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Synthesis and characterization of new, modified terphenyl ligands: Increasing the rotational barrier for flanking rings

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Abstract

The synthesis and characterization of some new terphenyl ligands, modified by *meta* alkyl substitution on the central ring are described. The new ligands were designed for potential applications in the stabilization of novel low valent main group species or transition metal heteronuclear multiply bonded compounds. Compounds 1-I-C_6H_1-2, 6-Ph_2-3, 5-Pr^i_2 (**1**), 1-I-C_6H_1-2, 6-Mes_2-3, 5-Pr^i_2 (**3**) (Mes = 2,4,6-trimethylphenyl), 1-I-C_6H_1-2, 6-$Trip_2$-3, 5-Pr^i_2 (**5**) (Trip = 2,4,6-triisopropylphenyl) and 1-I-C_6H_1-2, 6-$Dipp_2$-3, 5-Pr^i_2 (**6**) (Dipp = 2,6-diisopropylphenyl) were obtained by addition of two equivalents of the corresponding aryl Grignard reagent to the benzyne intermediate generated by lithiation with Bu^nLi of the starting material 2,4-dichloro-5-isopropylcumene, followed by quenching with iodine. The lithium salts of **2** and **4** were obtained treatment of the parent terphenyl iodides with one equivalent of *n*BuLi. All compounds were isolated as either colorless crystals or as white powders. They were characterized by ^{1}H and ^{13}C NMR spectroscopy and (in the case of **1** and **3**) by X-ray crystallography. DFT calculations were performed on model terphenyl molecules in an attempt to estimate how much the rotation barriers of the flanking aryls can be influenced by substitution by alkyl groups of the two meta positions on central ring.

Keywords: Terphenyl; Rotational barrier; Steric hindrance

1. Introduction

Sterically crowding ligands have been used with remarkable success in inorganic and organometallic chemistry over the past three decades [1]. They have allowed the first syntheses of molecules featuring previously unknown bonding types, geometries, electron configurations or oxidation states. The major types of ligands used include $-CH(SiMe_3)_2$ [2], $-C(SiMe_3)_3$ [3,4], $-N(SiMe_3)_2$ [5–8], $-C_6H_2$-2,4,6-R_3 (R = Pr^i or Bu^t) [9–11] or various silyls, such as $-Si(SiMe_3)_3$ or $SiBu^t_3$ [12]. Recent work has also described the use of meta-terphenyls [13–23] that allowed the synthesis of several new compound classes that were not accessible by using other bulky ligands. Examples of such ligands are given in Scheme 1.

In these ligands two substituted aryl groups flanking the central ring in the 2,6(or ortho) positions provide an area of protected space surrounding a reactive moiety at the *ipso* (or 1-) position. Their use has resulted in the stabilization of many new compound classes including the first crystalline heavier group 14 radicals $(GeAr^{\#})_3$ [24], the multiply bonded species $Na_2Ar^*MMAr^*$ (M = Ge, Sn) [25] or $[K(THF)_6][Ar^*SnSnAr^*]$ [26], $Cp(CO)_2M{\equiv}GeAr^{\#}$ (M = Mo, W) [27], $Cp(CO)_2M{\equiv}GeAr^*$ (M = Cr, Mo, W) [28], *trans*-$[Cl(PMe_3)_4W{\equiv}SnAr^*]$ [29], *trans*-$[Br(PMe_3)_4Mo{\equiv}PbAr^*]$ [30], alkene and alkyne analogs of groups 13 and 14 elements $Na_2[Ar^*GaGaAr^*]$ [31] and Ar′MMAr′ (M = Al [21], Ga [32], In [33], Ge [17], Sn [18], Pb [19]) or the hydride $(Ar^*SnH)_2$ [13]. Attempts to extend the range of such compounds to include boron or silicon species such as ArBBAr or ArSiSiAr have encountered problems with activation of the substituents on the flanking aryls that yield products incorporating boron [34–36] or

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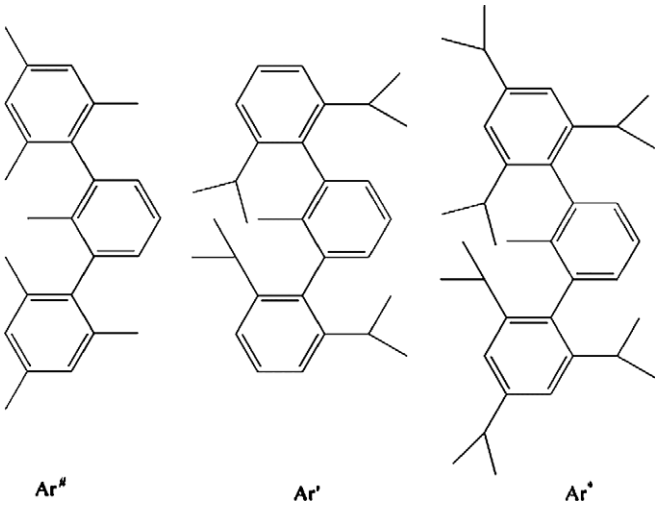
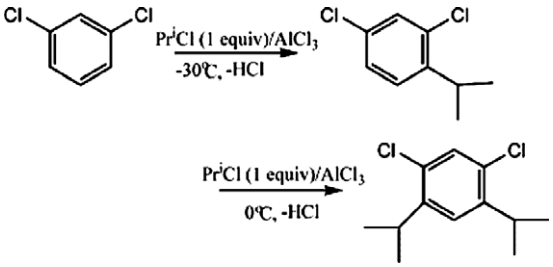


Scheme 1.

silicon [37–43] in the rings rather than the desired multiply bonded species. However, in parallel work by Rothwell and coworkers on related 2,6-diarylphenoxide ligands [44], it has been shown that the introduction of alkyl groups on the central aryl ortho to the flanking aryl rings confers lower susceptibility, if not immunity, to undesirable reactions of this type. This is because rotation of the flanking ring into the plane of the central ring, which facilitates undesirable activation, is made more difficult. In addition related systems involving meta-substitution by aryl groups have been investigated by Protasiewicz and his group [45–47]. Therefore, we aimed to modify the classical terphenyl ligands by introducing alkyl groups in the two meta positions of the central ring. It was hoped that these alkyl groups would exert two main effects: (a) due to the spatial proximity to the flanking aryls the angle formed by the latter decreases and thus the pocket-like cavity they form would provide more protection to the active site at the *ipso* position on central phenyl; (b) if crowding is increased by the presence of two alkyl groups, rotation of the flanking aryls into the plane of the central ring may be prevented, thereby "freezing" the molecule in a specific configuration. As a result, interaction between the reactive center and the flanking aryl groups would be very difficult, thus increasing the possibility of isolating the desired reaction products. We now describe the synthesis of four new terphenyls and two of their lithium salts 1-I-C_6H_1-2, 6-Ph_2-3, 5-Pr^i_2 (**1**), 1-Li-C_6H_1-2, 6-Ph_2-3, 5-Pr^i_2 (**2**), 1-I-C_6H_1-2, 6-Mes_2-3, 5-Pr^i_2 (**3**), 1-Li-C_6H_1-2, 6-Mes_2-3, 5-Pr^i_2 (**4**), 1-I-C_6H_1-2, 6-$Trip_2$-3, 5-Pr^i_2 (**5**) and 1-I-C_6H_1-2, 6-$Dipp_2$-3, 5-Pr^i_2 (**6**) and the structural characterization of **1** and **3**.

2. Discussion

The precursor for the terphenyl ligands synthesis, 2,4-dichloro-5-isopropylcumene, was obtained in one step by a Friedel-Crafts alkylation reaction of *meta*-dichlorobenzene [48], as shown in the scheme below:



Once the precursor is in hand, the ligand synthesis was achieved by using the classical reaction protocol described by Hart and co-workers [49a] and detailed by Power et al. [49b]. The yield was moderate to good for **3**, **5** and **6**, moderate to low for **1** (ca. 35%) and virtually quantitative for **2** and **4**.

The modified terphenyl ligands were synthesized under anaerobic and anhydrous conditions by dissolving the starting material 2,4-dichloro-5-isopropylcumene in THF, cooling to −78 °C and treatment of this solution with *n*BuLi. Subsequently, a freshly prepared solution of the desired Grignard reagent was added and the reaction mixture was allowed to warm to room temperature overnight. After refluxing the resultant solution, iodine was added and the solution was stirred for 6 h. The excess iodine was quenched with a Na_2SO_3 solution, the organic layer was separated, dried, the solvent was evaporated and the solid residue was refluxed in ethanol whereupon a white precipitate of the iodine derivative was formed. The corresponding terphenyl lithium salts were obtained by reacting a suspension of the parent terphenyl iodide with 1.1 equivalents of Bu^nLi in hexane at ca. 0 °C, which resulted in a white precipitate of the lithium salt. The reaction mixture was then allowed to settle and the precipitate was washed with cold hexane. The white solid was dried under reduced pressure to afford the lithium salt in >80% yield.

3. Structures and spectroscopy

The thermal ellipsoid plots for **1** and **3** are presented in Figs. 1 and 2 below. Some relevant bond distances and angles for compounds **1** and **3** are presented in the Table 1, and selected data collection and refinement parameters are presented in Table 2.

Both the ^1H and ^{13}C NMR spectra displayed the normal signals expected for meta terphenyl ligands. The ^{13}C NMR signal for the *ipso* carbon in **1**, **3**, **5** and **6** appeared in the expected range for terphenyl iodides (107–113 ppm) [50]. All other ring and substituent signals appeared in the expected ranges and were easily and unambiguously attributable to specific carbons. Both structures **1** and **3** are characterized by the presence of a symmetry plane incorporating the iodine and carbons C(1) and C(4). The angles between the *ipso* and *ortho* carbons on the central ring and the *ipso*

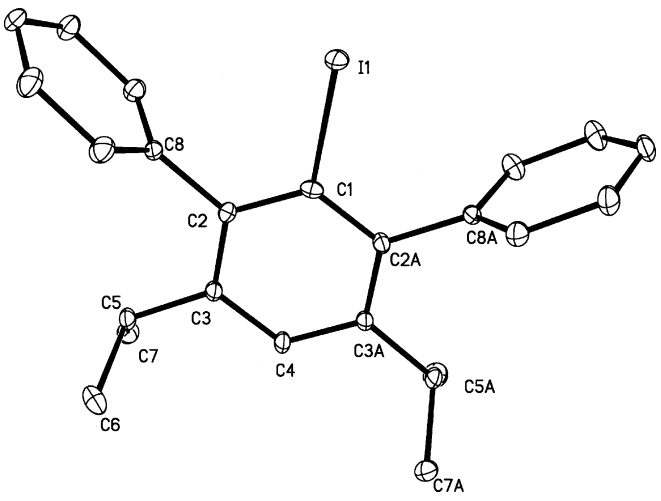


Fig. 1. Thermal ellipsoid plot for **1**. H atoms are not shown.

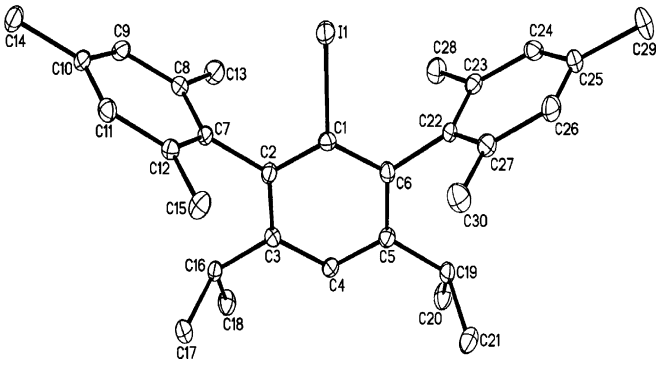


Fig. 2. Thermal ellipsoid plot for **3**. H atoms are not shown.

Table 1
Selected bond distances (Å) and angles (°) for **1** and **3**

*Compound **1***			
C(1)–I(1)	2.107(3)	C(1)–C(2)–C(8)	120.10(19)
C(1)–C(2)	1.399(2)	C(2)–C(1)–I(1)	118.44(13)
C(1)–C(2A)	1.399(2)	C(1)–C(2)–C(3)	118.50(19)
C(2)–C(8)	1.498(3)	C(3)–C(2)–C(8)	121.40(18)
C(3)–C(5)	1.525(3)	C(2)–C(1)–C(2A)	123.1(3)
*Compound **3***			
C(1)–I(1)	2.111(2)	C(1)–C(2)–C(7)	120.83(14)
C(1)–C(6)	1.400(2)	C(6)–C(1)–C(2)	123.79(15)
C(1)–C(2)	1.404(2)	C(6)–C(1)–I(1)	117.74(11)
C(2)–C(7)	1.505(2)	C(2)–C(1)–I(1)	118.44(12)
C(6)–C(22)	1.503	C(1)–C(2)–C(3)	117.64(15)

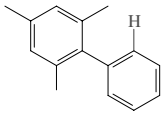
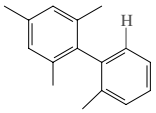
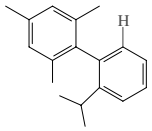
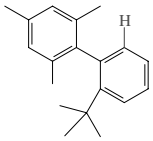
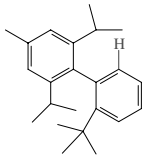
carbons on the flanking aryls are: C(1)–C(2)–C(8) = 120.10(19)° and C(1)–C(2)–C(7) = 120.83(14)° for **1** and **3**, respectively. When compared to the wider corresponding angle for 1-I-C_6H_3-2,6(C_6H_3-2′,6′-Pr^i_2)$_2$ [51] (C(1)–C(2)–C(13) = 122.33(13)°) it can be seen that the introduction of the two isopropyl groups on the central phenyl resulted in a decrease of the two angles. This is what is expected based on the higher steric interactions between the flanking aryl groups and the two meta isopropyls. The carbon–iodine distances of 2.107(3) and 2.111(2) Å for **1** and **3**, respectively, are nominally larger than the C–I bond distance in 1-I-C_6H_3-2,6(C_6H_3-2′,6′-Pr^i_2)$_2$, [51] which is 2.106(2) Å, although the values are within 3σ of each other. This is consistent with the inductive electron-donating effects of the alkyl groups on the central phenyl ring which are expected to result in the slight elongation of the C–I bond. The increased steric repulsion between the flanking aryl groups and different substituents in the meta positions of the central phenyl can also be appreciated from the calculated rotation barrier values for some selected model molecules in Table 3 (**M1**–**M5**). These simple models were chosen in order to minimize computational costs, which was achieved by using approximately half the molecule [52,53]. The primary purpose was to obtain approximate values for the increase in the rotation barrier when the substituents are changed.

Table 2
Selected crystallographic data for compounds **1** and **3**

Compound	**1**	**3**
Formula	$C_{24}H_{25}I$	$C_{30}H_{37}I$
Formula weight	440.34	524.50
Crystal color and habit	Colorless block	Colorless irregular block
Crystal system	Monoclinic	Triclinic
Space group	*I*2/*a*	$P\bar{1}$
a (Å)	11.3380(10)	8.3057(3)
b (Å)	8.8937(8)	12.0968(5)
c (Å)	20.035(2)	13.6505(6)
α (°)	90	96.5140(10)
β (°)	93.4150(10)	91.9130(10)
γ (°)	90	109.1190(10)
V (Å^3)	2016.7(3)	1283.84(9)
Z	4	2
Crystal size (mm)	0.45 × 0.35 × 0.27	0.37 × 0.22 × 0.16
Density *d* (calculated) (g cm^{-3})	1.450	1.357
Absorption coefficient, μ (mm^{-1})	1.591	1.262
Number of independent reflections	3213	5848
Number of observed reflections	2555	5335
R, observed reflections	0.0807	0.0551
wR_2, all data	0.0850	0.0567

Even though these are only approximate values (the calculation [50,53] was carried out for only one half of the molecule, for symmetry reasons), the variation observed clearly shows (for **M1**–**M4**) that increasing the bulkiness of the alkyl substituents (from hydrogen to *tert*-butyl) substantially increases the barrier to rotation of the flanking mesityls (from 17.8 to 95.4 kcal/mol). If, in addition, the side aryls are further substituted by larger alkyl groups, the rotation barrier is seen to increase dramatically, as illustrated by molecule **M5**. Thus, a change from methyl to isopropyl (as it is the case for **M4**–**M5**) allowed the energy to reach a value of 147.2 kcal/mol, suggesting that there is virtually no more free rotation of the flanking substituents. While molecule **M3** in Table 3 above is analogous to the compound **3** we synthesized, molecules **M4** and **M5** remain future targets. Based on the qualitative values for the rotation barriers presented in Table 3 as well as based on some preliminary results we obtained by employing **3** in different reactions, work is in progress for synthesizing the precursor molecule (1,3-dichloro-4,6-di-*tert*-butylben-

Table 3
Model molecules used for some preliminary calculations of the rotational barriers

M1	M2	M3	M4	M5
				
17.8 kcal/mol	> 39.1 kcal/mol	> 41.8 kcal/mol	> 95.4 kcal/mol	>147.2kcal/mol

zene) that would enable the formation of the *meta*-terphenyl ligands bearing two *tert*-butyl groups on the central ring.

4. Conclusion

In this paper we described the synthesis and characterization of four new terphenyl ligands bearing two isopropyl groups on the central phenyl ring. Analogous molecules to $Ar^{\#}I$, Ar′I and $Ar^{*}I$ were isolated along with a *meta*-terphenyl species bearing unsubstituted phenyl groups as side aryls. Two lithium derivatives of interest were also synthesized and characterized. Compounds **1** and **3** were characterized by single-crystal X-ray diffraction.

5. Experimental

$Ar^{\#}I$ (M1 in scheme above) was prepared according to the known literature procedures [49]. Here, we describe the first synthesis of modified terphenyl ligands, bearing two isopropyl groups on the central phenyl ring. The *t*-butyl analogs have not been obtained yet, but work regarding their synthesis is in progress.

A typical procedure for the synthesis of the modified terphenyl ligands consisted of dissolving 0.1 mol of 2,4-dichloro-5-isopropylcumene in ca. 300 mL THF, cooling to −78 °C in a dry ice/acetone bath and treatment of this solution with 0.11 mol $Bu^{n}Li$. To the white suspension formed, a freshly prepared solution of the desired Grignard reagent (0.25 mol, excess) was added dropwise, via cannula, at −78 °C. After the addition was complete, the reaction mixture was allowed to reach room temperature (RT) overnight. Next day, after refluxing the solution for ca. 2 h and subsequent cooling in an ice bath, I_2 (0.15 mol, excess) was added and the solution was stirred for 6 h. Then, the excess iodine was quenched with a 10% Na_2SO_3 solution, the organic layer was separated, dried over anhydrous $MgSO_4$, the solvent was pumped off and the solid residue was refluxed in ethanol overnight. Next day, the white precipitate was filtered off, washed with cold methanol and dried. The corresponding terphenyl lithium salts were obtained by reacting a suspension of the parent terpheyl iodide with 1.1 equivalents of *n*BuLi in hexane at ice-bath temperature. The reaction mixture was then allowed to settle, the supernatant liquid was discarded, the white precipitate formed was washed again with cold hexane and the white solid was dried and stored under inert atmosphere in a glove box.

The starting material for the modified terphenyl ligands syntheses, 2,4-dichloro-5-isopropylcumene, was obtained in 95% yield by employing a known literature procedure [45]. The product was analyzed by ^{1}H and ^{13}C NMR. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.26$ (d, $^{3}J_{H-H} = 6.9$ Hz, 6H, CH_3), 3.36 (sept, $^{3}J_{H-H} = 6.9$ Hz, 2H, $CH(CH_3)_2$), 7.21 (s, 1H, H-1). ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 22.88$ (CH_3), 30.22 (CH), 124.26 (C-6), 129.56 (C-3), 130.91 (*ipso*-Cl), 144.38 (*ipso*-Pr^{i}) ppm.

5.1. 1-I-C_6H_1-2,6-Ph_2-3,5-Pr^{i}_2 (1)

According to the general procedure described in Section 5, **1** was obtained as a white, microcrystalline powder. Large, colorless crystals, suitable for X-ray crystallography, were isolated after the initial microcrystalline material was dissolved in ether and stored for 3 days in a ca. 5 °C refrigerator. Yield 13.5 g (0.3 mol, 31%). M.p. = 198–200 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.15$ (d, $^{3}J_{H-H} = 6.8$ Hz, 12H, $CH(CH_3)_2$), 2.74 (sept, $^{3}J_{H-H} = 6.6$ Hz, 2H, $CH(CH_3)_2$), 7.19 (d, $^{3}J_{H-H} = 6.8$ Hz, 4H, *o*-C_6H_5), 7.38 (s, 1H, *p*-C_6H_1), 7.41 (t, $^{3}J_{H-H} = 7.6$ Hz, 2H, *p*-C_6H_5), 7.44 (t, $^{3}J_{H-H} = 6.4$ Hz, 4H, *m*-C_6H_5). ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 24.29$ ($CH(CH_3)_2$), 32.02 ($CH(CH_3)_2$), 108.32 (*i*-C_6H_1), 122.15 (*p*-C_6H_1), 127.31 (*p*-C_6H_5), 128.22 (*m*-C_6H_5), 129.79 (*o*-C_6H_5), 143.16 (*m*-C_6H_1), 145.78 (*i*-C_6H_5), 147.57 (*o*-C_6H_1) ppm.

5.2. 1-Li-C_6H_1-2,6-Ph_2-3,5-Pr^{i}_2 (2)

To a stirred suspension of 4.40 g **1** (10 mmol) in 80 mL hexane, 6.8 mL of a 1.6 M solution of $Bu^{n}Li$ in hexane (10.88 mmol, ca. 0.1 mmol excess) was syringed in at 0 °C. The initial suspension became clear and after about 15 min a white powder precipitated out. The reaction was allowed to run, after which the reaction mixture was allowed to settle, the supernatant liquid was decanted off, the remaining white precipitate was washed with 2×30 mL hexane and dried under vacuum. Attempts to grow X-ray quality crystals remained unsuccessful. Yield

3.1 g (97%). M.p. = 183–185 °C (decomposition to brown). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.25$ (d, $^3J_{H-H} = 6.8$ Hz, 12H, $CH(CH_3)_2$), 3.10 (sept, $^3J_{H-H} = 6.8$ Hz, 2H, $CH(CH_3)_2$), 6.94 (t, $^3J_{H-H} = 6.8$ Hz, 2H, *p*-C_6H_5), 7.09 (t, $^3J_{H-H} = 7.2$ Hz, 4H, *m*-C_6H_5), 7.20 (s, 1H, *p*-C_6H_1), 7.21 (d, $^3J_{H-H} = 7.8$ Hz, 4H, *o*-C_6H_5). ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): $\delta = 24.95$ ($CH(CH_3)_2$), 30.58 ($CH(CH_3)_2$), 119.51 (*p*-C_6H_1), 126.67 (*p*-C_6H_5), 129.27 (*m*-C_6H_5), 129.67 (*o*-C_6H_5), 141.68 (*m*-C_6H_1), 147.41 (*i*-C_6H_5), 147.76 (*o*-C_6H_1) ppm.

5.3. 1-I-C_6H_1-2,6-Mes_2-3,5-Pr^i_2 (Mes = 2,4,6-trimethylphenyl (**3**))

According to the general synthetic procedure, the product was obtained as a white powder. Crystallization from ether afforded large, colorless crystals (m.p. = 216–218 °C, decomp.), which were suitable for X-ray crystallographic analysis. Yield 55%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.23$ (d, $^3J_{H-H} = 6.9$ Hz, 12H, $CH(CH_3)_2$), 2.06 (s, 12H, *o*-CH_3), 2.45 (s, 6H, *p*-CH_3), 2.60 (sept, $^3J_{H-H} = 6.9$ Hz, 2H, $CH(CH_3)_2$), 7.05 (s, 4H, *m*-C_6H_2), 7.48 (s, 1H, *p*-C_6H_1). ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 20.56$ (*o*-CH_3), 21.55(*p*-CH_3), 24.59 ($CH(CH_3)_2$), 32.12 ($CH(CH_3)_2$), 109.65 (*i*-C_6H_1), 123.05 (*m*-C_6H_1), 128.23 (*m*-C_6H_2), 135.78 (*p*-C_6H_1), 136.76 (*p*-C_6H_2), 141.49 (*i*-C_6H_2), 141.63 (*o*-C_6H_1), 147.01 (*o*-C_6H_2) ppm.

5.4. 1-Li-C_6H_1-2,6-Mes_2-3,5-Pr^i_2 (Mes = 2,4,6-trimethylphenyl (**4**))

To a solution of 2.62 g (5 mmol) of **3** in 40 mL hexane, 3.2 mL 1.6 M Bu^{n}Li solution was added slowly via syringe at 0 °C. After ca. 10 min from addition, the solution became milky and was then allowed to warm to RT with stirring overnight. Next day the solution was allowed to settle, the mother liquor was decanted off, the precipitate washed with cold hexane (40 mL), allowed to settle again and the supernatant layer was discarded. The remaining white solid was dried under vacuum, and analyzed by NMR techniques. Yield 1.65 g (82%). M.p. = 201–203 °C. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 1.12$ (d, $^3J_{H-H} = 6.6$ Hz, 12H, $CH(CH_3)_2$), 1.80 (s, 12H, *o*-CH_3), 2.15 (s, 6H, *p*-CH_3), 2.38 (sept, $^3J_{H-H} = 6.6$ Hz, 2H, $CH(CH_3)_2$), 6.86 (s, 4H, *m*-C_6H_2), 7.23 (s, 1H, *p*-C_6H_1). ^{13}C NMR (75.4 MHz, C_6D_6, 25 °C): $\delta = 120.18$ (*m*-C_6H_1), 129.93 (*m*-C_6H_2), 136.11 (*p*-C_6H_2), 136.8 (*p*-C_6H_1), 141.16 (*i*-C_6H_2), 142.72 (*o*-C_6H_1), 146.81 (*o*-C_6H_2) ppm.

5.5. 1-I-C_6H_1-2,6-$Trip_2$-3,5-Pr^i_2 (Trip = 2,4,6-triisopropylphenyl (**5**))

In a similar manner to that described above, the crude product was obtained as a white powder (m.p. = 225–227 °C). Yield 32%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.15$ (d, $^3J_{H-H} = 6.0$ Hz, 12H, *o*-$CH(CH_3)_2$), 1.21 (d, $^3J_{H-H} = 3.3$ Hz, 24H, *o*-$CH(CH_3)_2$) + *m*-$CH(CH_3)_2$, 1.31 (d, $^3J_{H-H} = 6.3$ Hz, 12H, *p*-$CH(CH_3)_2$), 2.48 (sept, $^3J_{H-H} = 6.2$ Hz, 4H, *o*-$CH(CH_3)_2$), 2.74 (sept, $^3J_{H-H} = 6.0$ Hz, 2H, *m*-$CH(CH_3)_2$), 2.96 (sept, $^3J_{H-H} = 6.0$ Hz, 2H, *p*-$CH(CH_3)_2$), 7.03 (s, 4H, *m*-C_6H_2), 7.38 (s, 1H, *p*-C_6H_1) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 24.36$ (*m*-$CH(CH_3)_2$), 24.90 (*o*-$CH(CH_3)_2$), 25.15 (*o*-$CH(CH_3)_2$), 25.34 (*p*-$CH(CH_3)_2$), 30.63 (*m*-$CH(CH_3)_2$), 31.71 (*o*-$CH(CH_3)_2$), 34.23 (*p*-$CH(CH_3)_2$), 112.94 (*i*-C_6H_1), 121.10 (*m*-C_6H_2), 122.60 (*p*-C_6H_1), 139.78 (*i*-C_6H_2), 141.36 (*o*-C_6H_1), 145.95 (*o*-C_6H_2), 147.73 (*m*-C_6H_1), 148.06 (*p*-C_6H_2) ppm.

5.6. 1-I-C_6H_1-2,6-$Dipp_2$-3,5-Pr^i_2 (Dipp = 2,6-diisopropylphenyl (**6**))

Similar to **1**, **3** and **5**, **6** was obtained as a white product. After recrystallization from toluene, colorless crystals (m.p. = 219–222 °C) were obtained, but they were not of crystallographic quality. Yield 44.5%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 1.01$ (d, $^3J_{H-H} = 6.9$ Hz, 12H, *m*-$CH(CH_3)_2$), 1.17 (d, $^3J_{H-H} = 2.1$ Hz, 12H, *o*-$CH(CH_3)_2$), 1.19 (d, $^3J_{H-H} = 2.1$ Hz, 12H, *o*-$CH(CH_3)_2$), 2.51 (sept, $^3J_{H-H} = 6.6$ Hz, 2H, *m*-$CH(CH_3)_2$), 2.65 (sept, $^3J_{H-H} = 7.5$ Hz, 4H, *o*-$CH(CH_3)_2$), 7.20 (s, 1H, *p*-C_6H_1), 7.23 (d, $^3J_{H-H} = 7.5$ Hz, 4H, *m*-Dipp), 7.32 (t, $^3J_{H-H} = 7.2$ Hz, 2H, *p*-Dipp) ppm. ^{13}C NMR(300 MHz, $CDCl_3$, 25 °C): $\delta = 23.81$ (*o*-$CH(CH_3)_2$), 24.61 (*o*-$CH(CH_3)_2$), 26.03 (*m*-$CH(CH_3)_2$), 30.34 (*o*-$CH(CH_3)_2$), 30.67 (*m*-$CH(CH_3)_2$), 109.21 (*i*-C_6H_1), 122.60 (*m*-Dipp), 123.29 (*p*-C_6H_1), 127.47 (*p*-Dipp), 135.08 (*o*-C_6H_1), 137.76 (*i*-Dipp), 146.16 (*m*-C_6H_1), 147.42 (*o*-Dipp) ppm.

6. X-ray crystallographic studies

X-ray data were collected on a Bruker SMART 1000 diffractometer at 90(2) K with use of Mo Kα ($\lambda = 0.71073$ Å) radiation. Absorption corrections were applied using SADABS [54]. The structures were solved with use of direct methods or the Patterson option in SHELXS and refined by the full-matrix least-squares procedure in SHELXL [55]. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms 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 2. Further details can be found in the supporting information.

7. Calculations

The DFT calculations were carried out using the GAUSSIAN 03 package [56] and the representations of the molecular structures were generated with the MOLEKEL program [57]. Full optimizations of the geometries were performed at each step of the conformational scan using the hybrid B3LYP functional, including Becke's three-parameter non-local exchange potential and the non-local correlation functional of Lee–Yang–Parr. For all the calculations of the rotational barriers, 3-21 g* basis set was used. The

lowest and highest energy conformations were fully reoptimized with 6-31 g* basis set. The optimized geometries were verified for the minima by careful analysis of the calculated vibrational frequencies (second derivative of the energy). The use of such inexpensive basis set as 3-21 g* was dictated mainly by two reasons: The computational limitations (e.g., the real computational time for the full optimization of the geometries at each conformational step for the calculated rotational barrier in case of **M4** on our fastest processor (3.2 GHz) approaches 5 weeks) and the fact that we are estimating the height of the barriers which involves the calculations of the differences in energies only between different optimized conformations. Our primary objective was to obtain information on the relative values of the rotational barriers rather than highly accurate values on each individual barrier.

8. Supplementary information

CIF files for **1** and **3** may be obtained from the Cambridge Crystallographic Data Centre as supplementary publications CCDC 292518 and 252519 upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk.

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