

Synthesis of Sterically Encumbered Terphenyls and Characterization of Their Metal Derivatives

$\text{Et}_2\text{OLiC}_6\text{H}_3\text{-2,6-Trip}_2$ and $\text{Me}_2\text{SCuC}_6\text{H}_3\text{-2,6-Trip}_2$ (Trip = 2,4,6-*i*-Pr₃C₆H₂⁻)

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The synthesis and characterization of sterically encumbered terphenyl compounds are described. These are 2,6-Dipp₂C₆H₃I (Dipp = 2,6-*i*-Pr₂C₆H₃⁻), **1**, 2,6-Trip₂C₆H₃I (Trip = 2,4,6-*i*-Pr₃C₆H₂⁻), **2**, and 1,3-Mes^{*}C₆H₄ (Mes^{*} = 2,4,6-*t*-Bu₃C₆H₂⁻), **3**, and the solvated metal derivatives Et₂OLiC₆H₃-2,6-Trip₂, **4**, and Me₂SCuC₆H₃-2,6-Trip₂, **5**. They were characterized by ¹H and ¹³C NMR spectroscopy and, in the case of **3**–**5**, by X-ray crystallography. The monomeric structures of **4** and **5** and the two-coordinate nature of the metals underline the very bulky characteristics of these ligands. In addition the isolation of **3** rather than the intended iodine derivative 2,6-Mes^{*}₂C₆H₃I suggests that the synthetic route to the precursor halides can be limited by very large ring substituents.

Introduction

Sterically encumbered aryl groups have been shown to have widespread utility in the synthesis of numerous species with unusual bonding and/or coordination numbers. Classic examples of such compounds were the first stable disilene Mes₂SiSiMes₂ (Mes = 2,4,6-Me₃C₆H₂)¹ and the first uncomplexed diphosphene Mes^{*}PPMes^{*} (Mes^{*} = 2,4,6-*t*-Bu₃C₆H₂)². Other bulky aryl substituents that have proven useful include the isopropyl-substituted aryls 2,4,6-*i*-Pr₃C₆H₂⁻³ and 2,6-*i*-Pr₂C₆H₃⁻⁴ and silyl-substituted species such as 2,6-(Me₃Si)₂C₆H₃⁻⁵ and 2,4,6{[(Me₃Si)₂CH]₃C₆H₂⁻⁶. A characteristic feature of these aryls is that the steric crowding is provided, in the main, by two alkyl (or alkylsilyl) substituents at the ortho positions. Corresponding species in which the crowding is a result of bulky ortho aryl substituents have received rather less attention. These compounds feature two phenyl, or substituted phenyl, rings at the ortho positions of a central aryl ring and form part of a larger class of compounds, the terphenyls, owing to the fact that they contain three aromatic rings. Derivatization of such species is usually accomplished by the use of a reactive substituent such as halide, and it has been shown that it is possible to synthesize iodo compounds of the type 1-*I*-2,6-Ar₂C₆H₃ through a five-step route commencing with commercially available 2,6-dichloroaniline. The ortho aryl groups employed have included Ph,⁷ 2,6-Me₂C₆H₃⁻⁸

and Mes.⁷ Recent investigations involving the 2,6-Mes₂C₆H₃- terphenyl group have demonstrated that it is capable of stabilizing unusual or unique structural types through the synthesis and characterization of the dimeric lithium aryl {LiC₆H₃-2,6-Mes₂}₂⁹ and the two-coordinate arenethiolato and areneseleolato compounds Fe{SC₆H₃-2,6-Mes₂}₂¹⁰ and Mn{SeC₆H₃-2,6-Mes₂}₂¹¹. In contrast, similar compounds involving the Mes^{*} ligand were found to be more highly aggregated.^{11,12} These initial results suggested that the synthesis of more crowding terphenyl groups such as 2,6-Dipp₂C₆H₃⁻ (Dipp = 2,6-*i*-Pr₂C₆H₃⁻), 2,6-Trip₂C₆H₃⁻ (Trip = 2,4,6-*i*-Pr₃C₆H₂⁻), or 2,6-Mes^{*}₂C₆H₃⁻ might allow the synthesis of stable, hitherto unknown, types of compounds, for example, a crystalline species containing a one-coordinate metal or certain monomeric compounds with unusually low oxidation state such as a stable univalent phosphorus species. In this paper the synthesis and characterization of the key halide derivatives of these crowding ligands as well as two of their metal complexes are now reported.

Experimental Section

All experiments were performed under a nitrogen atmosphere either by using modified Schlenk techniques or in a Vacuum Atmospheres H43-2 drybox. Solvents were freshly distilled from a sodium–potassium alloy and degassed twice prior to use. ¹H and ¹³C NMR spectra were recorded in CDCl₃ or C₆D₆ solution by using a General Electric QE-300 spectrometer. IR spectra were recorded as Nujol mulls on a Perkin-Elmer PE 1430 spectrometer. The compound 2,6-*i*-Pr₂C₆H₃I was prepared by diazotization of commercially available 2,6-*i*-Pr₂C₆H₃NH₂; 2,4,6-*i*-Pr₃C₆H₂Br and Mes^{*}Br were purchased from commercial suppliers and used as received.

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Grignard reagents were prepared as described previously for these aryl halides.^{13,14}

2,6-Dipp₂C₆H₃I, 1. A solution of 200 mmol of DippMgI in THF (200 mL), freshly prepared from magnesium (4.86 g, 200 mmol) and DippI (48.23 g, 200 mmol), was added dropwise to a stirred solution of 2,6-dichloro-1-iodobenzene (13.64 g, 50 mmol) in THF (100 mL) with cooling in an ice bath. Stirring was continued for 1 h at ambient temperature, after which time the mixture was heated to reflux for 16 h. The reaction mixture was then cooled in an ice bath, and a solution of iodine (39.0 g, 150 mmol) in THF (200 mL) was added dropwise. After the mixture was stirred for 10 h at room temperature, a solution of Na₂SO₃ (20 g) in water (300 mL) was added to destroy the excess iodine and to dissolve the magnesium halides. The aqueous layer was separated and washed three times with Et₂O (100 mL). The solvents were evaporated, and the pale brown residue was dried at 100 °C under reduced pressure (0.1 mmHg). All volatile side products (mostly DippI) were then removed by distillation at 140 °C at 0.1 mmHg. Upon cooling, EtOH (250 mL) was added to the remaining solid and the mixture was heated to reflux for 16 h. After cooling of the suspension in a -20 °C freezer (10 h), a pale brown solid was isolated by filtration, washed twice with 30 mL of MeOH, and dried. Sublimation of the solid at 180 °C at 0.01 mmHg yields 16.52 g (31.5 mmol, 63%) of pure 2,6-Dipp₂C₆H₃I: Mp 151–153 °C; ¹H NMR (CDCl₃) δ = 1.09 (d, 12H, (o-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 1.23 (d, 12H, (o-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 2.53 (sept, 4H, (o-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 7.15 (d, 2H, m-C₆H₃)³J_{HH} = 7.5 Hz, 7.23 (d, 4H, m-Dipp)³J_{HH} = 7.8 Hz, 7.40 (t, 2H, p-Dipp)³J_{HH} = 7.8 Hz, 7.43 (t, 1H, p-Ph)³J_{HH} = 7.5 Hz; ¹³C NMR (CDCl₃) δ = 23.24 (o-CH(CH₃)₂), 24.84 (o-CH(CH₃)₂), 30.84 (o-CH(CH₃)₂), 110.08 (i-C₆H₃), 122.79 (m-Dipp), 127.45 (p-Ph), 128.11 (m-Dipp), 128.37 (m-Ph), 142.60 (i-Dipp), 146.02 (o-Dipp), 146.44 (o-Ph).

2,6-Trip₂C₆H₃I, 2. A solution of 75 mmol of EtMgBr in THF (200 mL) was added dropwise to a stirred solution of 2,6-dichloro-1-iodobenzene (20.47 g, 75 mmol) in THF (100 mL) with cooling in an ice bath. Stirring was continued for 1 h, after which time the resulting solution was added dropwise to a solution of 200 mmol of TripMgBr in 300 mL of THF (freshly prepared from magnesium (4.86 g, 200 mmol) and TripBr (56.65 g, 200 mmol)) at room temperature (30 min). Stirring was continued for 1 h at ambient temperature, after which time the mixture was heated to reflux for 16 h. The reaction mixture was then cooled to room temperature and allowed to settle. The supernatant liquid was then added to a solution of iodine (76.0 g, 300 mmol) in THF (200 mL) with cooling in an ice bath. After the mixture was stirred for 10 h, a solution of Na₂SO₃ (20.0 g) in water (300 mL) was added to destroy the excess iodine and to dissolve the magnesium halides. The aqueous layer was separated and washed three times with Et₂O (100 mL). The solvents were evaporated, and the pale brown residue was dried at 100 °C under reduced pressure (0.1 mmHg). All the volatile side products (mostly TripI) was then removed by distillation (at a bath temperature of 140 °C) at 0.1 mmHg. EtOH (250 mL) was added to the remaining solid and was heated to reflux for 16 h. After cooling of the suspension to -20 °C a pale brown solid was isolated by filtration, washed twice with MeOH (30 mL), and dried. Sublimation of the solid at 190 °C at 0.01 mmHg yielded 38.5 g (63.3 mmol, 83.3%) of pure **2** as a white solid: Mp 229 °C; ¹H NMR (CDCl₃) δ = 1.10 (d, 12H, o-CH(CH₃)₂), ³J_{HH} = 6.9 Hz, 1.23 (d, 12H, o-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 1.32 (d, 12H, p-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 2.53 (sept, 4H, o-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 2.97 (sept, 2H, p-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 7.06 (s, 4H, m-Trip), 7.15 (d, 2H, m-C₆H₃)³J_{HH} = 7.5 Hz, 7.39 (t, 1H, p-Ph)³J_{HH} = 7.5 Hz. ¹³C NMR (CDCl₃) δ = 23.35 (o-CH(CH₃)₂), 24.08 (p-CH(CH₃)₂), 24.90 (o-CH(CH₃)₂), 30.87 (o-CH(CH₃)₂),

34.20 (p-CH(CH₃)₂), 110.04 (i-C₆H₃), 120.72 (m-Trip), 127.23 (p-C₆H₃), 128.25 (m-C₆H₃), 140.33 (i-Trip), 145.59 (o-Trip), 146.75 (o-C₆H₃), 148.41 (p-Trip).

1,3-Mes*₂C₆H₄, 3. Compound **3** was prepared from Mes*-MgBr (200 mmol) and 2,6-dichloro-1-iodobenzene (13.64 g, 50 mmol) by a procedure similar to that described above: yield 17.75 g (62%) of 1,3-Mes*₂C₆H₄ after sublimation at 230 °C as a colorless solid; mp 243 °C; ¹H NMR (CDCl₃) δ = 1.21 (s, 36H, (o-C(CH₃)₃), 1.36 (s, 18H, (p-C(CH₃)₃), 7.18 (t, 1H, p-C₆H₄)³J_{HH} = 7.5 Hz, 7.29 (d, 2H, m-C₆H₄)³J_{HH} = 7.5 Hz, 7.52 (s, 4H, m-Mes*), 7.56 (s, 1H, i-Ph); ¹³C NMR (C₆D₆) δ = 31.56 (p-C(CH₃)₃), 34.82 (o-C(CH₃)₃), 35.33 (p-C(CH₃)₃), 38.61 (p-C(CH₃)₃), 123.02 (m-Mes*), 124.20 (i-C₆H₄), 135.23 (m-C₆H₄), 135.62 (p-C₆H₄), 138.29 (i-Mes*), 142.69 (o-Ph), 148.22 (p-Mes*), 148.90 (o-Mes*).

Et₂OLiC₆H₃-2,6-Trip₂, 4. A 3.56 g (6 mmol) amount of 2,6-Trip₂C₆H₃I was dissolved in a mixture of diethyl ether (15 mL) and hexane (50 mL) with rapid stirring. The solution, which gave a fine precipitate upon cooling to ca. -70 °C, was then treated with a 1.6 M solution of n-BuLi in hexane (3.75 mL, 6 mmol). The solution was warmed slowly to room temperature over 6 h, and stirring was continued for a further 4 h. The resulting clear solution was concentrated to incipient crystallization (ca. 25 mL) under reduced pressure (0.1 mmHg) and cooled in a -20 °C freezer for several hours to afford Et₂OLiC₆H₃-2,6-Trip₂ as large colorless crystals. Concentration of the mother liquid yields a second crop of crystals: combined yield 2.90 g, 86%; mp 141 °C (dec); ¹H NMR (C₆D₆) δ = 0.31 (t, 6H, OCH₂CH₃)³J_{HH} = 7.2 Hz, 1.18 (d, 12H, p-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 1.24 (d, 12H, o-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 1.25 (d, 12H, o-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 2.53 (q, 4H, OCH₂CH₃)³J_{HH} = 7.2 Hz, 2.84 (sept, 2H, p-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 3.51 (sept, 4H, o-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 7.11 (s, 4H, m-Trip), 7.23 (d, 2H, m-Ph)³J_{HH} = 6.9 Hz, 7.35 (t, 1H, p-Ph)³J_{HH} = 6.9 Hz; ¹³C NMR (C₆D₆) δ = 13.85 (OCH₂CH₃), 24.60 (o-CH(CH₃)₂), 24.68 (p-CH(CH₃)₂), 24.83 (o-CH(CH₃)₂), 30.17 (o-CH(CH₃)₂), 34.89 (p-CH(CH₃)₂), 66.28 (O-CH₂), 120.40 (m-Trip), 123.03 (m-C₆H₃), 123.45 (p-C₆H₃), 145.92 (i-Trip), 146.92 (o-Trip), 147.51 (p-Trip), 150.60 (m-Ph), 176.59 (i-Ph); ⁷Li NMR (C₆D₆) δ = 1.40; IR (cm⁻¹) 3180 w, 2720 w, 1900 w, 1840 w, 1780 w, 1760 w, 1603 m, 1558 m, 1531 m, 1418 sh, 1310 m, 1238 m, 1220 sh, 1180 sh, 1160 m, 1150 sh, 1095 sh, 1075 sh, 1055 s, 1035 sh, 938 m, 9155 h, 872 m, 844 m, 798 m, 788 m, 780 sh, 752 w, 695 m, 645 w, 608 m, 595 sh, 550 br, w, 492 w, 480 w, 375 w, 265 s.

Me₂SCuC₆H₃-2,6-Trip₂, 5. A 1.69 g (3 mmol) amount of Et₂OLiC₆H₃-2,6-Trip₂ in diethyl ether (40 mL) was added to a suspension of CuBr (0.43 g, 3 mmol) in diethyl ether (10 mL) with cooling in an ice bath and the exclusion of light. The reaction mixture was stirred for 45 min, and 1 mL of S(CH₃)₂ was added via syringe. The resultant pale yellow suspension was stirred for 1 h and was filtered over a pad of Celite. Concentration to incipient crystallization (ca. 15 mL) under reduced pressure and cooling in a -20 °C freezer afforded Me₂SCuC₆H₃-2,6-Trip₂ as colorless crystals: Yield 1.24 g, 68%; mp 189–191 °C (dec turns red at 140 °C); ¹H NMR (C₆D₆) δ = 1.04 (s, 6H, S(CH₃)₂), 1.16 (d, 12H, p-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 1.21 (d, 12H, p-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 1.31 (d, 12H, o-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 2.77 (sept, 2H, p-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 3.34 (sept, 4H, o-CH(CH₃)₂)³J_{HH} = 6.9 Hz, 7.09 (s, 4H, m-Trip), 7.16–7.26 (mult, 3H, m-Ph and p-Ph); ¹³C NMR (C₆D₆) δ = 18.55 (S(CH₃)₂), 24.52 and 24.91 (o- and p-CH(CH₃)₂), 30.55 (o-CH(CH₃)₂), 34.81 (p-CH(CH₃)₂), 120.38 (m-Trip), 124.80 (m-Ph), 125.27 (p-Ph), 145.78 (i-Trip), 146.48 (o-Trip), 146.96 (p-Trip), 149.57 (m-Ph), 168.09 (i-Ph); IR (cm⁻¹) 3180 w, 2708 w, 1910 w, 1850 w, 1608 m, 1562 m, 1535 w, 1428 m, 1378 s, 1358 s, 1310 m, 1240 m, 1180 w, 1162 m, 1150 sh, 1098 m, 1070 m, 1065 sh, 1035 m, 972 m, 940 m, 912 w, 872 s, 795 s, 645 w, 582 w, 482 w, 285 w.

X-ray Data Collection, Solution, and Refinement of Structures. Crystals of **3–5** were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. Suitable

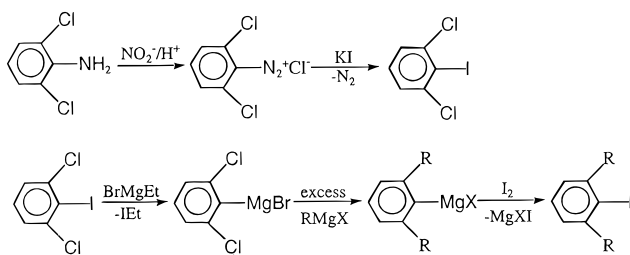
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Table 1. Selected Crystallographic Data^a for 3–5

	1,3-Mes* ₂ C ₆ H ₄ (3)	Et ₂ OLiC ₆ H ₃ -2,6-Trip ₂ (4)	Me ₂ SCuC ₆ H ₃ -2,6-Trip ₂ (5)
formula	C ₄₂ H ₆₂	C ₄₀ H ₅₉ LiO	C ₃₈ H ₅₅ CuS
fw	566.92	562.81	607.42
cryst color and habit	colorless blocks	colorless blocks	colorless blocks
cryst system	triclinic	monoclinic	orthorhombic
space group	P $\bar{1}$	P2 ₁ /n	P2 ₁ 2 ₁ 2 ₁
crystal dims, mm	0.4 × 0.3 × 0.25	0.5 × 0.4 × 0.4	0.4 × 0.4 × 0.25
a, Å	6.260(2)	8.765(3)	8.774(1)
b, Å	10.557(4)	17.178(8)	15.974(4)
c, Å	28.794(24)	24.267(14)	24.860(6)
α, deg	78.98(5)		
β, deg	84.08(5)	93.84(4)	
γ, deg	75.79(3)		
V, Å ³	1807.5(18)		
Z	2	4	4
d _{calc} , g cm ⁻³	1.042	1.025	1.158
μ, mm ⁻¹	0.422	0.433	1.595
no. of obsd rflns	2902 (I > 2σ(I))	3598 (I > 2σ(I))	2385 (I > 2σ(I))
R (all data)	0.0831, 0.2553	0.0618, 0.1574	0.0495, 0.1429

^a Data were collected at 130 K with a Syntex P2₁ diffractometer using Cu Kα (λ = 1.541 78 Å) radiation.

Scheme 1

crystals were selected, attached to a glass fiber by silicon grease, and immediately placed in the low-temperature N₂ stream. X-ray data were collected with a Syntex P2₁ diffractometer equipped with a graphite monochromator and a locally modified LT-1 apparatus. Calculations were carried out on an IBM-compatible 486 PC using the SHELXTL 5 program system. Neutral atom scattering factors and the correction for anomalous dispersion were those supplied by SHELXTL 5. Some details of the data collections and the refinements are provided in Table 1. Further details are in the Supporting Information. The structures were solved by direct methods. The compounds were refined by full-matrix least-squares procedures. Hydrogen atoms were included by the use of a riding model with C–H distances of 0.96 Å and isotropic thermal parameters. Important atom coordinates and bond distances and angles are given in Tables 2 and 3.

Results

Synthesis. The compounds **1–3** were synthesized by the route^{7,8} illustrated in Scheme 1. The first two steps may be avoided by using the commercially available, but considerably more expensive, starting material 1-I-2,6-Cl₂C₆H₃. The reactions proceed smoothly to give the products **1** and **2**. However, the iodo product is not isolated in the case of the Mes*-substituted ring. Instead, the compound **3** is obtained. It is possible that the aryl Grignard BrMgC₆H₃-2,6-Mes*₂ formed in the penultimate step is unstable—perhaps for steric reasons. It is notable that the addition of a large excess of iodine or bromine did not result in the isolation of the desired XC₆H₃-2,6-Mes*₂ (X = Br or I) species.

Structural Descriptions. **1,3-Mes*₂C₆H₄ (**3**).** The compound crystallizes as discrete monomers in the space group P $\bar{1}$. The compound is illustrated in Figure 1. There are no unusual C–C bond lengths within the rings, and the range of C–C distances in the central

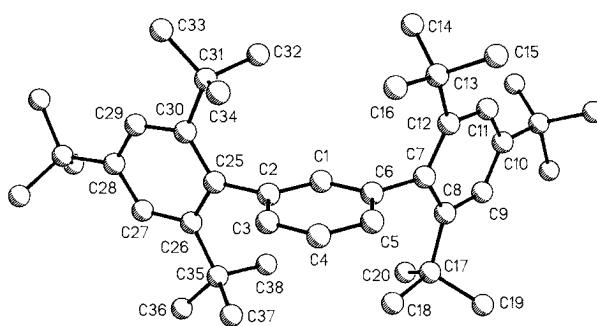


Figure 1. Computer-generated drawing of **3**. H atoms are not shown.

C(1) ring is 1.375(7)–1.401(6) Å. There are also some deviations from the expected internal 120° ring angles in the C(1) ring; the widest such angle (123.6(5)°) is observed at C(1), and the narrowest are observed at C(2) (115.9(4)°) and C(6) (117.9(4)°). The external angles at the ring carbons substituted by the Mes* groups (i.e. C(2) and C(6)) also display asymmetry. Thus, C(1)–C(2)–C(25) (125.2(4)°) is 6.4° greater than C(3)–C(2)–C(25) (118.8(4)°) whereas C(1)–C(6)–C(7) (118.7(4)°) is 4.7° less than C(7)–C(6)–C(5) (123.4(4)°). The angles between perpendiculars to plane of the central ring and those of the Mes* rings are 88.1° for the C(7) ring and 89.5° for the C(25) ring. There are also significant deviations involving the Mes* ring planes and central ring–Mes* C–C bonds. Thus, the C(2)–C(25)–C(28) and C(6)–C(7)–C(10) angles are 169.6 and 176.9° instead of the expected 180°.

Et₂OLiC₆H₃-2,6-Trip₂ (4**).** Compound **4** crystallizes as monomers of formula Et₂OLiC₆H₃-2,6-Trip₂ with no required crystallographic symmetry. The compound is shown in Figure 2. The Li⁺ ion is bound only to C(1) (Li–C = 2.017(7) Å) and O(1) (Li–O = 1.850(7) Å) with a C–Li–O angle of 171.9(5)°. There is very little asymmetry in the angles surrounding the ortho carbon atoms C(2) and C(6) bearing the Trip substituents, and the maximum deviation from 120° that is observed is only 2.6°. In addition, the planes of the Trip rings are bent away from the C(2)–C(22) and C(6)–C(7) vectors by only 2.0 and 1.2°, respectively. The angle between the perpendiculars to the central (C(1)) ring and the C(2) and C(7) Trip rings are 77.3 and 76.1°.

Me₂SCuC₆H₃-2,6-Trip₂ (5**).** The structure of **5** bears a close resemblance to that of **4** (see Figure 3). The

Table 2. Atomic Coordinates ($\times 10^4$) for 3–5

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Compound 3							
C(1)	609(8)	5039(4)	2523(2)	C(22)	2449(21)	7566(12)	−47(4)
C(2)	47(8)	4490(4)	2988(2)	C(23)	3422(25)	9178(11)	366(4)
C(3)	−2129(8)	4399(4)	3083(2)	C(24)	5875(18)	6904(13)	415(5)
C(4)	−3645(8)	4821(5)	2740(2)	C(25)	1622(8)	3998(4)	3385(2)
C(5)	−3050(8)	5375(5)	2285(2)	C(26)	1807(8)	4867(4)	3700(2)
C(6)	−884(8)	5482(4)	2168(2)	C(27)	3157(8)	4332(4)	4078(2)
C(7)	−71(8)	6061(5)	1674(2)	C(28)	4322(8)	3035(4)	4171(2)
C(8)	−27(9)	7433(5)	1567(2)	C(29)	4113(8)	2222(5)	3863(2)
C(9)	1163(9)	7855(5)	1149(2)	C(30)	2777(8)	2648(4)	3475(2)
C(10)	2183(9)	7058(5)	830(2)	C(31)	2797(3)	1588(4)	3162(2)
C(11)	1942(8)	5771(5)	927(2)	C(32)	3942(10)	1942(5)	2672(2)
C(12)	815(8)	5231(5)	1337(2)	C(33)	4115(10)	199(5)	3372(2)
C(13)	735(9)	3752(5)	1353(2)	C(34)	488(9)	1411(5)	3110(2)
C(14)	3154(11)	2911(6)	1363(2)	C(35)	696(8)	6370(4)	3645(2)
C(15)	−234(12)	3661(6)	898(2)	C(36)	1111(10)	6997(5)	4057(2)
C(16)	−567(10)	3101(5)	1761(2)	C(37)	−1834(8)	6655(5)	3633(2)
C(17)	−1067(10)	8570(5)	1853(2)	C(38)	1675(9)	7124(4)	3198(2)
C(18)	−2604(11)	8245(5)	2286(2)	C(39)	5750(8)	2541(5)	4600(2)
C(19)	−2496(12)	9699(6)	1516(2)	C(40)	4238(9)	2613(5)	5055(2)
C(20)	796(12)	9080(6)	2011(2)	C(41)	7410(9)	3398(5)	4585(2)
C(21)	3529(10)	7565(6)	390(2)	C(42)	7046(10)	1101(5)	4616(2)
Compound 4							
O(1)	7084(3)	1145(1)	1639(1)	C(20)	6897(5)	584(2)	4252(1)
Li(1)	5362(8)	1759(4)	1683(3)	C(21)	4669(5)	1085(2)	4739(1)
C(1)	3340(3)	2290(2)	1768(1)	C(22)	3091(3)	2509(2)	747(1)
C(2)	2476(3)	2603(2)	1306(1)	C(23)	4324(3)	2972(2)	600(1)
C(3)	1112(3)	3008(2)	1354(1)	C(24)	4917(4)	2860(2)	88(1)
C(4)	558(4)	3115(2)	1867(1)	C(25)	4341(4)	2308(2)	−288(1)
C(5)	1358(3)	2824(2)	2330(1)	C(26)	3143(4)	1852(2)	−132(1)
C(6)	2720(3)	2414(2)	2281(1)	C(27)	2503(4)	1941(2)	372(1)
C(7)	3571(3)	2117(2)	2799(1)	C(28)	1171(4)	1424(2)	504(1)
C(8)	4460(3)	2622(2)	3147(1)	C(29)	−214(7)	1560(5)	107(3)
C(9)	5199(3)	2338(2)	3631(1)	C(30)	1592(7)	573(3)	517(3)
C(10)	5109(3)	1562(2)	3784(1)	C(31)	4960(4)	3627(2)	972(1)
C(11)	4266(3)	1068(2)	3432(1)	C(32)	6696(4)	3575(3)	1084(2)
C(12)	3501(3)	1321(2)	2944(1)	C(33)	4485(4)	4411(2)	730(1)
C(13)	2606(4)	728(2)	2585(1)	C(34)	4991(7)	2206(2)	−849(2)
C(14)	3687(5)	176(2)	2306(2)	C(35)	5557(7)	1454(3)	−954(2)
C(15)	1491(4)	268(2)	2914(2)	C(36)	5557(7)	2887(3)	−1090(2)
C(16)	4693(3)	3471(2)	2983(1)	C(37)	7284(6)	648(3)	1184(2)
C(17)	4736(5)	4031(2)	3469(1)	C(38)	6079(6)	791(4)	738(2)
C(18)	6133(4)	3549(2)	2669(1)	C(39)	8232(5)	1076(3)	2084(2)
C(19)	5844(4)	1282(2)	4331(1)	C(40)	7864(7)	1554(4)	2545(3)
Compound 5							
Cu(1)	4656(1)	5845(1)	2377(1)	C(19)	5682(8)	5718(5)	4843(3)
S(1)	6682(2)	6632(1)	2375(1)	C(20)	6633(10)	6503(6)	4762(3)
C(1)	2975(7)	5102(4)	2393(2)	C(21)	4589(10)	5837(6)	5309(3)
C(2)	2179(8)	4873(4)	1921(2)	C(22)	2683(7)	5262(4)	1399(2)
C(3)	961(8)	4312(4)	1935(2)	C(23)	4031(8)	4997(4)	1146(3)
C(4)	501(7)	3976(4)	2420(3)	C(24)	4556(9)	5408(4)	686(2)
C(5)	1246(7)	4176(4)	2893(3)	C(25)	3771(8)	6079(4)	463(3)
C(6)	2465(7)	4736(4)	2885(3)	C(26)	2434(8)	6315(4)	704(3)
C(7)	3283(8)	4972(4)	3390(2)	C(27)	1857(7)	5937(4)	1163(2)
C(8)	4482(8)	4491(4)	3589(2)	C(28)	398(8)	6253(4)	1416(2)
C(9)	5257(9)	4740(4)	4052(2)	C(29)	−885(8)	6367(5)	1010(3)
C(10)	4859(8)	5466(4)	4329(2)	C(30)	694(9)	7081(5)	1721(3)
C(11)	3650(8)	5928(5)	4134(3)	C(31)	4899(8)	4236(4)	1344(2)
C(12)	2861(8)	5711(4)	3671(3)	C(32)	6620(8)	4410(5)	1409(3)
C(13)	1500(8)	6221(4)	3492(3)	C(33)	4636(10)	3501(4)	960(3)
C(14)	213(11)	6188(7)	3908(4)	C(34)	4317(8)	6526(5)	−39(3)
C(15)	1930(10)	7131(5)	3370(4)	C(35)	5970(9)	6376(6)	−175(3)
C(16)	4983(8)	3684(4)	3299(3)	C(36)	3301(10)	6292(5)	−507(3)
C(17)	5250(10)	2948(4)	3684(3)	C(37)	8122(9)	5970(5)	2675(3)
C(18)	6415(9)	3843(5)	2956(3)	C(38)	6421(10)	7342(5)	2929(3)

metal atom (i.e. copper) is almost linearly (S–Cu–C = 176.3(2)°) coordinated. The copper is bound to Me₂S instead of Et₂O with a Cu–S distance of 2.177(2) Å. It is notable that the geometry at sulfur is pyramidal with $\Sigma^\circ\text{S} = 306.4(3)^\circ$. The disposition of the –C₆H₃–2,6-Trip₂ group is very similar to that observed in **4**. The asymmetry in the exo-ring angles at C(2) and C(6) is *ca.* 1°, and the bending angle between the ortho-Trip rings and the C(2)–C(2) or C(6)–C(7) bonds is 4.3 and

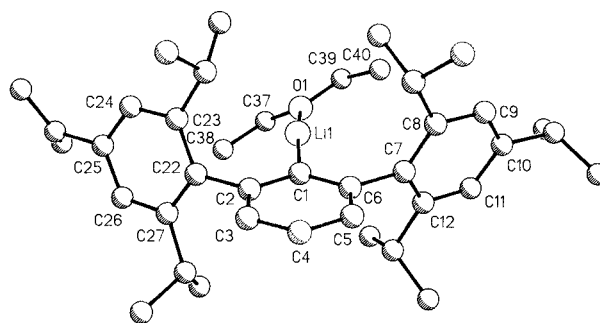
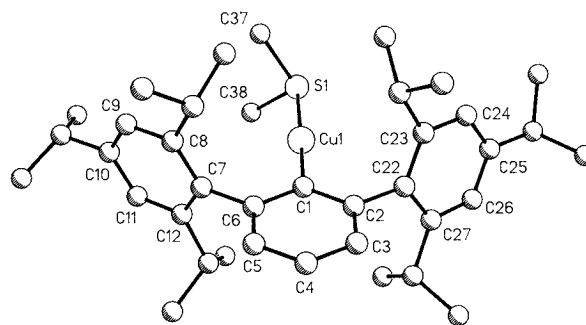
1.8°, respectively. The angles between the perpendiculars to the C(1) and C(7) or C(22) Trip rings are 85.7 and 77.3°.

Discussion

The major objective in synthesizing the sterically encumbered terphenyl ligands described here was their eventual application in the stabilization of new com-

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compounds 3-5

Compound 3			
C(1)–C(6)	1.391(6)	C(2)–C(1)–C(6)	123.6(5)
C(1)–C(2)	1.401(6)	C(1)–C(2)–C(3)	115.9(4)
C(2)–C(3)	1.385(7)	C(3)–C(2)–C(25)	118.8(4)
C(2)–C(25)	1.517(6)	C(1)–C(2)–C(25)	125.2(4)
C(3)–C(4)	1.375(7)	C(2)–C(3)–C(4)	122.0(4)
C(4)–C(5)	1.383(7)	C(3)–C(4)–C(5)	120.8(5)
C(5)–C(6)	1.389(7)	C(4)–C(5)–C(6)	119.8(5)
C(6)–C(7)	1.525(7)	C(5)–C(6)–C(1)	117.9(4)
C(7)–C(8)	1.429(7)	C(5)–C(6)–C(7)	123.4(4)
C(7)–C(12)	1.412(7)	C(1)–C(6)–C(7)	118.7(4)
		C(8)–C(7)–C(12)	119.7(4)
		C(12)–C(7)–C(6)	120.5(4)
		C(30)–C(25)–C(26)	119.3(4)
		C(30)–C(25)–C(2)	120.3(4)
		C(26)–C(25)–C(2)	120.1(4)
Compound 4			
Li(1)–C(1)	2.017(7)	O(1)–Li(1)–C(1)	171.9(5)
O(1)–Li(1)	1.850(7)	C(37)–O(1)–C(39)	114.9(3)
C(1)–C(6)	1.408(4)	C(37)–O(1)–Li(1)	122.1(3)
C(1)–C(2)	1.416(4)	C(39)–O(1)–Li(1)	122.6(3)
C(2)–C(3)	1.394(4)	C(6)–C(1)–C(2)	115.1(2)
C(2)–C(22)	1.502(4)	C(6)–C(1)–Li(1)	123.6(3)
C(3)–C(4)	1.378(4)	C(2)–C(1)–Li(1)	121.2(3)
C(4)–C(5)	1.378(4)	C(3)–C(2)–C(1)	122.6(3)
C(5)–C(6)	1.397(4)	C(3)–C(2)–C(22)	119.4(2)
C(6)–C(7)	1.509(4)	C(1)–C(2)–C(22)	118.0(2)
C(22)–C(23)	1.407(4)	C(4)–C(3)–C(2)	119.9(3)
C(22)–C(27)	1.408(4)	C(3)–C(4)–C(5)	119.8(3)
O(1)–C(37)	1.416(5)	C(4)–C(5)–C(6)	120.2(3)
O(1)–C(39)	1.430(5)	C(5)–C(6)–C(1)	122.3(2)
		C(5)–C(6)–C(7)	118.5(2)
		C(1)–C(6)–C(7)	119.2(2)
		C(8)–C(7)–C(6)	120.9(2)
		C(12)–C(7)–C(6)	120.5(2)
Compound 5			
Cu(1)–C(1)	1.894(6)	C(1)–Cu(1)–S(1)	176.3(2)
Cu(1)–S(1)	2.177(2)	C(38)–S(1)–C(37)	98.1(4)
S(1)–C(38)	1.799(8)	C(38)–S(1)–Cu(1)	104.9(3)
S(1)–C(37)	1.810(8)	C(37)–S(1)–Cu(1)	103.4(3)
C(1)–C(2)	1.414(9)	C(2)–C(1)–C(6)	116.8(5)
C(1)–C(6)	1.428(9)	Cu(1)–C(1)–C(2)	122.0(5)
C(2)–C(3)	1.394(9)	Cu(1)–C(91)–C(6)	121.2(5)
C(2)–C(22)	1.504(9)	C(2)–C(1)–Cu(1)	122.0(5)
C(3)–C(4)	1.380(8)	C(6)–C(1)–Cu(1)	121.2(5)
C(4)–C(5)	1.383(9)	C(1)–C(2)–C(3)	121.5(6)
C(5)–C(6)	1.395(9)	C(1)–C(2)–C(22)	117.6(6)
C(6)–C(7)	1.494(9)	C(3)–C(2)–C(22)	120.9(6)
		C(4)–C(3)–C(2)	119.8(6)
		C(3)–C(4)–C(5)	121.0(6)
		C(4)–C(5)–C(6)	119.9(6)
		C(5)–C(6)–C(1)	121.0(6)
		C(1)–C(6)–C(7)	117.8(5)
		C(5)–C(6)–C(7)	121.2(6)

**Figure 2.** Computer-generated drawing of **4**. H atoms are not shown.**Figure 3.** Computer-generated drawing of **5**. H atoms are not shown.

instances involve thiolate and selenolate derivatives of Fe or Mn where the steric properties of the Mes* and $-C_6H_3-2,6-Mes_2$ groups can be directly compared tend to support this view.^{10–12}

In addition to these steric considerations it should be noted that ortho-aryl groups attached to the central aromatic ring introduce electronic effects that differ from those provided by ortho-alkyl or alkylsilyl substituents. Aryl groups, since they contain six π -electrons, may provide electron density that can aid in the stabilization of species that contain low-coordination metal ions. A classic example of this behavior is the complexation and stabilization of Ga(I) species by neutral arene ligands.¹⁷ On the other hand, the ortho-alkyl substituents can provide stabilization of low-coordination numbers at metals by interactions between the metal center and the C–H groups of the alkyl. This can be illustrated in the case of the Mes* substituents by the recent synthesis^{16,18–20} of Mes*MX₂ and Mes*₂-MX compounds (M = Al, Ga, In; X = halide) which display close M...H approaches and do not form donor complexes with diethyl ether.

Of the new compounds described in this paper the structure of the lithium derivative **4** most readily illustrates the high steric requirements of the $-C_6H_3-2,6-Trip_2$ ligand. Its structural details may be compared to those of related ether-solvated lithium aryls^{21–24} provided in Table 4. It can be seen that there is a substantial decrease in the Li–C distance with decreas-

pounds with unusual structures, coordination numbers, or oxidation states. The synthetic route to such ligands has already been established with (relatively) less crowding ortho aryl groups such as Ph,⁷ 2,6-Me₂C₆H₃–,⁸ and mesityl.⁷ In addition, recently published work has shown that metal derivatives such as (LiC₆H₃-2,6-Mes₂)₂⁹ or ClGa(C₆H₃-2,6-Mes₂)₂¹⁵ can be readily obtained. These results have suggested that the $-C_6H_3-2,6-Mes_2$ ligand can often produce a more crowded environment than related bulky ligands such as $-C_6H_2-2,4,6-t-Bu_3$ (i.e. Mes*). For example, the C–Ga–C angle in Mes*₂GaCl¹⁶ is 135.6(2)° whereas in {2,6-Mes₂C₆H₃}₂GaCl the corresponding angle is 153.3(5)°. Other

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Table 4. Important Structural Parameters for Ether-Solvated Aryllithium Compounds

compd	Li coord no.	C coord no.	Li-C(Å)	ref
(Et ₂ O)LiPh ₄	4	5	2.31(4)	21
{(THF) ₂ LiMes ₂ }	4	4	2.271(3)	22
(Et ₂ O)LiTrip ₂	3	4	2.203(3)	23
(Et ₂ O) ₂ LiTrip ^a	3	3	2.074(16)	24
Et ₂ O)LiC ₆ H ₃ -2,6-Trip ₂	2	3	2.017(7)	this work

^a Trip^h = 2,4,6-Ph₃C₆H₂⁻.

ing coordination number of lithium or carbon. The structure of **4** in effect represents the lowest degree of aggregation for an ether-solvated organolithium compound. The Li-C distance 2.017(7) Å is nominally the shortest Li-C bond length to have been observed in the solid state. It is, however, within the standard deviations seen in the vapor phase structure of LiCH(SiMe₃)₂²⁵ (Li-C = 2.03(6) Å) which features a unique one-coordinate Li⁺ ion bound to an alkyl group. The Li-O distance, 1.850(7) Å, is also very short and is consistent with the two-coordination of the Li⁺ ion.²⁶ In spite of the crowding in **4** there is no evidence for a significant amount of strain in the molecule. The angles surrounding the carbons to which the Trip substituents are attached are close to 120°. Furthermore, there is almost perfect alignment of the planes of the Trip rings with the C-C bonds through which they are connected to the central phenyl ring. There is no evidence that the ortho Trip substituents interact with the lithium center. Thus, it may be concluded that the monomeric structure of **4** and the two-coordinate nature of the Li⁺ ion are a consequence of the size of the -C₆H₃-2,6-Trip₂ ligand rather than to electronic effects introduced by the Trip substituents.

The structure of the copper derivative **5** has many similarities to that of **4**. The copper is two-coordinate, being bound to SMe₂ and -C₆H₃-2,6-Trip₂, and the interligand angle is 176.3(2)°. The Cu-C (1.894(6) Å) and the Cu-S (2.177(2) Å) distances may be compared to those observed in Me₂SCuMes*, Cu-C = 1.916(3) Å and Cu-S = 2.185(1) Å.²⁷ The reasons for the slightly shorter metal-ligand distances in **5** are not clear. It is possible that the ortho t-Bu substituents on the Mes* group interact weakly with the Cu atom, thereby increasing slightly the electron density and coordination number at the metal which would account for the observed differences. There is no evidence in the structure of **5** for any such secondary metal-ligand interactions.

Like the Li-C bond length in **4** the Cu-C distance in **5** represents the shortest Cu-C (alkyl or aryl) bond length that has been authenticated to date. It is of interest to note that it is practically identical to the Cu-C bond length (Cu-C = 1.890(6) Å) reported for CuTrip^h (Trip^h = 2,4,6-Ph₃C₆H₃⁻), which was said to contain a unique one-coordinate metal.²⁸ A recent

publication, however, has suggested that this result is in error and that the compound studied was, most probably, the TriphBr starting material.²⁹ CuTrip^h may, nonetheless, be isolated as the solvate (Me₂S)₂Cu-(μ-Trip^h)CuTrip^h (**6**)²⁷ from a Me₂S solution. The structure of both **5** and **6** also offer circumstantial evidence that the description of the structure of "CuTrip^h" as monomeric is incorrect. For instance, it is odd that the uncomplexed monomer CuTrip^h forms the aggregate **6** when crystallized from a donor solvent such as Me₂S. Usually, the addition of donors to metal complexes results in a lower, not a higher, degree of aggregation. Furthermore, the almost identical Cu-C distances observed in **5** and in "CuTrip^h" are inconsistent with the different metal coordination numbers observed since a longer Cu-C distance should have been obtained in the case of the higher metal coordination number in **5**. In addition to the structural arguments it is notable that the solution ¹³C NMR data for **5** and (Me₂S)₂Cu-(μ-Trip^h)CuTrip^h (most probably monomeric in solution with one or two Me₂S ligands solvating the copper) display ipso-C signals at relatively low field (i.e. 154.9 ppm for (Me₂S)₂Cu-(μ-Trip^h)CuTrip^h and 168.09 ppm for **5**) that are consistent with substitution at this carbon by copper. In contrast, the ipso-C signal for "CuTrip^h" was reported to occur at 122.11 ppm which is almost identical to the value recorded for TriphBr.²⁹ Attempts to obtain crystalline CuC₆H₃-2,6-Trip₂ in the absence of a Me₂S donor have not been successful to date.

Turning now to the compound 1,3-Mes*C₆H₄ (**3**), it is notable that this species was consistently obtained in spite of numerous attempts to effect halogenation and obtain 2,6-Mes*₂C₆H₃X (X = Br, I). Although it is likely that the halide derivatives will be obtained eventually, it seems that an alternative route to the one described here will have to be used. It is not possible to say at present why **3** is formed in preference to the halide. One explanation is that in the last step the Grignard XMgC₆H₃-2,6-Mes*₂ may be unstable (possibly for steric reasons) and thus the Mg-C bond may be cleaved in which case the hydrogen derivative **3** is formed by hydrogen abstraction from a solvent molecule. The crowding in **3** is evident from the crystal structure which shows some deviation from the expected 120° angles at the substituted carbons from the central aryl ring. In addition to this there are significant deviations (up to ca. 10°) of the Mes* ring planes from the line of the C-C bonds through which they are connected to the C₆H₄ aryl ring.

In addition to the compounds described in this paper the iodo compound **1** may be converted to the lithium derivative LiC₆H₃-2,6-Dipp₂. This compound does not crystallize well from diethyl ether solutions. Nonetheless, it can be crystallized as the dimer (LiC₆H₃-2,6-Dipp₂)₂ from noncoordinating solvents. Its structure, as well as those of other "nonsolvated", sterically encumbered, lithium aryls, will be reported separately.³⁰

Conclusion

The bulky aryl iodides 2,6-Dipp₂C₆H₃I and 2,6-Trip₂C₆H₃I may be relatively easily synthesized. They

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may be transformed by simple, known, routes to their lithium derivatives. The structures of the lithium and copper salts **4** and **5** attest to the very bulky character of these aryl groups which should have widespread applicability throughout the periodic table.

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Supporting Information Available: Tables of data collection parameters, hydrogen coordinates and *U* values, bond distances and angles, and anisotropic thermal parameters (29 pages). Ordering information is given on any current mast-head page.

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