The reaction vessel was charged with 5 mL (48 mmol) of benzyl alcohol, 10 mL of $(CH_2)_2Cl_2$, 0.02 g (0.077 mmol) of $RuCl_3 \cdot 3H_2O$, and 1 mL (1 mmol) of DDAB, 50% in toluene. The H_2O_2, 30% (15 mL), was fed into the reaction mixture by a syringe pump at a constant feed rate of 0.3 mL/min.

When the isolation of pure products was wanted, the organic phase was separated, solvent evaporated, and the residue chromatographed on a silica gel column by gradient elution, beginning with CH_2Cl_2 up to CH_2Cl_2:MeOH, 80:20%.

The procedures for all the other cited substrates are exactly the same as for benzyl alcohol.

Analysis. The progress of the reactions was checked by GLC analysis. When the product was an acid, the sample was first methylated by diazomethane. The column was OV-101 15% on Chromosorb 100/120 WAW for primary aliphatic and benzylic alcohols at a temperature of 100 °C (3 min), 25 °C/min, 250 °C (5 min) and OV 210 10% on Chromosorb 80/100 WHP for secondary alcohols at a temperature of 60 °C (5 min), 25 °C/min, 250 °C (5 min). The identification of the products was done by comparing with a standard and also by CGMS analysis.

Acknowledgment. We are grateful to Abic Ltd. Ramal-Gan for the donation of DDAB.

Registry No. $RuCl_3$, 10049-08-8; $PdCl_2$, 7647-10-1; $CoCl_2$, 7646-79-9; $MnCl_2$, 7773-01-5; didecyldimethylammonium bromide, 19959-22-9; cyclohexanol, 108-93-0; 2-octanol, 123-96-6; *sec*-phenethyl alcohol, 98-85-1; benzyl alcohol, 100-51-6; *p*-methylbenzyl alcohol, 589-18-4; *p*-nitrobenzyl alcohol, 619-73-8; *p*-bromobenzyl alcohol, 873-75-6; 1-decanol, 112-30-1; 1-octanol, 111-87-5; 1-heptanol, 111-70-6; 1-hexanol, 111-27-3; cyclohexanone, 108-94-1; 2-octanone, 111-13-7; acetophenone, 98-86-2; benzaldehyde, 100-52-7; benzoic acid, 65-85-0; *p*-methylbenzaldehyde, 104-87-0; *p*-nitrobenzaldehyde, 555-16-8; *p*-bromobenzaldehyde, 1122-91-4; 1-decanoic acid, 334-48-5; 1-octanoic acid, 124-07-2; 1-heptanoic acid, 111-14-8; 1-butanoic acid, 107-92-6; benzyl benzoate, 120-51-4; 1-octen-3-ol, 3391-86-4; 1-octen-3-one, 4312-99-6.

Synthesis of Triarylbenzenes via Tandem Aryne Reactions of Aryl Grignards with Polyhalobenzenes

Tirthankar Ghosh and Harold Hart*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

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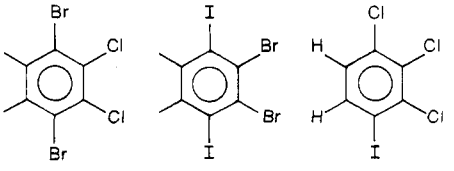
Aryl Grignards react with 1,2,3,4-tetrahalobenzenes to give primarily (2,3,4-triarylphenyl)magnesium halides. The mechanism involves Grignard exchange at one of the "outer" halogens followed by three cycles of magnesium halide loss and regioselective capture of the resulting aryne by the aryl Grignard agent (Scheme II).

Introduction

The use of multi-aryne reactions as a synthetic tool for multiple carbon–carbon bond constructions to an arene ring has now been well established. Recently we described general syntheses of biaryls[1] (from 1,2-dihalobenzenes), *p*-terphenyls[1] (from 1,2,4,5-tetrahalobenzenes), *m*-terphenyls[2] (from 1,2,3-trihalobenzenes), and 1,2,4,5-tetraarylbenzenes[3] (from hexahalobenzenes). A similar one-pot synthesis of *o*-terphenyls is lacking. We imagined that such a synthesis might be possible from an appropriate 1,2,3,4-tetrahalobenzene if the reaction were to proceed via a 1,4-diGrignard intermediate (Scheme I).

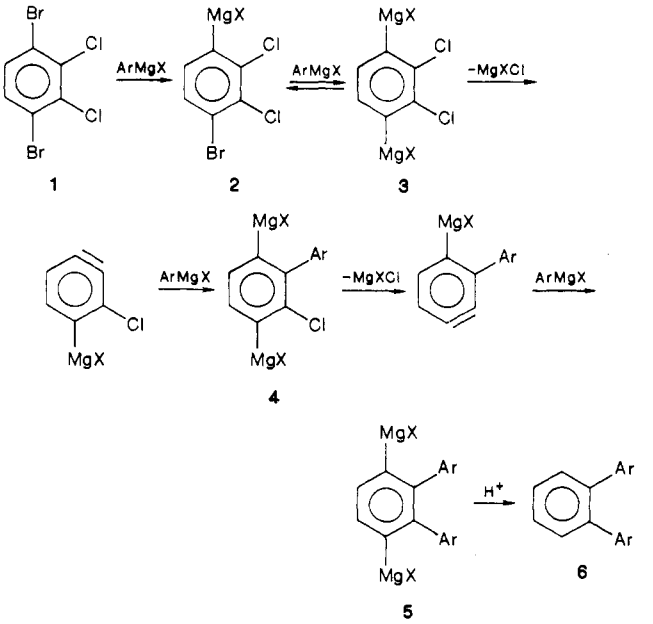
According to our earlier work, exchange should occur predominantly at Br instead of Cl to give first **2** and then **3**. Assuming that 1,4-diGrignards will be preferred over 1,3-diGrignards, the regiochemistry should be as shown, giving **6**.

Here we report on our first efforts in this area. Instead of **1**, we used the more easily synthesized dimethyl analogues **7**[4] and **8**,[5] together with the trichloroiodobenzene **9**. Although the desired *o*-terphenyl synthesis was not



7 **8** **9**

Scheme I



achieved as anticipated by Scheme I, the results are novel and useful.

Results

Heating **7** at reflux with 5–8 equiv of phenylmagnesium bromide followed by aqueous quench gave 1,2-dimethyl-3,4,5-triphenylbenzene (**10**) in 40% yield, together with 5% of the 1,3-diaryl derivative **11**.[6] Although ^1H NMR

(1) Hart, H.; Harada, K.; Du, C-J. F. *J. Org. Chem.* **1985**, *50*, 3104.
(2) Du, C-J. F.; Hart, H.; Ng, D.K.-K. *J. Org. Chem.* **1986**, *51*, 3162.
(3) Harada, K.; Hart, H.; Du, C.-J. F. *J. Org. Chem.* **1985**, *50*, 5524.
(4) Hinkel, L. E.; Ayling, E. E.; Walters, T. M. *J. Chem. Soc.* **1934**, 283.
(5) Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427.

(6) Although we were not able to obtain a pure sample of **11** from this reaction, its ^1H NMR spectrum was identical with that of the sample isolated in the reaction of **8** with phenylmagnesium bromide at 25 °C.

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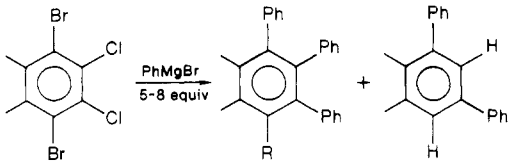
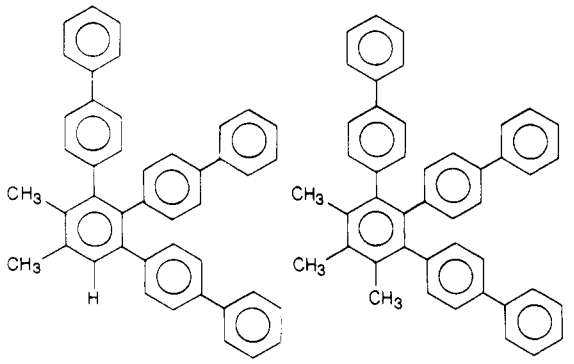


7 10: R=H (40%) 11 (5%)
12: R=CH$_3$

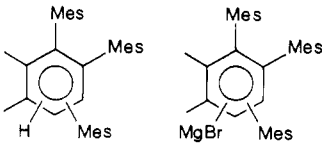
spectroscopy was ambiguous as to the location of the phenyl substituents in **10**, quenching with CH_3I was unequivocal, giving a product whose ^1H NMR spectrum showed only two methyl signals, in a 2:1 ratio. This result is only consistent with the formation of the symmetrical trimethyltriphenylbenzene **12** and not its 1,2,4-triaryl isomer.

An identical experiment using the Grignard reagent from 4-bromobiphenyl gave a 30% yield of 1,2,3-tris(biphenylyl)-4,5-dimethylbenzene (**13**). Here also the position of the biphenyls was established by quenching with CH_3I, which gave the corresponding symmetrical trimethyl derivative **14**.

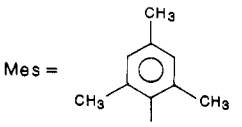


13 14

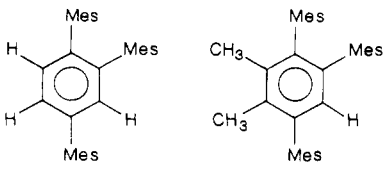
Similarly we have been able to synthesize a trimesityl derivative **15** by this methodology. In this case the final product **16** could not be trapped with CH_3I, probably



15 16

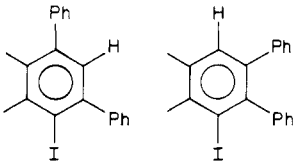


because of steric hindrance. As a result we have been unable to determine with certainty the position of the mesityl groups in **15**. However, an identical reaction, but with **9** instead of **7** as the polyhalo precursor, gave 1,2,4-trimesitylbenzene (**17**) after aqueous quench. The unsymmetrical nature of **17** was evident from the methyl region of its ^1H NMR spectrum, which had three 6-proton peaks and three 3-proton peaks. Thus it seems likely that the product from **7** also has the unsymmetric structure **18**.



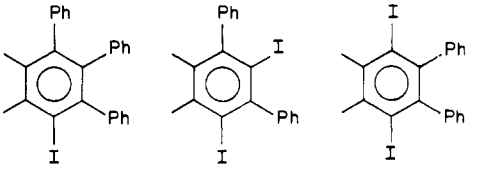
17 18

We next decided to determine the effect, if any, of changing the halogens on the polyhaloarene precursor. When an 8-fold excess of phenylmagnesium bromide was heated at reflux in THF with **8**, there was obtained, together with **10** (50%), an inseparable two-component mixture (4:1 ratio, 16%). The ^1H NMR spectrum indicated that these compounds were structural isomers, and the mass spectrum was consistent with the incorporation of only two phenyl groups, with one iodine atom still present. Thus, the most probable structures of the two isomers are **19** and **20**. When the same reaction mixture



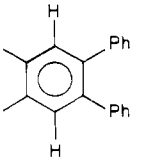
19 20

was quenched with iodine, we isolated the triphenyliodo derivative **21** (50%) and only one diphenyldiiodoarene, **22** (20%). The ^1H NMR spectrum of **22** showed two different methyl signals at δ 2.60 and 2.15. We conclude that in the proton quenching experiment the structure of the major diphenyliodoarene is **19**, because if the major isomer had been **20**, then iodine quenching should have afforded **23**, which, due to its symmetry, would have exhibited only one methyl signal in its ^1H NMR spectrum. When carried out



21 22 23

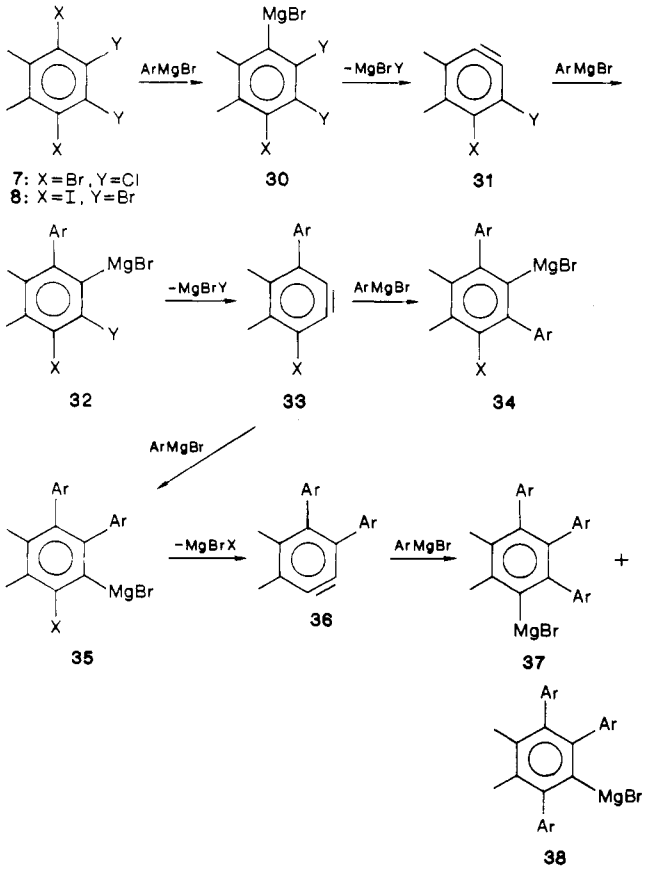
at 25 °C instead of at reflux, **10** was again the major product (51%) together with the 1,3-diaryl products **11** (28%) and **19** (14%). Quenching with iodine gave, as expected, only **21** and **22**. (Since the other possible isomer of **11**, i.e. **24**, is symmetric, it would show one methyl peak in its ^1H NMR spectrum. Since we observe two singlets at δ 2.40 and 2.20, we assign structure **11** to the diaryl product).



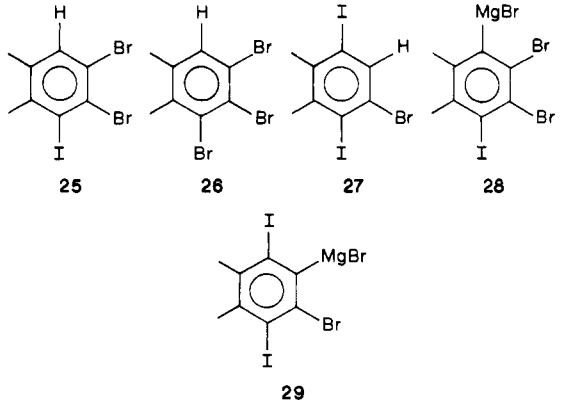
24

To gain insight regarding the initial exchange site, **8** was stirred with 2.5 equiv of phenylmagnesium bromide at −78 °C for 3 h and then quenched with aqueous acid. Apart from 50% unreacted **8**, a mixture of three different polyhalobenzenes was isolated and analyzed by capillary chromatography (ratio 4:1.7:1). GC/MS analysis indicated the bromine and iodine content of each component. The major component contained two bromines and one iodine and is assigned structure **25**, presumably derived from metal–halogen exchange at iodine to give monoGrignard **28**. The predominant minor product contained *three* bromines; formation of a tribromo product from a dibromo precursor has precedent[1] and its origin will be discussed later. Finally, the minor product had two iodines and one bromine, and is thought to be **27**, presumably derived from metal–halogen exchange at bromine to give monoGrignard

Scheme II



29. Since we have been unable to separate the individual components, the structural assignments for **25–27** are based in part on reasonable mechanism and are not fully established.

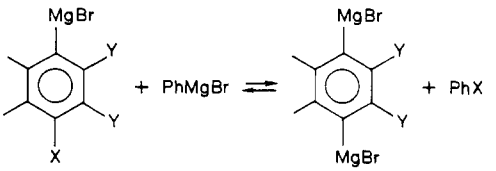


Discussion

The formation of trisubstituted benzenes from either **7** or **8** can be rationalized by a tandem aryne sequence (Scheme II). The low temperature exchange studies show that the major species in solution is the monoGrignard **30**. The first aryne **31**, generated by the loss of magnesium halide, is captured by excess aryl Grignard regiospecifically to give the *o*-halo stabilized Grignard **32**. This intermediate is now well poised for the elimination of a second mole of magnesium halide to give aryne **33**. Like **31**, **33** undergoes nucleophilic capture to give predominantly the halogen-substituted Grignard **35**, together with a minor amount of **34**. Intermediate **35** can undergo further elimination to give the third aryne in the sequence, **36**, which is then trapped by another molecule of the Grignard reagent to give the ultimate triaryl Grignards **37** and **38**. Except for mesityl where nucleophilic capture of **36** takes place adjacent to the methyl group, the major mode of capture for unhindered Grignard reagents is meta to the methyl group. Such a regioselectivity is in contrast with recent observations where 3-tolyne[7a] and 1,2-dimethyl-3-benzyne[7b] exhibited no regioselectivity on nucleophilic capture.

Minor intermediate **34**, if it undergoes no further exchanges, will account for the formation of minor product **19** (aqueous quench) or **22** (iodine quench).

Minor product **11** may arise in any of several ways. One possibility is that **34** may undergo a second metal–halogen exchange to produce a 1,3-diGrignard which, on aqueous quench, would give **11**. Alternatively, initial intermediate **30** may undergo a second metal–halogen exchange (either 1,3 or 1,4) leading ultimately to **11**. The fact that more **11** is formed at room temperature than at reflux favors a diGrignard precursor for **11**, since the opportunity for diGrignard formation vis-â-vis elimination to form aryne from monoGrignard intermediates should be favored at lower temperatures. However, at this point, we have been unable to design a simple experiment that will distinguish among the possibilities for formation of minor product **11**.



Finally it remains to account for minor tribromo product **26** in the exchange studies. It seems that this product arises from *reversible* diGrignard formation from **30**. DiGrignard **39** could react with any aryl bromide in solution in a back-exchange, to give a tribromide; indeed, some **25** may also arise in this way, although most of it probably comes from monoGrignard **28**. Similar results were obtained previously,[1] in solutions where diGrignard formation was clearly demonstrated.

To summarize, the reaction of several 1,2,3,4-tetrahalobenzenes with excess aryl Grignard reagent gives good yields of 1,2,3-triarylbenzenes, but with hindered Grignards such as mesityl 1,2,4-triarylbenzenes are obtained. The products are thought to arise from tandem aryne reactions (Scheme II). In view of our recent demonstration that vinyl Grignards can replace aryl Grignards in similar reactions,[8] it seems likely that 1,2,3-trivinylbenzenes could arise from reactions similar to those described here.

Experimental Section

General Procedures. ^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer in $CDCl_3$ solution containing $(CH_3)_4Si$ as an internal standard. Chemical shifts are reported in δ units. Mass spectra were recorded at 70 eV on a Finnigan 4000 spectrometer. High-resolution mass spectra were obtained on a JEOL IMSHX100 spectrometer. Melting points, taken on a Thomas-Hoover Unimelt apparatus, are uncorrected. Silica gel for chromatography was 230–400 mesh.

1,2,3-Trichloro-4-iodobenzene (9). To a well-stirred suspension of 2,3,4-trichloroaniline (19.7 g, 0.1 mol) in concentrated hydrochloric acid (25 mL) kept at 0–10 °C was added dropwise

(7) (a) Levine, R.; Biehl, E. R. *J. Org. Chem.* **1975**, *40*, 2416. (b) Biehl, E. R.; Razzuk, A.; Jovanovic, M. V.; Khanapure, S. *J. Org. Chem.* **1986**, *51*, 5157.

(8) Du, C.-J. F.; Hart, H. *J. Org. Chem.* **1987**, *52*, 4311. Hart, H.; Ghosh, T. *Tetrahedron Lett.* **1988**, *29*, 881. Vinod, T. K.; Hart, H. *Tetrahedron Lett.* **1988**, *29*, 885.

an aqueous solution of sodium nitrite (8.0 g in 10 mL of water). After addition was complete, the solution was stirred for 1 h. The diazotized solution was then slowly poured into a well-stirred solution of sodium iodide (50 g) in 100 mL of water. The mixture was stirred at room temperature overnight. Methylene chloride (100 mL) was added, and the iodine color discharged by adding sodium sulfite. The organic layer was separated, washed with 15% sodium hydroxide followed by brine, and dried (Na_2SO_4). Removal of the solvent gave a dark solid, which was chromatographed over silica gel to give **9** (14 g, 50%) as a white crystalline solid: recrystallized from petroleum ether, mp 50–52 °C (lit.[9] mp 66.0–66.5 °C).

1,2-Dimethyl-3,4,5-triphenylbenzene (10). To a refluxing solution of phenylmagnesum bromide (12 mmol) was added a solution of **7**[4] (500 mg, 1.5 mmol) in THF (25 mL). After 6.5 h at reflux, the reaction was quenched with saturated ammonium chloride solution and extracted with ether. The ether layer was washed with brine and dried (Na_2SO_4). The gum obtained after removal of the ether was chromatographed over silica gel with hexane–methylene chloride (85:15) as eluent. The first fractions gave a mixture of **10** and **11** (150 mg) followed by pure **10** (200 mg, 40%): mp 78–80 °C; ^{1}H NMR δ 7.00–7.48 (series of m, 16 H), 2.20 (s, 3 H), 2.10 (s, 3 H); mass spectrum calcd for $C_{26}H_{22}$ 334.1722, obsd 334.1728.

Methyl Iodide Quench. Phenylmagnesium bromide (6.4 mmol) and 0.75 mmol of **7** were heated at reflux for 6 h after which CH_3I (5 mL) was added and the mixture heated at reflux for an additional 4 h. After being quenched with aqueous hydrochloric acid, the reaction mixture was extracted with ether. The crude oil obtained after removal of the ether was chromatographed over silica gel with hexane–methylene chloride (75:25) as eluent. First to elute was unreacted **8** (80 mg) followed by **12** (100 mg, 40%); mp 100–105 °C; ^{1}H NMR δ 6.95–7.50 (series of m, 15 H), 2.05 (s, 6 H), 1.70 (s, 3 H); mass spectrum calcd for $C_{27}H_{24}$ 348.1878, obsd 348.1883.

1,2,3-Tris(4-biphenylyl)-4,5-dimethylbenzene (13). To a refluxing solution of 4-biphenylylmagnesium bromide (prepared from 4-bromobiphenyl (1.4 g, 6 mmol) and Mg (150 mg, 6.25 mmol) in 15 mL of THF) was added a solution of **7** (250 mg, 0.75 mmol) in THF (10 mL). The mixture was heated at reflux for 16 h, then quenched with aqueous acid (HCl), and extracted with ether. After removal of the ether the crude product was chromatographed over silica gel with hexane–methylene chloride (4:1) as eluent. First to elute was unreacted **7** (40 mg) followed by biphenyl (700 mg) and ultimately **13** (120 mg). Based on recovered **7**, the yield of **13** was 33%; mp 210–213 °C; ^{1}H NMR δ 7.15–7.75 (series of m, 28 H), 2.38 (s, 3 H), 2.25 (s, 3 H); mass spectrum calcd for $C_{44}H_{34}$ 562.2661, obsd 562.2709.

Methyl Iodide Quench. 4-Biphenylylmagnesium bromide (6.0 mmol) and 0.75 mmol of **7** were heated at reflux for 8 h after which CH_3I (7 mL) was added and the mixture was heated at reflux for an additional 12 h. After being quenched with aqueous HCl, the reaction mixture was extracted with ether. The crude oil after removal of the ether was chromatographed over silica gel with hexane–CH_2Cl_2 (7:3) as eluent, giving 120 mg (28%) of **14** as a white solid: mp 200–205 °C; ^{1}H NMR δ 7.05–7.75 (series of m, 27 H), 2.12 (s, 6 H), 1.85 (s, 3 H); mass spectrum calcd for $C_{45}H_{36}$ 576.2817, obsd 576.2816.

1,2,4-Trimesityl-5,6-dimethylbenzene (18). To a refluxing solution of mesitylmagnesium bromide (prepared from mesityl bromide (1.2 g, 6 mmol) and Mg (150 mg, 6.25 mmol) in 15 mL of THF) was added dropwise a solution of **7** (200 mg, 0.6 mmol) in THF (10 mL). The reaction mixture was heated at reflux for 16 h and then worked up as described previously. The crude product was chromatographed over silica gel with hexane–methylene chloride (4:1) as eluent to give 100 mg (37%) of **18** as a white solid: mp 150–155 °C; ^{1}H NMR δ 6.95 (s, 2 H), 6.75 (s, 2 H), 6.70 (s, 1 H), 6.65 (s, 2 H), 2.35 (s, 3 H), 2.20 (s, 3 H), 2.17 (s, 3 H), 2.03 (s, 6 H), 2.00 (s, 3 H), 1.95 (s, 3 H), 1.92 (s, 6 H), 1.90 (s, 6 H); mass spectrum calcd for $C_{35}H_{40}$ 460.3130, obsd 460.3120.

1,2,4-Trimesitylbenzene (17). To a refluxing solution of mesitylmagnesium bromide (prepared from bromomesitylene (1.0 g, 5 mmol) and Mg (120 mg, 5 mmol) in 20 mL of THF) was added dropwise a solution of **9** (310 mg, 1.0 mmol) in THF (5 mL). The reaction mixture was heated at reflux for 16 h and then worked up as described previously. The crude product was chromatographed over silica gel with hexane followed by hexane–methylene chloride (3:1) as eluent to give 230 mg (53%) of **17**: ^{1}H NMR δ 7.22 (s, 1 H), 7.13 (d, 1 H), 7.00 (d, 1 H), 6.95 (s, 2 H), 6.76 (s, 2 H), 6.71 (s, 2 H), 2.33 (s, 3 H), 2.23 (s, 3 H), 2.20 (s, 3 H), 2.10 (s, 6 H), 1.98 (s, 6 H), 1.95 (s, 6 H); mass spectrum calcd for $C_{33}H_{36}$ 432.2817, obsd 432.2799.

Reactions with 8[5] as Aryne Precursor. A solution of phenylmagnesium bromide (5 mmol) and **8** (310 mg, 0.6 mmol) in THF (20 mL) was heated at reflux for 5 h. After the usual acid quench and workup, the crude product was chromatographed over silica gel with hexane–methylene chloride (9:1) as eluent. First to elute was a mixture of **19** and **20** in a 4:1 ratio (50 mg, 22%). For **19**: ^{1}H NMR δ 7.35 (m, 10 H), 7.05 (s, 1 H), 2.68 (s, 3 H), 2.32 (s, 3 H). For **20**: ^{1}H NMR δ 7.35 (m, 10 H), 7.08 (s, 1 H), 2.55 (s, 3 H), 2.30 (s, 3 H); mass spectrum calcd for $C_{20}H_{17}I$ 384.0375, obsd 384.0393. Next to elute was **10** (100 mg, 50%).

A solution of phenylmagnesium bromide (5 mmol) and **8** (310 mg, 0.6 mmol) in THF (20 mL) was heated at reflux for 5 h. After cooling 1.3 g of iodine was added and the reaction mixture stirred for 3 h. After the mixture was quenched with aqueous acid (HCl), 75 mL of ether was added. The ether layer was separated, washed with brine, and dried (Na_2SO_4). The crude product obtained after removal of the ether was triturated with hexane to give 140 mg (52%) of **21** as a white crystalline solid. The hexane-soluble fraction, on preparative TLC over silica gel with hexane as eluent, gave 70 mg (23%) of **22**. For **21**: mp 165–170 °C; ^{1}H NMR δ 6.95–7.55 (m, 15 H), 2.10 (s, 3 H), 2.00 (s, 3 H); mass spectrum calcd for $C_{26}H_{21}I$ 460.0688, obsd 460.0676. For **22**: mp 125–130 °C; ^{1}H NMR δ 7.10–7.55 (m, 10 H), 2.60 (s, 3 H), 2.15 (s, 3 H); mass spectrum calcd for $C_{20}H_{16}I_2$ 509.9341, obsd 509.9348.

A solution of phenylmagnesium bromide (5 mmol) and **8** (310 mg, 0.6 mmol) was stirred at 25 °C in THF (35 mL) for 5 h. The reaction was quenched with aqueous acid (HCl) followed by extraction with ether (70 mL). The ether layer was separated, washed with brine, and dried (Na_2SO_4). Removal of the ether gave 200 mg of a colorless gum. ^{1}H NMR analysis of this gum showed three products in a ratio of 1:2:4. The gum was subjected to column chromatography over silica gel with hexane as eluent. First to elute was **10** (100 mg, 50%) followed by a mixture of **11** and **19** (70 mg). Repetitive chromatography of this mixture gave a sample of pure **11**. For **11**: ^{1}H NMR δ 7.25–7.50 (m, 12 H), 2.40 (s, 3 H), 2.20 (s, 3 H); mass spectrum, *m/e* (relative intensity) 258 (M^+, 35), 243 (9), 154 (24), 93 (66), 77 (40).

Low-Temperature Experiment. A solution of **8** (516 mg, 1 mmol) in THF (10 mL) was added slowly to a well-stirred solution of phenylmagnesium bromide (2.5 mmol) in THF (10 mL) kept at −78 °C. The solution was stirred at −78 °C for 2 h and then quenched at −78 °C with 2 mL of 10% HCl in 2 mL of THF. Ether (50 mL) was added and the ether layer separated. The crude product obtained after removal of the ether was chromatographed over silica gel with hexane as eluent. First to elute was a mixture of **25**, **26**, and **27** (100 mg). Next to elute was unreacted **8** (200 mg). For **25**: ^{1}H NMR δ 7.73 (s, 1 H), 2.65 (s, 3 H), 2.45 (s, 3 H); mass spectrum, *m/e* (relative intensity) 392 (20), 390 (62), 388 (25), 265 (3), 263 (13), 261 (4), 184 (16), 182 (22), 127 (81), 77 (60). For **26**: ^{1}H NMR δ 7.72 (s, 1 H), 2.68 (s, 3 H), 2.55 (s, 3 H); mass spectrum, *m/e* (relative intensity) 346 (1), 344 (24), 343 (9), 342 (44), 265 (20), 263 (68), 262 (13), 261 (17), 182 (11), 103 (52), 102 (100), 77 (52). For **27**: ^{1}H NMR δ 8.00 (s, 1 H), 2.52 (s, 3 H), 2.40 (s, 3 H); mass spectrum, *m/e* (relative intensity) 438 (37), 436 (51), 184 (8), 182 (10), 127 (100), 103 (78), 77 (40).

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