{Cy}-H] 2,4-di-*tert*-butyl-6-((cyclohexyl(methyl)amino)methyl)phenol,[15] [L^{C12}-H] 2,4-di-*tert*-butyl-6-((dodecyl(methyl)amino)methyl)phenol,[16] [L^{Me}-H] 2,4-di-*tert*-butyl-6-((dimethylamino)methyl)phenol,[17] [L^{Bn}-L] 2,4-di-*tert*-butyl-6-((dibenzylamino)methyl)phenol,[18] [L^{Pic}-H] 2-((bis(pyridin-2-ylmethyl)amino)methyl)-4,6-di-*tert*-butylphenol,[19] [L^{Ox}-H] 2-((((1,3-dioxolan-2-yl)methyl)(methyl)amino)methyl)-4,6-di-*tert*-butylphenol.[15]

The detailed synthesis and isolation of the product is presented for [$L^{Cy}_{O\text{-}Me}$] and [$L^{Cy}_{O,N\text{-}Me}$]. The syntheses for all aminophenols proceed in the same manner; therefore, the description and details for the methylated forms of L^{C12}, L^{Me}, L^{Bn}, L^{Pic}, and L^{Ox} are omitted.

N-(3,5-Di-tert-butyl-2-methoxybenzyl)-N-methylcyclohexanamine [$L^{Cy}_{O\text{-}Me}$]. To solution of [L^{Cy}-H] (1.00 g, 3.00 mmol) in THF, NaH (0.09 g, 3.75 mmol, 1.25 equiv) was added under inert atmosphere of N_2. The solution turned cloudy, and gas evolution was observed. After 1 h, MeI (0.28 mL, 4.50 mmol, 1.5 equiv) was added via syringe. The solution was stirred at 70 °C for 4 h, after which it was cooled and extracted with DCM/H_2O. The organic layer was dried over $MgSO_4$, filtered, and evaporated to give yellow oil (0.69 g, 66%), which was purified by column chromatography on silica gel using dichloromethane/methanol (19/1) as an eluent to give the main product [$L^{Cy}_{O\text{-}Me}$] as a white powder (0.34 g, 0.98 mmol) in 33% yield. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.42 (d, J = 2.4 Hz, 1H, ArCH), 7.22 (d, J = 2.4 Hz, 1H, ArCH), 3.78 (s, 3H, OCH_3), 3.71 (s, 2H, $ArCH_2N$), 2.49 (tt, J = 11.4, 3.1 Hz, 1H, NCH), 2.25 (s, 3H, NCH_3), 1.87 (dd, J = 12.2, 1.9 Hz, 2H, CH_2), 1.79 (dd, J = 9.7, 2.9 Hz, 2H, CH_2), 1.65−1.58 (m, 1H, CH_2), 1.40 (s, 9H, $C(CH_3)_3$), 1.30 (s, J = 3.7 Hz, 9H, $C(CH_3)_3$), 1.29−1.04 (m, 5H, CH_2). ^{13}C NMR (126 MHz, CDCl3) δ: 157.3 (s, 1C, ArCO), 146.4 (s, 1C, ArC), 142.4 (s, 1C, ArC), 127.1 (s, 1C, ArCH), 124.6 (s, 1C, ArC), 123.8 (s, 1C, ArCH), 63.3 (s, 1C, NCH), 63.1 (s, 1C, OCH_3), 53.7 (s, 1C, $ArCH_2N$), 38.3 (s, 1C, NCH_3), 36.4 (s, 1C, $C(CH_3)_3$), 35.7 (s, 1C, $C(CH_3)_3$), 32.7 (s, 3C, $C(CH_3)_3$), 32.3 (s, 3C, $C(CH_3)_3$), 29.6 (s, 2C, CH_2), 27.6 (s, 1C, CH_2), 27.2 (s, 2C, CH_2). HRMS(ESI): calcd for $C_{23}H_{39}NO$: 345.303 $[M + H]^+$, found 345.30. Anal. calcd (found) for $C_{23}H_{39}NO$: C, 79.94 (78.77); H, 11.38 (10.56); N, 4.05 (3.63)%.

The next methylated product [$L^{Cy}_{O,N\text{-}Me}$] was purified in the same manner and was obtained as white powder (0.12g, 0.25 mmol) in 11% yield.

N-(3,5-Di-tert-butyl-2-methoxybenzyl)-N,N-dimethylcyclohexaminium iodide [$L^{Cy}_{O,N\text{-}Me}$]. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.59 (d, J = 2.5 Hz, 1H, ArCH), 7.50 (d, J = 2.5 Hz, 1H, ArCH), 4.80 (s, 2H, $ArCH_2N$), 3.79 (s, 3H, OCH_3), 3.72−3.60 (m, 1H, NCH), 3.07 (s, 6H, NCH_3), 2.37 (t, J = 20.6 Hz, 2H, CH_2), 2.03 (d, J = 13.4 Hz, 2H, CH_2), 1.73−1.51 (m, 4H, CH_2), 1.40 (s, 9H, $C(CH_3)_3$), 1.33 (s, 9H, $C(CH_3)_3$), 1.27−1.22 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.77 (s, 1C, ArCO), 147.38 (s, 1C, ArC), 144.73 (s, 1C, ArC), 130.84 (s, 1C, ArCH), 128.23 (s, 1C, ArCH), 120.80 (s, 1C, ArC), 72.40 (s, 1C, NCH), 63.85 (s, 1C, OCH_3), 61.60 (s, 1C, $ArCH_2N$), 47.57 (s, 1C, NCH_3), 35.46 (s, 1C, $C(CH_3)_3$), 34.78 (s, 1C, $C(CH_3)_3$), 31.49 (s, 3C, $C(CH_3)_3$), 31.18 (s, 3C, $C(CH_3)_3$), 27.19 (s, 2C, CH_2), 25.47 (s, 1C, CH_2), 24.84 (s, 2C, CH_2). HRMS(ESI): calcd for $C_{24}H_{42}NO^+$: 360.324 $[M + H]^+$, found 360.33. Anal. calcd (found) for $C_{24}H_{42}NO^+I^-$: C, 59.13 (58.85); H, 8.68 (9.12); N, 2.87 (2.99)%.

N-(3,5-Di-tert-butyl-2-methoxybenzyl)-N-methyldodecan-1-amine [$L^{C12}_{O\text{-}Me}$]. Synthesis of [$L^{Cy}_{O\text{-}Me}$] was performed by using appropriate substrates as follows: [L^{C12}-H] (1.00 g, 2.40 mmol), NaH (0.072 g, 3.00 mmol, 1.25 equiv), and MeI (0.22 mL, 3.60 mmol, 1.5 equiv). Compound was obtained as white powder, yield: (0.40 g, 0.92 mmol, 39%). ^1H NMR (500 MHz, C_6D_6) δ 7.78 (d, J = 2.6 Hz, 1H, ArCH), 7.46 (d, J = 2.6 Hz, 1H, ArCH), 3.62 (s, 2H, $ArCH_2N$), 3.58 (s, 3H, OCH_3), 2.47−2.33 (m, 2H, NCH_2), 2.23 (s, 3H, NCH_3), 1.53 (s, 9H, $C(CH_3)_3$), 1.38 (s, 9H, $C(CH_3)_3$), 1.35−1.26 (m, 20H, $CH_2-(CH_2)_{10}-CH_3$), 0.92 (t, J = 6.9 Hz, 3H, CH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 157.0 (s, 1C, ArCO), 145.6 (s, 1C, ArC), 141.7 (s, 1C, ArC), 132.5 (s, 1C, ArCH), 126.4 (s, 1C, ArCH), 122.8 (s, 1C, ArC), 61.9 (s, 1C, OCH_3), 57.9 (s, 1C, NCH_2), 57.6 (s, 1C, $ArCH_2N$), 42.5 (s, 1C, NCH_3), 35.6 (s, 1C, $C(CH_3)_3$), 34.8 (s, 1C, $C(CH_3)_3$), 32.4 (s, 1C, CH_2), 31.5 (s, 3C, $C(CH_3)_3$), 31.2 (s, 3C, $C(CH_3)_3$), 30.2 (m, 5C, CH_2), 29.9 (s, 1C, CH_2), 28.0 (s, 1C, CH_2), 27.9 (s, 1C, CH_2), 23.1 (s, 1C, CH_2), 14.4 (s, 1C, CH_3). HRMS(ESI): calcd for $C_{29}H_{53}NO$: 417.396 $[M + H]^+$, found 431.41. Anal. calcd (found) for $C_{29}H_{53}NO$: C, 80.68 (80.31); H, 12.37 (12.01); N, 3.24 (3.03)%.

N-(3,5-Di-tert-butyl-2-methoxybenzyl)-N,N-dimethyldodecan-1-aminium iodide [$L^{C12}_{O,N\text{-}Me}$]. Compound was obtained as white powder (0.17 g, 0.30 mmol) in 16% yield. ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 2.4 Hz, 1H, ArCH), 7.43 (d, J = 2.4 Hz, 1H, ArCH), 4.80 (s, 2H, $ArCH_2N$), 3.74 (s, 3H, OCH_3), 3.41−3.34 (m, 2H, NCH_2), 3.14 (s, 6H, NCH_3), 1.79−1.65 (m, 2H, CH_2), 1.33 (s, 9H, $C(CH_3)_3$), 1.26 (s, 9H, $C(CH_3)_3$), 1.23−1.15 (m, 18H, $CH_2-(CH_2)_9-CH_3$), 0.80 (d, J = 7.1 Hz, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9 (s, 1C, ArCO), 147.8 (s, 1C, ArC), 143.8 (s, 1C, ArC), 131.0 (s, 1C, ArCH), 128.3 (s, 1C, ArCH), 120.8 (s, 1C, ArC), 64.5 (s, 1C, OCH_3), 64.1 (s, 1C, $ArCH_2N$), 64.0 (s, 1C, NCH_2), 50.4 (s, 2C, NCH_3), 35.7 (s, 1C, $C(CH_3)_3$), 34.9 (s, 1C, $C(CH_3)_3$), 32.0 (s, 1C, CH_2), 31.6 (s, 3C, $C(CH_3)_3$), 31.3 (s, 3C, $C(CH_3)_3$), 29.8−29.3 (m, 6C, CH_2), 26.5 (s, 1C, CH_2), 23.4 (s, 1C, CH_2), 22.8 (s, 1C, CH_2), 14.3 (s, 1C, CH_3). HRMS(ESI): calcd for $C_{30}H_{56}NO^+$: 446.442 $[M - I]^+$, found 446.44. Anal. calcd (found) for $C_{30}H_{56}NO^+I^-$: C, 62.81 (62.12); H, 9.84 (10.38); N, 2.44 (2.82)%.

1-(3,5-Di-tert-butyl-2-methoxyphenyl)-N,N-dimethylmethanamine [$L^{Me}_{O\text{-}Me}$]. Synthesis of [$L^{Me}_{O\text{-}Me}$] was was performed by using appropriate substrates as follows: compound [L^{Me}-H] (1.00 g, 3.80 mmol), NaH (0.11 g, 4.75 mmol, 1.25 equiv), and MeI (0.35 mL, 5.70 mmol, 1.5 equiv). Compound was obtained as white powder, yield: (0.36 g, 1.30 mmol, 34%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, J = 2.5 Hz, 1H, ArCH), 7.25 (d, J = 2.5 Hz, 1H, ArCH), 3.79 (s, 3H, OCH_3), 3.52 (s, 2H, $ArCH_2N$), 2.27 (s, 6H, NCH_3), 1.39 (s, 9H, $C(CH_3)_3$), 1.30 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3 (s, 1C, ArCO), 145.5 (s, 1C, ArC), 141.7 (s, 1C, ArC), 130.9 (s, 1C, ArC), 126.3 (s, 1C, ArCH), 123.2 (s, 1C, ArCH), 62.2 (s, 1C, $ArCH_2N$), 59.0 (s, 1C, OCH_3), 45.5 (s, 2C, NCH_3), 35.4 (s, 1C, $C(CH_3)_3$), 34.6 (s, 1C, $C(CH_3)_3$), 31.7 (s, 3C, $C(CH_3)_3$), 31.4 (s, 3C, $C(CH_3)_3$). HRMS(ESI): calcd for $C_{18}H_{31}NO$: 277.243 $[M + H]^+$, found 277.24. Anal. calcd (found) for $C_{18}H_{31}NO$: C, 77.92 (77.64); H, 11.26 (11.02); N, 5.05 (4.81)%.

1-(3,5-Di-tert-butyl-2-methoxyphenyl)-N,N,N-trimethylmethanaminium iodide [$L^{Me}_{O,N\text{-}Me}$]. Compound was obtained as white powder

https://dx.doi.org/10.1021/acs.inorgchem.0c00310
Inorg. Chem. XXXX, XXX, XXX−XXX

(0.19 g, 0.45 mmol) in 18% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 2.5 Hz, 1H, ArCH), 7.50 (d, J = 2.5 Hz, 1H, ArCH), 4.87 (s, 2H, $ArCH_2N$), 3.83 (s, 3H, OCH_3), 3.36 (s, 9H, NCH_3), 1.39 (s, 9H, $C(CH_3)_3$), 1.32 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.7 (s, 1C, ArCO), 147.5 (s, 1C, ArC), 143.8 (s, 1C, ArC), 130.8 (s, 1C, ArC), 128.2 (s, 1C, ArCH), 120.8 (s, 1C, ArCH), 65.8 (s, 1C, $ArCH_2N$), 64.1 (s, 1C, OCH_3), 53.4 (s, 3C, NCH_3), 35.6 (s, 1C, $C(CH_3)_3$), 34.9 (s, 1C, $C(CH_3)_3$), 31.5 (s, 3C, $C(CH_3)_3$), 31.3 (s, 3C, $C(CH_3)_3$). HRMS(ESI): calcd for $C_{19}H_{34}NO^+$: 292.262 [M − I]$^+$, found 292.26. Anal. calcd (found) for $C_{19}H_{34}NO^+I^-$: C, 54.41 (53.95); H, 8.17 (8.54); N, 3.34 (2.81)%.

N,N-Dibenzyl-1-(3,5-di-tert-butyl-2-methoxyphenyl)-methanamine [$L^{Bn}_{O\text{-}Me}$]. Synthesis of [$L^{Bn}_{O\text{-}Me}$] was performed by using appropriate substrates as follows: compound [L^{Bn}-H] (1.00 g, 2.41 mmol), NaH (0.072 g, 3.00 mmol, 1.25 equiv), and MeI (0.23 mL, 3.61 mmol, 1.5 equiv). Compound was obtained as white powder, yield: (0.84 g, 1.96 mmol, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72−7.69 (m, 1H, ArCH), 7.44−7.40 (m, 4H, ArCH), 7.30 (dd, J = 10.9, 4.3 Hz, 4H, ArCH), 7.23−7.18 (m, 3H, ArCH), 3.64−3.63 (s, 2H, $ArCH_2N$), 3.63−3.62 (s, 3H, OCH_3), 3.56 (s, 4H, NCH_2Ar), 1.39 (d, J = 1.8 Hz, 9H, $C(CH_3)_3$), 1.34 (t, J = 3.4 Hz, 9H, $C(CH_3)_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3 (s, 1C, ArCO), 145.4 (s, 1C, ArC), 141.4 (s, 1C, ArC), 140.0 (s, 1C, ArC), 132.1 (s, 1C, ArC), 128.9 (s, 4C, ArCH), 128.3 (s, 4C, ArCH), 126.9 (s, 2C, ArCH), 125.3 (s, 1C, ArCH), 122.6 (s, 1C, ArCH), 62.0 (s, 1C, $ArCH_2N$), 58.4 (s, 2C, NCH_2Ar), 52.5 (s, 1C, OCH_3), 35.4 (s, 1C, $C(CH_3)_3$), 34.7 (s, 1C, $C(CH_3)_3$), 31.8 (s, 3C, $C(CH_3)_3$), 31.3 (s, 3C, $C(CH_3)_3$). HRMS(ESI): calcd for $C_{30}H_{39}NO$: 429.301 [M + H]$^+$, found 429.30. Anal. calcd (found) for $C_{30}H_{39}NO$: C, 83.87 (83.75); H, 9.15 (8.93); N, 3.26 (3.06)%.

N-(3,5-Di-tert-butyl-2-methoxybenzyl)-1-(pyridin-2-yl)-N-(pyridin-2-ylmethyl)methanamine [$L^{Pic}_{O\text{-}Me}$]. Synthesis of [$L^{Pic}_{O\text{-}Me}$] was performed by using appropriate substrates as follows: compound [L^{Pic}-H] (1.00 g, 2.40 mmol), NaH (0.072 g, 3.00 mmol, 1.25 equiv), and MeI (0.22 mL, 3.60 mmol, 1.5 equiv). Product was obtained as white powder, yield: (0.72 g, 1.67 mmol, 69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56−8.45 (m, 2H, ArCH), 7.68−7.57 (m, 5H, ArCH), 7.20 (d, J = 2.5 Hz, 1H, ArCH), 7.15−7.11 (m, 2H, ArCH), 3.82 (s, 4H, NCH_2Ar), 3.79−3.75 (m, 2H, $ArCH_2N$), 3.64 (s, 3H, OCH_3), 1.37 (d, J = 4.4 Hz, 9H, $C(CH_3)_3$), 1.29 (d, J = 3.7 Hz, 9H, $C(CH_3)_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2 (s, 1C, ArCO), 156.3 (s, 1C, ArC), 149.1 (s, 2C, ArCH), 145.5 (s, 1C, ArC), 141.7 (s, 2C, ArC), 136.5 (s, 4C, ArCH), 125.1 (s, 1C, ArCH), 122.9 (s, 1C, ArC), 122.9 (s, 1C, ArCH), 122.0 (s, 2C, ArCH), 62.0 (s, 1C, OCH_3), 60.5 (s, 2C, NCH_2Ar), 53.3 (s, 1C, $ArCH_2N$), 35.4 (s, 1C, $C(CH_3)_3$), 34.7 (s, 1C, $C(CH_3)_3$), 31.8 (s, 3C, $C(CH_3)_3$), 31.3 (s, 3C, $C(CH_3)_3$). HRMS(ESI): calcd for $C_{28}H_{37}N_3O$: 431.29 [M + H]$^+$, found 431.29. Anal. calcd (found) for $C_{28}H_{37}N_3O$: C, 77.92 (77.71); H, 8.64 (8.59); N, 9.74 (9.62)%.

N-((1,3-Dioxolan-2-yl)methyl)-1-(3,5-ditert-butyl-2-methoxyphenyl)-N-methylmethanamine [$L^{Ox}_{O\text{-}Me}$]. Synthesis of [$L^{Ox}_{O\text{-}Me}$] was performed by using appropriate substrates as follows: compound [L^{Ox}-H] (1.00 g, 2.98 mmol), NaH (0.089 g, 3.72 mmol, 1.25 equiv), and MeI (0.28 mL, 4.47 mmol, 1.5 equiv). Product was obtained as white powder, yield: (0.41 g, 1.17 mmol, 39%). ^{1}H NMR (500 MHz, C_6D_6) δ 7.70 (d, J = 2.6 Hz, 1H, ArCH), 7.36 (d, J = 2.6 Hz, 1H, ArCH), 5.03 (t, J = 4.3 Hz, 1H, CH), 3.66 (s, 2H, $ArCH_2N$), 3.45 (s, 3H, OCH_3), 3.42−3.35 (m, 2H, CH_2), 3.29−3.19 (m, 2H, CH_2), 2.71 (d, J = 4.3 Hz, 2H, NCH_2), 2.29 (s, 3H, NCH_3), 1.41 (s, 9H, $C(CH_3)_3$), 1.27 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (126 MHz, C_6D_6) δ 156.6 (s, 1C, ArCO), 145.3 (s, 1C, ArC), 141.4 (s, 1C, ArC), 131.9 (s, 1C, ArCH), 126.1 (s, 1C, ArCH), 122.5 (s, 1C, ArC), 104.2 (s, 1C, CH), 64.4 (s, 2C, CH_2), 61.5 (s, 1C, $ArCH_2N$), 60.4 (s, 1C, OCH_3), 57.5 (s, 1C, NCH_2), 43.3 (s, 1C, NCH_3), 35.3 (s, 1C, $C(CH_3)_3$), 34.5 (s, 1C, $C(CH_3)_3$), 31.5 (s, 3C, $C(CH_3)_3$), 31.2 (s, 3C, $C(CH_3)_3$). HRMS(ESI): calcd for $C_{21}H_{35}NO_3$: 349.26 [M + H]$^+$, found 349.26. Anal. calcd (found) for $C_{21}H_{35}NO_3$: C, 72.17 (71.87); H, 10.09 (9.89); N, 4.01 (3.85)%.

N-((1,3-Dioxolan-2-yl)methyl)-1-(3,5-di-tert-butyl-2-methoxyphenyl)-N,N-dimethylmethanaminium iodide [$L^{Ox}_{O,N\text{-}Me}$]. Compound was obtained as white powder (0.28 g, 0.57 mmol) in 27% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 2.5 Hz, 1H, ArCH), 7.44 (dd, J = 7.9, 2.5 Hz, 1H, ArCH), 5.42 (t, J = 4.6 Hz, 1H, CH), 4.97 (s, 2H, $ArCH_2N$), 4.11−3.90 (m, 4H, CH_2), 3.77 (s, 3H, OCH_3), 3.73 (d, J = 4.7 Hz, 2H, NCH_2), 3.25 (s, 6H, NCH_3), 1.3 (s, 9H, $C(CH_3)_3$), 1.26 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8 (s, 1C, ArCO), 147.3 (s, 1C, ArC), 143.6 (s, 1C, ArC), 131.1 (s, 1C, ArCH), 128.0 (s, 1C, ArCH), 120.6 (s, 1C, ArC), 98.1 (s, 1C, CH), 65.6 (s, 1C, $ArCH_2N$), 65.4 (s, 1C, OCH_3), 64.4 (s, 2C, CH_2), 64.1 (s, 1C, NCH_2), 51.4 (s, 2C, NCH_3), 35.4 (s, 1C, $C(CH_3)_3$), 34.7 (s, 1C, $C(CH_3)_3$), 31.5 (s, 3C, $C(CH_3)_3$), 31.1 (s, 3C, $C(CH_3)_3$). HRMS(ESI): calcd for $C_{22}H_{38}NO_3^+$: 364.28 [M − I]$^+$, found 364.28. Anal. calcd (found) for $C_{22}H_{38}NO_3^+I^-$: C, 53.77 (53.34); H, 7.79 (8.32); N, 2.85 (2.67)%.

1,4-Bis((cyclohexyl(methyl)amino)methyl)naphthalene-2,3-diol [LN^{Cy}-H_2]. To a solution of 2,3-dihydroxynaphthalene (0.613 g, 3.8 mmol) in methanol (20 mL), *N*-methylcyclohexylamine (1.0 mL, 7.7 mmol) was added. While the mixture was stirred on an ice bath, an aqueos solution of formaldehyde (0.65 mL, 8.6 mmol) was slowly added. After 15 min a crude product precipitated as a white solid. It was collected by filtration, washed with cold methanol, recrystallized from toluene, and dried in vacuo to give the main product (1.44 g, 3.5 mmol) as a white crystalline powder in 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.69 (br s, 1H), 7.73 (dd, J = 6.4, 3.3 Hz, 2H, ArCH), 7.25 (dd, J = 6.4, 3.2 Hz, 2H, ArCH), 4.26 (s, 4H, $ArCH_2N$), 2.67 (tt, J = 11.4, 3.2 Hz, 2H, NCH), 2.37 (s, J = 7.0 Hz, 6H, NCH_3), 1.99 (d, J = 11.2 Hz, 4H, CH_2), 1.84 (d, J = 13.1 Hz, 4H, CH_2), 1.66 (d, J = 12.7 Hz, 2H, CH_2), 1.41 (qd, J = 12.2, 2.9 Hz, 4H, CH_2), 1.27 (ddt, J = 25.5, 12.6, 3.3 Hz, 4H, CH_2), 1.15 (tt, J = 12.6, 3.3 Hz, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1 (s, 2C, ArOH), 127.0 (s, 2C, ArC), 122.5 (s, 2C, ArCH), 121.4 (s, 2C, ArCH), 110.8 (s, 2C, ArC), 62.5 (s, 2C, NCH), 53.3 (s, 2C, $ArCH_2N$), 37.0 (s, 2C, CH_3), 28.3 (s, 4C, CH_2), 26.2 (s, 2C, CH_2), 25.8 (s, 4C, CH_2). HRMS(ESI): calc for $C_{26}H_{38}N_2O_2$: 411.30 [M + H]$^+$, found: 411.30. Anal. calcd (found) for $C_{26}H_{38}N_2O_2$: C, 76.06 (75.69); H, 9.33 (10.46); N, 6.82 (6.68)%.

[L^{Cy}-Na]. In the glovebox, to the stirred solution of L^{Cy}-H (1.50 g, 4.50 mmol) in THF the NaH (0.11 g, 4.50 mmol, 1.00 equiv) was added. The solution turned cloudy, and gas evolution was observed. The mixture was stirred, until the solution was clear. Next the solution was placed at −15 °C, until colorless crystalline product appeared, which was filtered off and dried under vacuum to obtain L^{Cy}-Na (1.81 g, 94%). ^{1}H NMR (500 MHz, C_6D_6) δ 7.51 (s, 2H, ArCH), 7.13 (d, J = 1.9 Hz, 2H, ArCH), 3.70 (bs, 4H, $ArCH_2N$), 3.49−3.36 (m, 8H, CH_2^{THF}), 2.73 (s, 2H, NCH), 2.09 (s, 6H, NCH_3), 1.70 (s, 18H, $C(CH_3)_3$), 1.49 (s, 18H, $C(CH_3)_3$), 1.62−1.01 (m, 20H, CH_2), 1.37−1.28 (m, 8H, CH_2^{THF}). ^{13}C NMR (126 MHz, C_6D_6) δ 166.8 (s, 2C, ArCO), 155.8 (s, 2C, ArC), 140.4 (s, 2C, ArC), 136.2 (s, 2C, ArC), 130.7 (s, 2C, ArCH), 124.3 (s, 2C, ArCH), 68.0 (s, 4H, CH_2^{THF}), 62.0 (s, 2C, NCH_3), 58.9 (s, 2C, $ArCH_2N$), 58.5 (s, 2C, CH), 35.7 (s, 2C, $C(CH_3)_3$), 34.0 (s, 2C, $C(CH_3)_3$), 32.6 (s, 6C, $C(CH_3)_3$), 32.1 (s, 1C, CH_2), 30.7 (s, 6C, $C(CH_3)_3$), 30.1 (s, 1C, CH_2), 26.7 (s, 4C, CH_2), 26.4 (s, 4C, CH_2), 25.7 (s, 4C, CH_2^{THF}). Anal. calcd (found) for $C_{52}H_{86}N_2O_4Na_2$: C, 73.54 (74.01); H, 10.21 (10.43); N, 3.26 (3.11)%.

[L^{C12}-Na]. Compound L^{C12}-Na was synthesized by using 1.50 g (3.59 mmol) of L^{C12}-H and NaH (0.086 g, 3.59 mmol, 1.00 equiv). L^{C12}-Na was obtained as colorless crystalline product (1.62 g, 89%). ^{1}H NMR (500 MHz, C_6D_6) δ 7.52 (s, 2H, ArCH), 7.13 (s, 2H, ArCH), 4.26−2.94 (bs, 4H, $ArCH_2N$), 2.74−2.26 (m, 8H, CH_2^{THF}), 2.26−1.75 (bs, 4H, NCH_2), 1.71 (s, 6H, NCH_3, 4H, CH_2), 1,72 (s, 18H, $C(CH_3)_3$), 1.50 (s, 18H, $C(CH_3)_3$), 1.35−1.16 (m, 44H, CH_2, CH_2^{THF}), 0.93 (t, J = 6.8 Hz, 6H, CH_3). ^{13}C NMR (126 MHz, C_6D_6) δ 166.9 (s, 2C, ArCO), 155.4 (s, 2C, ArC), 140.6 (s, 2C, ArC), 136.0 (s, 2C, ArC), 129.1 (s, 2C, ArCH), 123.2 (s, 2C, ArCH), 67.9 (s, 4H, CH_2^{THF}), 63.7 (s, 2C, $ArCH_2N$), 62.6 (s, 2C, NCH_2), 57.0 (s, 2C, NCH_3), 40.8 (s, 2C, CH_2), 35.4 (s, 2C, $C(CH_3)_3$), 34.4 (s, 2C, $C(CH_3)_3$), 32.4 (s, 2C, CH_2), 32.0 (s, 6C, $C(CH_3)_3$), 30.6 (s, 6C, $C(CH_3)_3$), 29.9 (m, 10C, CH_2), 28.0 (s, 2C, CH_2), 27.5 (s, 2C, CH_2), 27.3 (s, 2C, CH_2), 25.7 (s, 4C, CH_2^{THF}), 23.2 (s, 2C, CH_2),

https://dx.doi.org/10.1021/acs.inorgchem.0c00310
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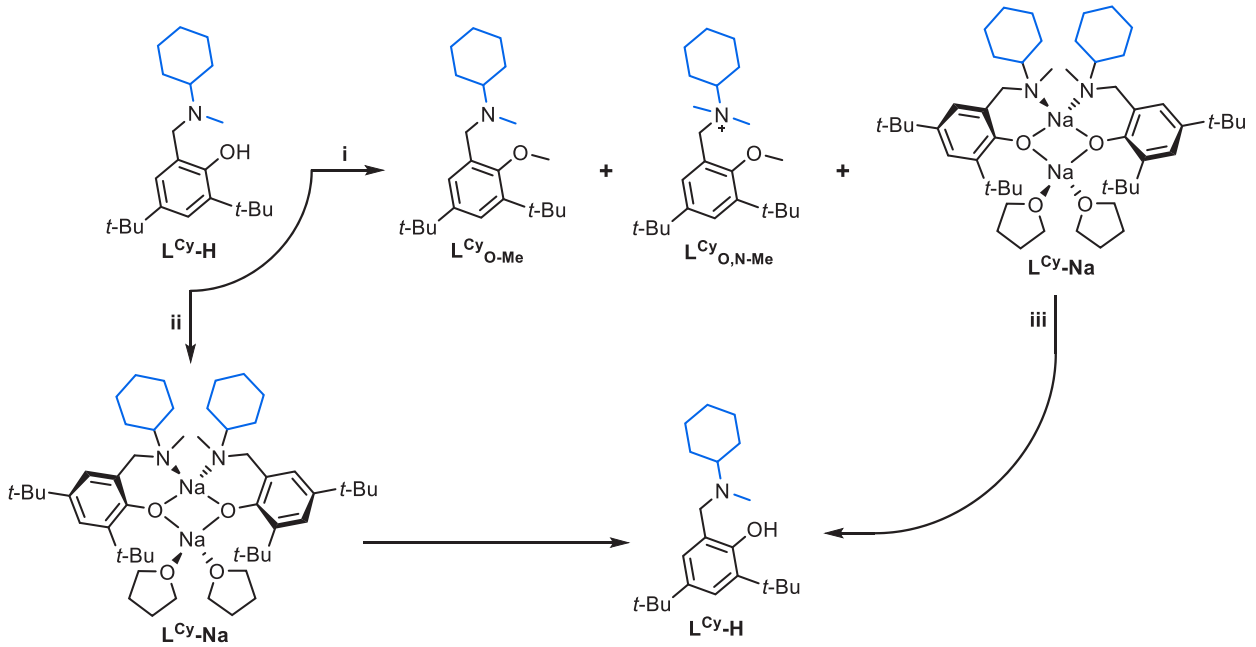
Scheme 1. Syntheses[a]



[a](i) NaH, THF, RT, 1 h, N_2; MeI added after 1 h, 70 °C, 4 h, N_2 (stoichiometry NaH/MeI = 1.25/1.5), extracted with DCM/H_2O air; (ii) NaH added (stoichiometry L^{Cy}-H/NaH = 1/1); (iii), DCM/H_2O, air.

14.4 (s, 2C, CH_3). Anal. calcd (found) for $C_{64}H_{114}N_2O_4Na_2$: C, 75.24 (75.68); H, 11.25 (11.51); N, 2.74 (2.84)%.

[L^{Me}-Na]. Compound L^{Me}-Na was synthesized by using 1.50 g (5.69 mmol) of L^{Me}-H and NaH (0.14 g, 5.69 mmol, 1.00 equiv). L^{Me}-Na was obtained as colorless crystalline product (2.14 g, 88%). ^{1}H NMR (500 MHz, C_6D_6) δ 7.53 (d, J = 2.3 Hz, 2H, ArCH), 7.02 (s, 2H, ArCH), 3.55−3.23 (m, 12H, $ArCH_2N$, CH_2^{THF}), 1.90 (s, 12H, NCH_3), 1.69 (s, 18H, $C(CH_3)_3$), 1.45 (s, 18H, $C(CH_3)_3$), 1.34−1.27 (m, 8H, CH_2^{THF}). ^{13}C NMR (151 MHz, C_6D_6) δ 166.6 (s, 2C, ArCO), 161.4 (s, 2C, ArC), 136.5 (s, 2C, ArC), 131.2 (s, 2C, ArC), 128.4 (s, 2C, ArCH), 124.7 (s, 2C, ArCH), 67.9 (s, 4H, CH_2^{THF}), 64.4 (s, 2C, $ArCH_2N$), 45.7 (s, 4C, NCH_3), 35.7 (s, 2C, $C(CH_3)_3$), 34.0 (s, 2C, $C(CH_3)_3$), 32.5 (s, 6C, $C(CH_3)_3$), 30.6 (s, 6C, $C(CH_3)_3$), 25.6 (s, 4C, CH_2^{THF}). Anal. calcd (found) for $C_{50}H_{84}N_2O_6Na_2$: C, 70.22 (70.59); H, 9.90 (9.95); N, 3.28 (3.59)%.

[L^{Bn}-Na]. Compound L^{Bn}-Na was synthesized by using 1.50 g (3.60 mmol) of L^{Bn}-H and NaH (0.087 g, 3.60 mmol, 1.00 equiv). L^{Bn}-Na was obtained as a colorless crystalline product (1.76 g, 84%). ^{1}H NMR (500 MHz, C_6D_6) δ 7.49 (d, J = 2.7 Hz, 2H, ArCH), 7.16 (d, J = 2.7 Hz, 2H, ArCH), 6.87−6.79 (m, 12H, ArCH), 6.67 (d, J = 7.0 Hz, 8H, ArCH), 3.75−3.59 (m, 4H, $ArCH_2N$), 3.59−3.26 (m, 16H, CH_2^{THF}), 34.60 (s, 8H, CH_2), 1.43 (s, 18H, $C(CH_3)_3$), 1.41 (s, 18H, $C(CH_3)_3$), 1.34−1.29 (m, 16H, CH_2^{THF}). ^{13}C NMR (126 MHz, C_6D_6) δ 167.1 (s, 2C, ArCO), 155.2 (s, 2C, ArC), 141.5 (s, 2C, ArC), 140.4 (s, 2C, ArC), 138.1 (s, 4C, ArC), 137.1 (s, 2C, ArCH), 130.1 (s, 8C, ArCH), 129.4 (s, 4C, ArCH), 125.0 (s, 8C, ArCH), 124.2 (s, 2C, ArCH), 68.4 (s, 8C, CH_2^{THF}), 63.4 (s, 2C, $ArCH_2N$), 58.9 (s, 4C, CH_2), 34.8 (s, 2C, $C(CH_3)_3$), 34.7 (s, 2C, $C(CH_3)_3$), 33.1 (s, 6C, $C(CH_3)_3$), 26.37 (s, 6C, $C(CH_3)_3$), 26.4 (s, 8C, CH_2^{THF}). Anal. calcd (found) for $C_{74}H_{100}N_2O_6Na_2$: C, 76.65 (77.13); H, 8.69 (8.25); N, 3.97 (3.80)%.

[L^{Pic}-Na]. Compound L^{Pic}-Nawas synthesized by using 1.50 g (3.60 mmol) of L^{Pic}-H and NaH (0.086 g, 3.60 mmol, 1.00 equiv). L^{Pic}-Na was obtained as a colorless crystalline product (1.41 g, 89%). ^{1}H NMR (500 MHz, C_6D_6) δ 8.31 (s, 4H, PyCH), 7.40 (d, J = 2.7 Hz, 2H, ArCH), 7.10 (d, J = 2.5 Hz, 2H, ArCH), 6.80 (t, J = 7.2 Hz, 4H, PyCH), 6.68−6.27 (m, 8H, PyCH), 4.73 (br s, 4H, $ArCH_2N$), 3.62 (br s, 4H, br s, 4H, $PyCH_2N$), 3.21 (br s, 6H, $ArCH_2N$, $PyCH_2N$), 1.89 (s, 18H, $C(CH_3)_3$), 1.55 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (126 MHz, C_6D_6) δ 167.3 (s, 2C, ArCO), 158.9 (s, 4C, PyCH), 145.7 (s, ArC), 140.0 (s, 2C, ArC), 138.1 (s, 2C, ArC), 136.6 (s, 4C, PyCH), 127.5 (s, 2C, ArCH), 124.0 (s, 2C, ArCH), 122.7 (s, 8C, PyCH), 120.5 (s, 4C, PyC), 58.8 (s, 2C, $ArCH_2N$), 41.3 (s, 2C, $PyCH_2N$), 36.2 (s, 2C, $C(CH_3)_3$), 34.6 (s, 2C, $C(CH_3)_3$), 33.4 (s, 6C, $C(CH_3)_3$), 31.3 (s, 6C, $C(CH_3)_3$). Anal. calcd (found) for $C_{54}H_{68}N_6O_2Na_2$: C, 73.77 (73.52); H, 7.80 (7.98); N, 9.56 (9.34)%.

[L^{Ox}-Na]. Compound L^{ox}-Na was synthesized by using 1.50 g (4.47 mmol) of L^{ox}-H and NaH (0.11 g, 4.47 mmol, 1.00 equiv). L^{ox}-Na was obtained as a colorless crystalline product (1.79 g, 93%). ^{1}H NMR (500 MHz, C_6D_6) δ 7.54 (d, J = 2.5 Hz, 2H, ArCH), 7.08 (d, J = 2.5 Hz, 2H, ArCH), 4.64 (d, J = 36.7 Hz, 2H, CH), 3.62−3.43 (m, 8H, CH_2^{THF}), 3.22 (bs, 4H, $ArCH_2N$), 3.04 (s, 8H, CH_2), 2.63 (bs, 4H, NCH_2), 2.07 (s, 6H, NCH_3), 1.76 (s, 18H, $C(CH_3)_3$), 1.47 (s, 18H, $C(CH_3)_3$), 1.40−1.34 (m, 8H, CH_2^{THF}). ^{13}C NMR (151 MHz, C_6D_6) δ 167.9 (s, 2C, ArCO), 158.6 (s, 2C, ArC), 138.2 (s, 2C, ArC), 136.0 (s, 2C, ArC), 128.9 (s, 2C, ArCH), 123.0 (s, 2C, ArCH), 100.9 (s, 2C, CH), 67.5 (s, 4C, CH_2^{THF}), 64.5 (s, 2C, $ArCH_2N$), 64.0 (s, 4C, CH_2), 60.0 (s, 2C, NCH_2), 42.0 (s, 2C, NCH_3), 35.1 (s, 2C, $C(CH_3)_3$), 33.7 (s, 2C, $C(CH_3)_3$), 32.1 (s, 6C, $C(CH_3)_3$), 30.1 (s, 6C, $C(CH_3)_3$), 25.4 (s, 4C, CH_2^{THF}). Anal. calcd (found) for $C_{48}H_{78}N_2O_8Na_2$: C, 67.26 (67.32); H, 9.17 (8.97); N, 3.27 (3.35)%.

[(BP-Na)$_2$]. Compound(BP-Na)$_2$ was synthesized by using 1.00 g (3.00 mmol) of L^{Cy}-H, 0.11 g (4.50 mmol, 1.5 equiv) of NaH, and 0.37 mL (6.00 mmol, 2.00 equiv) of MeI added simultaneously. (BP-Na)$_2$ crystallized from the parent solution under inert atmosphere as colorless crystals (0.43 g, 0.31 mmol) in 42% yield. ^{1}H NMR (500 MHz, C_6D_6) δ 7.37 (s, 4H, ArCH), 7.37 (s, 4H, ArCH), 4.03 (br s, 4H, $ArCH_2Ar$), 3.44−3.40 (m, 24H, CH_2^{THF}), 1.54 (s, 36H, $C(CH_3)_3$), 1.38 (s, 36H, $C(CH_3)_3$), 1.37−1.33 (m, 24H, CH_2^{THF}). ^{13}C NMR (126 MHz, C_6D_6) δ 168.2 (s, 4C, ArCO), 156.4 (s, 4C, ArC), 141.3 (s, 4C, ArC), 140.4 (s, 4C, ArC), 129.1 (s, 4C, ArCH), 122.2 (s, 4C, ArCH), 68.4 (s, 12C, CH_2^{THF}), 53.9 (s, 4C, $ArCH_2Ar$), 36.0 (s, 4C, $C(CH_3)_3$), 34.8 (s, 4C, $C(CH_3)_3$), 32.9 (s, 12C, $C(CH_3)_3$), 31.1 (s, 12C, $C(CH_3)_3$), 26.3 (s, 12C, CH_2^{THF}). Anal. calcd (found) for $C_{82}H_{126}O_{10}Na_4$: C, 72.21 (72.80); H, 9.31 (9.06)%.

[BN^{Cy}-Na]. Compound BN^{Cy}-Na was synthesized by using 0.41 g (1.00 mmol) of LN^{Cy}-H_2, 0.04 g (1.50 mmol, 1.5 equiv) of NaH, and 0.12 mL (2.00 mmol, 2.00 equiv) of MeI added simultaneously. BN^{Cy}-Na crystallized from parent solution under inert atmosphere as colorless crystals (0.12 g, 0.08 mmol) in 31% yield. ^{1}H NMR (500

https://dx.doi.org/10.1021/acs.inorgchem.0c00310
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MHz, C_6D_6) δ 13.42 (br s, 2H, Ar−OH), 8.08 (br s, 4H, ArCH), 7.42 (br s, 4H, ArCH), 6.96 (br s, 8H, ArCH), 4.63 (br s, 6H, $ArCH_2N$, $ArCH_2Ar$), 3.75 (br s, 8H, $ArCH_2N$, ArOH), 3.67−3.58 (m, 16H, CH_2^{THF}), 2.53 (s, 4H, NCH), 2.27 (s, 12H, NCH_3), 2.08−0.57 (m, 40H, CH_2), 1.77−1.69 (m, 16H, CH_2^{THF}). ^{13}C NMR (126 MHz, C_6D_6) δ 151.3 (s, 8C, ArCOH), 131.5 (s, 8C, ArC), 121.3 (s, 16C, ArCH), 109.2 (s, 8C, ArC), 68.4 (s, 8C, CH_2^{THF}), 63.9 (s, 4C, N−CH), 59.5 (s, 4C, $ArCH_2N$), 54.5 (s, 2C, $ArCH_2Ar$), 38.1 (s, 4C, NCH_3), 27.8 (s, 8C, CH_2), 27.4 (s, 8C, CH_2), 26.6 (s, 4C, CH_2), 26.4 (s, 8C, CH_2^{THF}). Anal. calcd (found) for $C_{90}H_{118}N_4O_{12}Na_2$: C, 72.36 (72.78); H, 7.96 (7.65); N, 3.75 (3.97)%.

Details of X-ray Data Analysis. X-ray diffraction data for a suitable crystal of each sample were collected using a KUMA KM4 CCD or Xcalibur CCD Ruby or Xcalibur CCD Onyx (see Supporting Information, Tables S1 and S2) with ω scan technique. The data collection and processing utilized the CrysAlis suite of programs.[20] The space groups were determined based on systematic absences and intensity statistics. Lorentz polarization corrections were applied. The structures were solved using intrinsic phasing SHELXT-2014/5 and refined by full-matrix least-squares on F^2. All calculations were performed using the SHELX suite of programs.[21] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were calculated with geometry and not allowed to vary. Coordination geometries of all five-coordinated complexes were estimated according to τ parameter values.[21,22] Thermal ellipsoid plots were prepared with 30% of probability displacements for non-hydrogen atoms by using Mercury 3.9 program.[23] All data were deposited with the Cambridge Crystallographic Data Centre: CCDC 1946311 for L^{Cy}-Na, 1946312 for L^{C12}-Na, 1946313 for L^{Met}-Na, 1946314 for L^{Bn}-Na, 1946315 for L^{Pic}-Na, 1946316 for L^{Ox}-Na, 1946317 for $(BP\text{-}Na)_2$, 1946318 for BP-Na, 1946319 for BN-Na, and 1946320 for $CyMe_3N^+I^-$. Additional crystallographic information is available in the Supporting Information.

The crystal of $BP\text{-}Na_2$ is pseudomerohedrally twinned according to Twin Law (211)[100] with batch scale factor (BASF) parameter = 0.218 64. Crystal structures of sodium complexes contain disordered THF ligands/molecules *tert*-butyl and benzyl groups, which were modeled using the following Shelxl commands: DELU/ISOR (L^{Cy}-Na, L^{Met}-Na, L^{Bn}-Na, L^{Pic}-Na, L^{Ox}-Na, BP-Na, BN-Na), RIGU/ISOR (L^{C12}-Na), and RIGU/ISOR/SAME ($BP\text{-}Na_2$) and refined anisotropically.

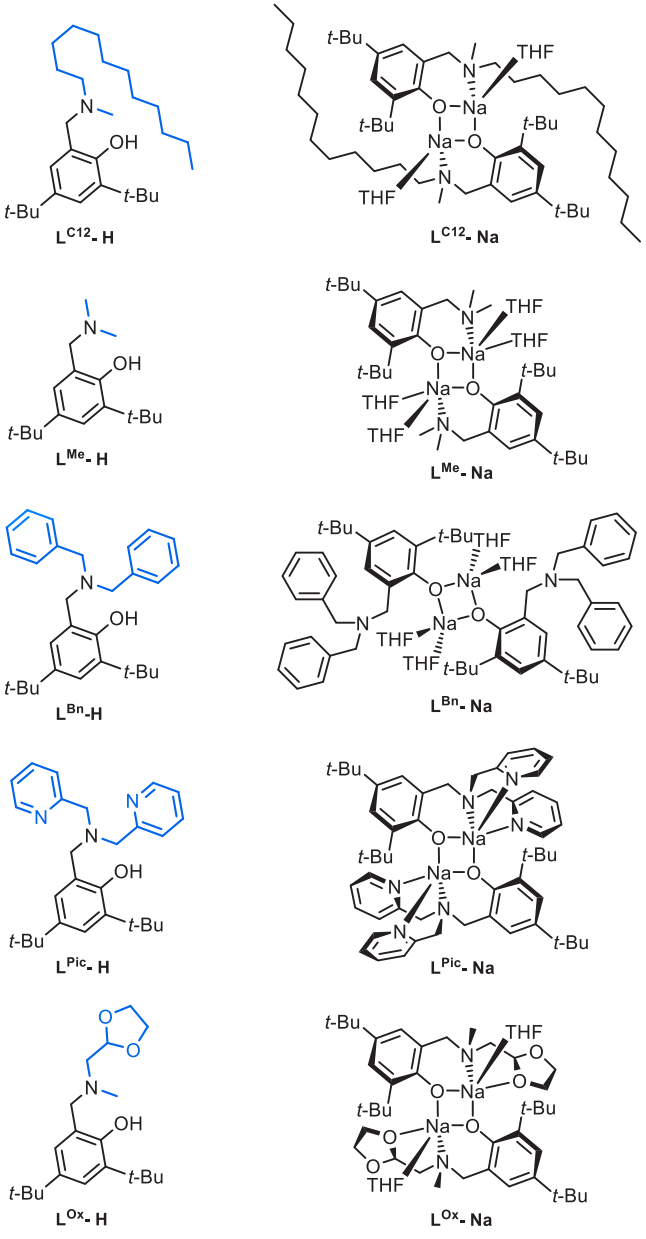
RESULTS AND DISCUSSION

The synthetic pathway involving the introduction of a methyl ether group for the protection of the hydroxyl of aminophenols is commonly used in organic synthesis, as it allows for the selective transformation of the OH function in the presence of the amine. A typical procedure consists of the deprotonation of aminophenol with sodium hydride, followed by the addition of methyl iodide to the solution of the reagents dissolved in tetrahydrofuran.[9]

Our initial attempts, aimed at the protection of the aminophenol L^{Cy}-H (Scheme 1), based on the procedure described in literature, resulted in an unsatisfactory yield of a methylated substrate (only O- or both O- and N-methylated), which was accompanied by a significant amount of unreacted aminophenol and small traces of an unexpected sodium complex with an aminophenol ligand.

Although the target products could be separated by laborious techniques, it became clear to us that the procedure described in the literature is not practical while using a specific group of reactants.[9] The rationale explaining the difficulties in the protection of L^{Cy}-H is based on the initial formation of the sodium complex as a result of the reaction of the aminophenol with NaH, preventing the methylation reaction of the starting material. It can be anticipated that, in the process of the isolation of the organic product, the sodium complex undergoes a hydrolysis reaction, restoring the aminophenol substrate. It was envisioned that the appropriate functionalization of aminophenol would suppress the coordination of sodium ions with the nitrogen atoms of the amine arm, leading eventually to higher yields of the target organic product. To test the hypothesis and gain insight into the structural limitations of the reaction, as well as to understand the effect of the substituents attached to the amine arm of the ligands on the sodium complex formation, a representative group of aminophenols was designed and synthesized. In the next step, all these compounds were evaluated as the reactants for the protection of the studied hydroxyl group (Scheme 2). The analysis of the reaction products led to the conclusion that the formation of sodium complexes is a prerogative, and only a small fraction of O-methylated aminophenols could be

Scheme 2. Functionalized Aminophenols and Their Sodium Complexes



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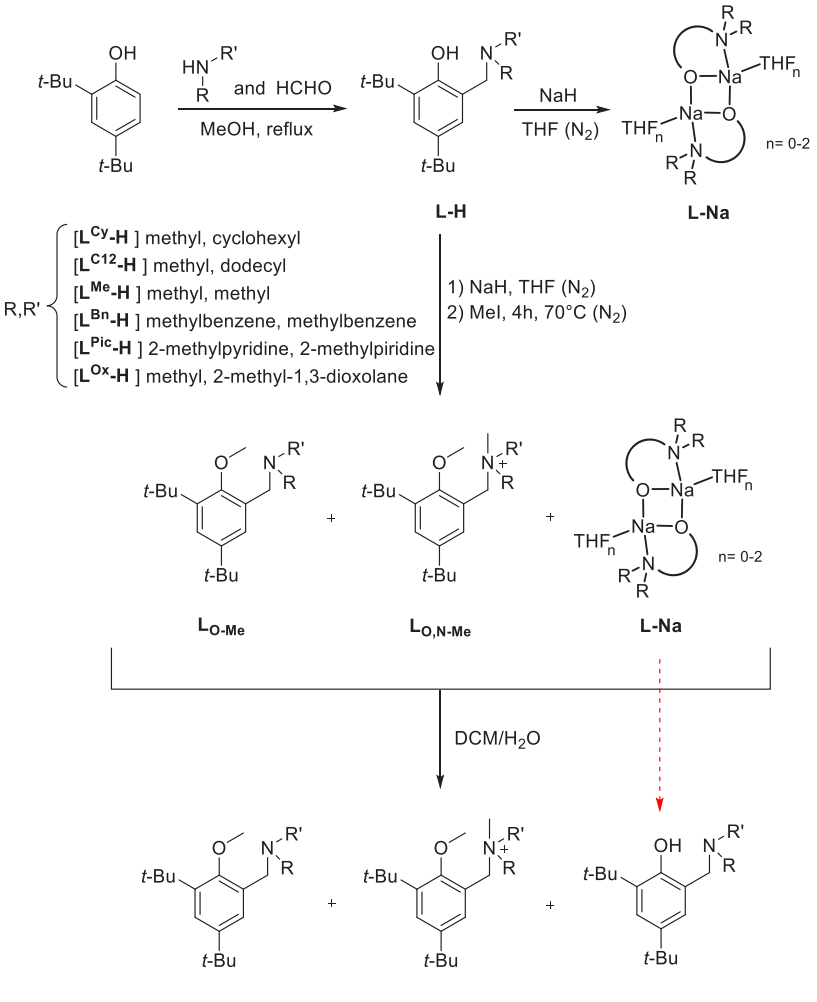
Scheme 3. General Synthesis to Obtain Methylated Aminophenols



	$L_{O\text{-}Me}$	$L_{O,N\text{-}Me}$	L-H
	Yields (%)		
L^{Cy}-H	66	11	23
L^{C12}-H	39	16	45
L^{Me}-H	34	18	52
L^{Bn}-H	82	<1	18
L^{Pic}-H	69	<1	31
L^{Ox}-H	39	27	66

isolated. The variations of all the conventional modifications of the reaction conditions, such as temperature, time, and change of the solvents employed for the effective synthesis of O-methylated aminophenols, did not produce the expected results. This can be explained, presumably, in terms of the easy availability of nitrogen donor atoms that show strong affinity for sodium cations. It would appear that a larger steric hindrance prevents the coordination of sodium atom to nitrogen and that the reaction of activated phenol with MeI could proceed readily. However, the reaction conducted for functionalized aminophenols proceeded in a similar manner and, in all the cases, resulted in the formation of sodium complexes (Scheme 2).

Methylated aminophenol derivatives were obtained in higher yield for $L^{Pic/Bn}$ containing bulky benzyl groups located on nitrogen atoms. The example described in literature indicated only one product, namely, $L_{O\text{-}Me}$. Here, we isolated a mixture of products: $L_{O\text{-}Me}$, $L_{O,N\text{-}Me}$, and L-Na. During the isolation of methylated aminophenols, the sodium complex undergoes hydrolysis, and the final product was aminophenol L-H (Scheme 3, red arrow). Therefore, the standard presentation including only one planned product of the reaction with a different yield (34−82%) is neither clarified nor precise.

The highest yield of sodium complexes was obtained when both the reaction and isolation process were conducted in an inert gas atmosphere. All sodium compounds were found to be dimeric, with bridging oxygen atoms of the aminophenol ligands and the nitrogen atoms of amine substituents or oxygen atoms of solvent molecules (e.g., tetrahydrofuran) fulfilling the coordination sphere of the sodium cations.

The molecular structures of all sodium complexes were determined by X-ray crystallography (Figure 1; for details see Supporting Information, Tables S1−S7). The molecular structure of L^{Cy}-Na presents a dimer containing sodium centers of tetragonal geometry but with a different coordination mode.

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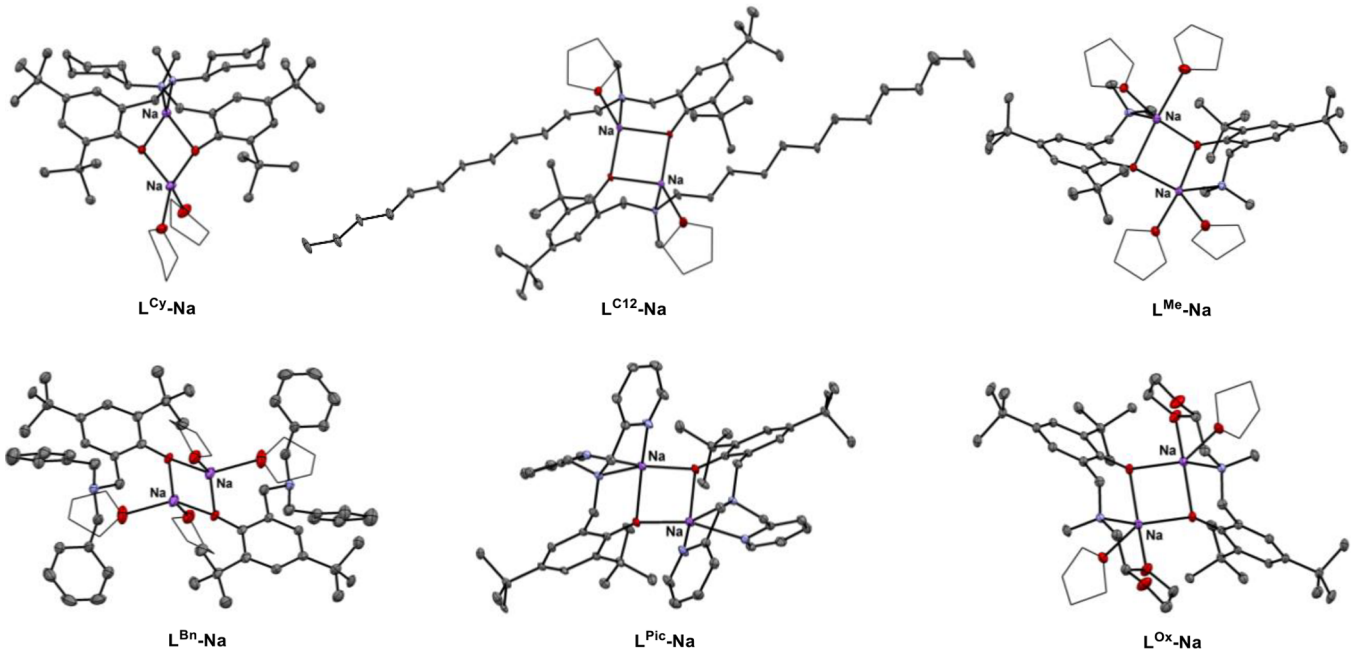
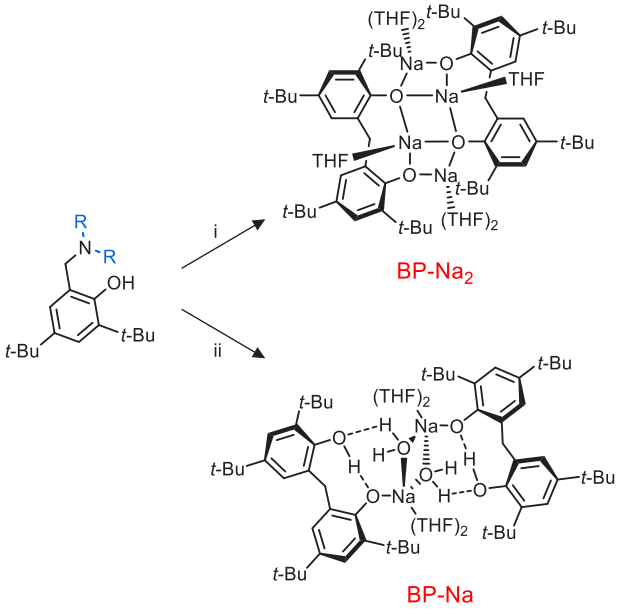


Figure 1. Molecular structures of sodium aminophenolate complexes.

One of the cations is surrounded by two ligands forming N-,O-donor bis-chelate, while the second one is coordinated by phenolate oxygen atoms and two THF molecules. Similar structural motifs have previously been reported in the literature.[24,25] Compounds L^{C12}-Na and L^{Bn}-Na also possess two sodium centers with distorted tetrahedral geometry bridged by phenolate oxygen atoms, but in their cases the coordination spheres of metals are complemented in a different way. Each sodium ion in L^{C12}-Na coordinates an N-donor atom of the amine arm of the aminophenolate ligand and a single THF molecule. However, each sodium atom in L^{Bn}-Na coordinates only two THF molecules; in this example, the aminophenolate ligands contain a long alkylamine arm. This structural motif adopts a coordination mode similar to that of aryloxide sodium compounds.[26,27] The sodium centers in L^{Met}-Na, L^{Ox}-Na, and L^{Pic}-Na exhibit geometries of distorted square pyramids (see Supporting Information, Table S8).[28,29] The metal cations are surrounded by both the bridging oxygen atoms and terminal nitrogen donors of the aminophenolate ligands, with their coordination spheres staffed additionally by THF molecules for L^{Met}-Na and L^{Ox}-Na complexes or N-donor atoms of the amine arm substituents for the L^{Pic}-Na complex. A dimeric structural motif of these compounds is rare in sodium chemistry—there are only two reported examples.[30] Other examples of sodium complexes cointaining similar substituents can also be found in the literature.[31−38]

Unarguably, the most interesting outcome of this reaction was observed when the process was performed with an excess of MeI. Under such conditions, an unexpected tetrameric sodium complex BP-Na_2, containing a bisphenol moiety, was isolated as the sole product (Scheme 4). X-ray quality crystals of the sodium bisphenolate complexes were obtained from parent solutions while using aminophenols with different substituents, and the same type of product was isolated in all cases. This result proves that the formation of bisphenolate sodium complexes does not depend on the structure of the amine arms of the aminophenol substrates. In addition, ammonium salts $[RMe_3N]I$ with an iodide counteranion

Scheme 4. Synthesis[a]



[a]Synthesis of bisphenolate sodium complexes, BP-Na_2 (top), BP-Na (bottom). (i) NaH and MeI added simultaneously (stoichiometry NaH/MeI = 1.5/2), THF; RT, 4 h, N_2; (ii) after procedure described as (i), THF (evaporated), DCM (added), moisture, air.

were detected in the parent solutions and characterized in the solid state (Supporting Information, Table S2). The proposed synthesis of bisphenol from aminophenols was outlined in Scheme 4.

The molecular structure of $(BP\text{-}Na)_2$ presents a tetramer with an open cage arrangement containing four metal centers with distorted tetrahedral geometries bridged through the phenolate oxygen atoms of two dianionic bisphenol ligands. The two internally located sodium cations are surrounded by two μ_3- and two phenolate μ_2-O donors of bisphenol, as well as one THF molecule. The two terminal sodium centers are

https://dx.doi.org/10.1021/acs.inorgchem.0c00310
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bonded by the phenolate one μ_3- and one μ_2-O atoms of the two bisphenol ligands and two THF molecules (Figure 2).

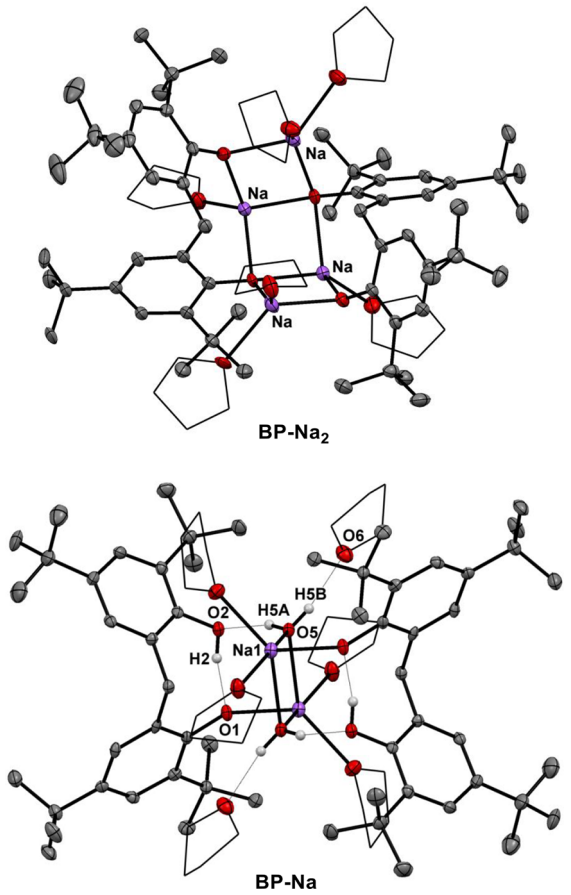


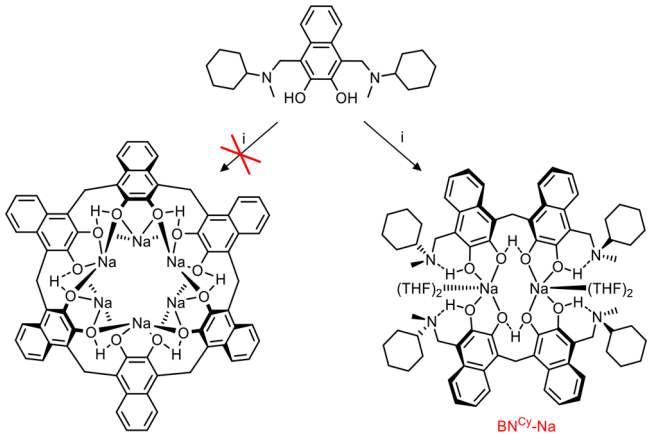
Figure 2. Molecular structures of sodium bisphenolate complexes.

Currently, this is the second example of a structure with this type of architecture.[39] The other interesting object stemming from this reaction is a product of the hydrolysis of tetrameric sodium complexes BP-Na_2. The dimer BP-Na was obtained when the isolation step was performed in aerobic conditions, in the presence of moisture; see Scheme 4.

BP-Na forms a centrosymmetric dimer containing metal centers with distorted square pyramidal geometry. The molecular structure reveals a dimeric motif, but in this case the sodium ions are bridged by a water molecule, and one of the oxygen atoms of bisphenol is protonated, while the other one forms a hydrogen bond with the bridging water molecule. Additionally, each sodium ion coordinates two THF molecules. The stability of the dimer likely originates from intramolecular (O2\H2···O1−2.443(5) Å, O5\H5A···O2−2.663(5) Å) and intermolecular (O5\H5B···O6−2.72(1) Å) hydrogen bonds (Figure 2). The coordination mode is similar to the one observed for the sodium bisphenolate complex described earlier, but the example reported in the literature presents sodium atoms with distorted tetrahedral geometry.[40] Most importantly, the molecular structure of the intermediary species involved in the hydrolysis process has provided insight into the mechanistic details of the reactions governing a typical postsynthetic workup procedure aimed at the isolation of the organic product.

To further confirm our findings, an intriguing synthetic scenario directed toward a more complex structural motif was targeted, namely, the macrocyclic system based on the functionalized dihydroxynaphthalene moieties. Despite our expectations, the planned macrocycle was found to be inaccessible via the established route, as only a single amine arm was cleaved from each ligand molecule, hampering the formation of a cyclic structure. Nevertheless, the applied one-pot synthetic procedure provided a new ligand system, stabilized by sodium cations (Scheme 5).

Scheme 5. Synthesis[a]



[a]Synthesis of bisnaphtholate sodium complexes BN^{Cy}-Na. (i) NaH and MeI added simultaneously (stoichiometry NaH/MeI = 1.5/2), THF; RT, 4 h, N_2.

The molecular structure of BN-Na presents a unique dimeric structural motif, in which each sodium center displays distorted octahedral geometry and coordination engaging four oxygen atoms of both monoanionic bisaminonaphthalene-2,3-diol ligands and two THF molecules (Figure 3). It can be anticipated that the intramolecular hydrogen bonds within the ligand moiety (O3\H3···O1−2.455(3) Å) and (O2\H2···N1−2.613(4) Å, O4\H4···N2−2.554(3) Å) play a crucial role in the stabilization of the complex and prevent the coordination of the nitrogen atoms to the metal centers.

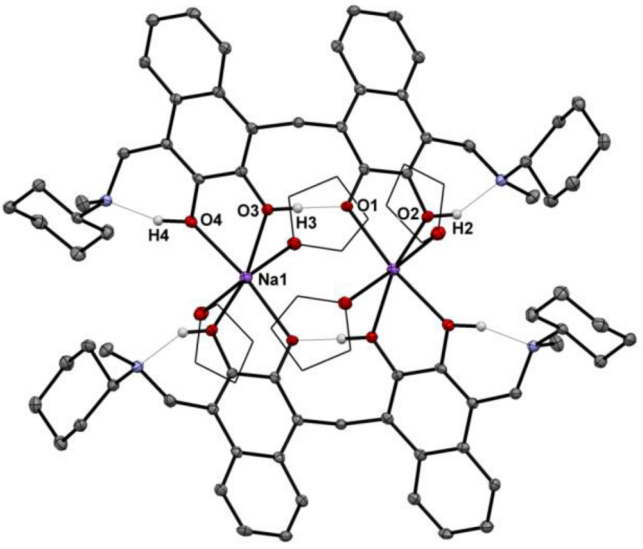


Figure 3. Molecular structure of sodium complex BN^{Cy}-Na.

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The methods of bisphenol synthesis are known in the literature;[41−43] however, our approach described here is new and was caught in the nuances of the masking reactions.

CONCLUSIONS

In summary, the protection of the hydroxyl group of aminophenols with the use of MeI—a general and, in many cases, excellent methylation reagent—was investigated. The role of the activating agent, that is, NaH, was established leading to in-depth understanding of the chemistry behind the widely used protocol of methyl ether-protective group introduction. Recognition of the influence of the functionalized amine arm of aminophenol in the course of the reaction allowed for the estimation of the possible stability of the sodium complex "coordination code", which can be considered as the essential factor to be considered in organic reactions involving NaH. The aminophenolate sodium complex generated in the first stage of the reaction should be treated as the key active intermediate with fixed coordination code, contrary to the common-sense expectation that the reaction proceeds through a simple phenoxide anion classically proposed in various organic reaction mechanisms. One of the most exciting findings in the current studies was establishing the influence of the "silent reagent" MeI on the transformation of aminophenols to bisphenols. Thorough insight into the structure−reactivity relationship of the aminophenolate substrates was gained upon analysis of the solid-state architectures of isolated products. In-depth understanding of the mechanistic aspects of methyl protective group incorporation provided a practical guide for its application in organic synthesis, but it also opened a new route for the synthesis of an original group of bisphenols. Finally, it was understood that the intermediacy of sodium compounds can be problematic in cases where the complex, being in fact an activated form of phenol, becomes involved in competitive processes, for example, reactions leading to decomposition. In addition, the provided synthetic plan offers a new protocol allowing for the selective methylation of the phenolic hydroxyl group in the presence of the amine functionality. It is expected that the potentially wide utility of the presented strategy might help to overcome obstacles in the syntheses of pharmaceuticals, agrochemicals, natural products, and other complex organic targets. Various applications of this methodology in the synthesis of different compounds, complexes, and ligands are in progress and will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00310.

Single-crystal X-ray crystallography, ^{1}H and ^{13}C NMR spectra, checkCIF alert B explanation (PDF)

Accession Codes

CCDC 1946311−1946320 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Jolanta Ejfler − *Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, Poland;* orcid.org/0000-0002-7467-1312; Email: jolanta.ejfler@chem.uni.wroc.pl

Authors

Aleksandra Marszałek-Harych − *Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, Poland*

Danuta Trybuła − *Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, Poland*

Dawid Jędrzkiewicz − *Faculty of Chemistry, University of Wrocław, 50-383 Wrocław, Poland*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c00310

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

OPUS Grant No. 2017/25/B/ST5/00597 founded by the National Science Centre in Poland.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors express their gratitude to the National Science Centre in Poland (Grant No. 2017/25/B/ST5/00597).

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https://dx.doi.org/10.1021/acs.inorgchem.0c00310
Inorg. Chem. XXXX, XXX, XXX−XXX