ipso-and para-Functionalization of meta-terphenyl ligands with substituted methyl groups: Unusual head-to-tail coupling of terphenyl moieties

Corneliu Stanciu, Alexander R. Fox, Anne F. Richards, James C. Fettinger, Philip P. Power *

Department of Chemistry, One Shields Avenue, University of California, Davis, CA 95616, United States

Abstract

The synthesis and characterization of several *ipso*-functionalized derivatives of the bulky terphenyl group C_6H_3-$2,6(C_6H_3$-$2',6'$-$Pr^i_2)_2(Ar')$ are described. These include the primary alcohol $Ar'CH_2OH$ (**1**), the bromo derivative $Ar'CH_2Br$ (**2**), and the terphenyl formate $Ar'CH_2OC(O)H$ (**3**). The alcohol **1** was obtained by treatment of $LiAr'$ with formaldehyde, and **1** was readily converted to the bromo derivative **2** using HBr. The reaction of **1** with formic acid afforded **3** in good yield. Attempts to form the Grignard derivative of **1**, i.e., $Ar'CH_2MgBr$, resulted in a head-to-tail reaction of the terphenyl benzyl units to yield an unusual coupled product **4**. An approach to the avoidance of this coupling involved the synthesis of the terphenyl derivatives 1-I-C_6H_2-$2,6(C_6H_3$-$2',6'$-$Pr^i_2)_2$-4-Me (**5**) and 1-I-C_6H_2-$2,6(C_6H_2$-$2',4',6'$-$Pr^i_3)_2$-4-Me (**6**), bearing methyl groups in the para positions of the central aryl ring, which could be prepared in good yield, and converted to their respective lithium salts **7** and **8** without complication . The compounds were characterized by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy (**1**) and X-ray crystallography (**2**, **4**, **5** and **6**).
© 2006 Elsevier B.V. All rights reserved.

Keywords: Terphenyl; Bulky aryl; Coupling; Lithium aryl

1. Introduction

Bulky *meta*-terphenyl ligands have been shown to be effective for the stabilization of numerous compounds with low coordination numbers [1–7], previously unknown multiple bonds [8–12], or heavier main group element compounds with unpaired electrons [13–16]. Usually the terphenyl ligand is attached directly to the reactive center through the *ipso* carbon of the central aryl ring and steric protection is provided by the flanking aryls attached at positions ortho to this carbon. Recently, this theme has been extended to include terphenyl derivatives that employ hetero atoms such as the pnictogens or chalcogens (or derivatives thereof) attached to the *ipso* carbon [17–22]. The resultant ligands (e.g., amides, phenolates or thiolates)

have also been shown to be effective as sterically encumbering groups. In contrast, less attention has been devoted to the use of terphenyl substituted group 14 elements as ligands where, for example, alkyl or silyl ligands with terphenyl substituents could be used in the stabilization of new compounds. We describe the synthesis and characterization of carbon ligands that have the bulky terphenyl group $Ar'(Ar' = C_6H_3$-$2,6(C_6H_3$-$2',6'$-$Pr^i_2)_2)$. In these ligands the terphenyl is substituted by the group $-CH_2X$, where $X = OH$, Br or $OC(O)H$, at the *ipso* position. In addition, we show that the reaction of the bromo derivative $Ar'CH_2Br$ with magnesium affords a unique head-to-tail coupled product, **4**, as shown by the formula rather than the expected Grignard reagent $Ar'CH_2MgBr$. Initial efforts to block this undesirable reaction, have involved the synthesis of two new terphenyl species 1-I-C_6H_2-$2,6(C_6H_3$-$2',6'$-$Pr^i_2)_2$-4-Me, $MeAr'I$ (**5**) and 1-I-C_6H_2-$2,6(C_6H_2$-$2',4',6'$-$Pr^i_3)_2$-4-Me, $MeAr^*I$ (**6**) that have methyl

---

substitution at the *para*-position of the central aryl ring and which could be converted to their respective lithium salts LiAr′Me (**7**), and LiAr*Me (**8**).
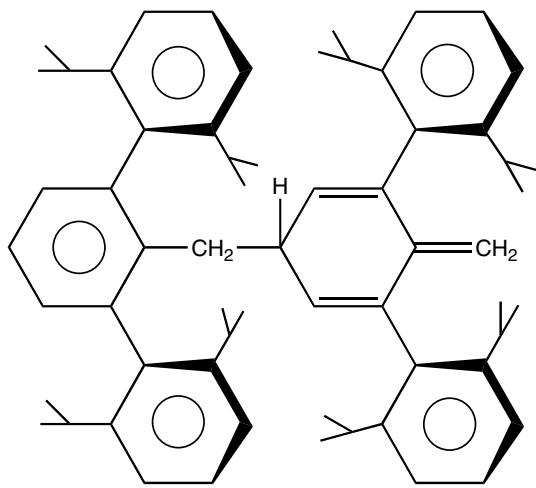
4

2. Results and discussion

Previous work that has dealt with the derivatization of terphenyl ligands with carbon based functional groups at the *ipso* position of the central ring has focused mainly on isolation of carboxylic derivatives and their subsequent use as bulky ligands for transition metal complexes. We were anxious to synthesize species with substituents at this position containing a C–X (X = halogen) in order to facilitate further derivatization. This was achieved with use of
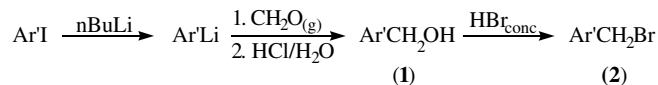
Scheme 1. The synthetic routes to **1** and **2**.

the route described in Scheme 1 which afforded **2** in ca. 87% overall yield based on LiAr′.

The reaction of **2** with Mg in THF resulted in almost complete consumption of the metal and the formation of a pale yellow solution. Attempts to react this solution with a suspension of $SnCl_2$ in diethyl ether afforded the product **4** rather than the expected Ar′CH₂SnCl. Further experiments involving the rapid quenching of the putative Grignard species Ar′CH₂MgBr with methanol afforded identical results. The identity of the product **4** was established by ^1H and ^{13}C NMR spectroscopy as well as X-ray crystallography. A possible mechanism for the formation of **4** is provided in Scheme 2.

2.1. Structures and spectroscopy

Compounds **1**–**8** were characterized by ^1H and ^{13}C NMR spectroscopy and the structures of **2**, **4**, **5**, and **6** were determined by X-ray crystallography.

The most striking feature of compound **1** is that it is an unassociated primary alcohol because of the steric effects of the flanking rings of the Ar′ group. The monomeric formulation is supported by the upfield chemical shift of the –OH proton in ^1H NMR spectrum (triplet at 0.92 ppm), as well as by the sharp absorption band at 3560 cm^{-1} in the IR spectrum. The OH ^1H NMR chemical shift is close to that expected for unassociated alcohols (ca. 0.5 ppm) [23a] and the sharp –OH stretching band lies in the higher frequency

Ar = –C₆H₃-2,6-Pr$^i_2$,2,6-di-isopropylphenyl (Dipp)
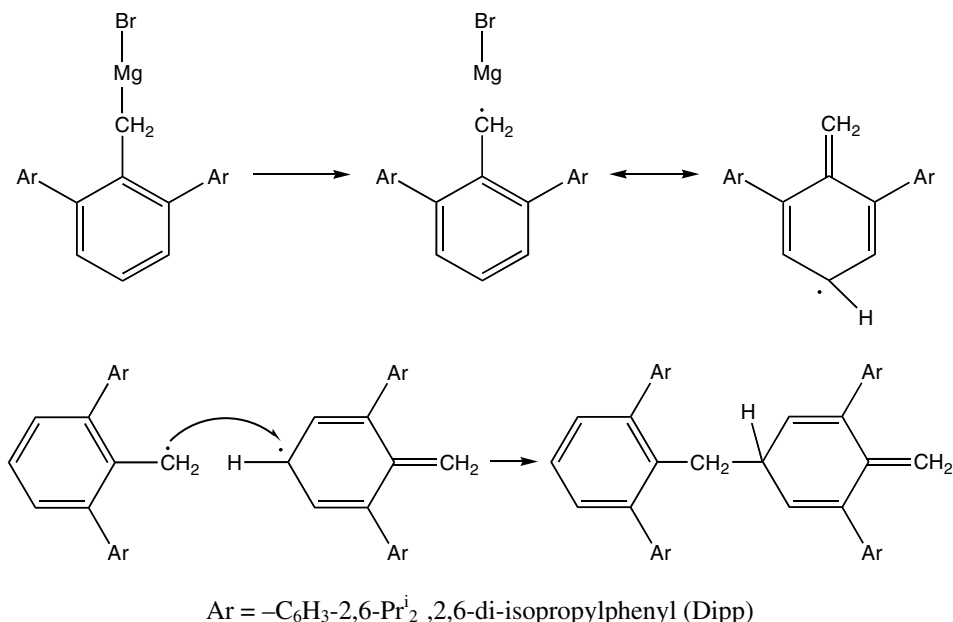
Scheme 2. A possible mechanism for the coupling reaction of two terphenyl methylene groups to produce **4**.
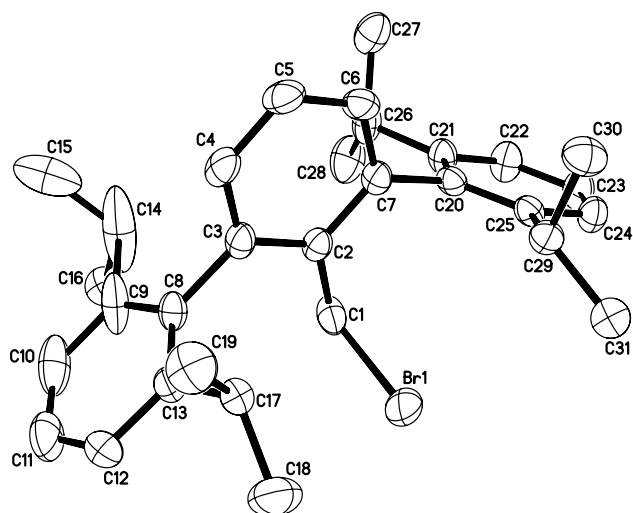
Fig. 1. Thermal ellipsoid plot of Ar′CH₂Br (**2**). H atoms are not shown.

range 3600–3650 cm^{-1} expected for an unassociated structure [23b]. The benzylic CH$_2$ group carrying the –OH appears as a doublet at 4.07 ppm.

In the case of **2**, the X-ray structure showed that it had a monomeric structure. A thermal ellipsoid plot of **2** is given in Fig. 1.

A relatively small number of benzyl-like bromides have been structurally characterized but it is known that the carbon–bromine bond distances vary in the general range 1.94–1.79 Å, depending on the hybridization of carbon [24]. Other authors found benzylic C–Br bond distances of 1.988 (7) Å [25] or 1.974 and 1.984 Å [26] (in 2,6-di(bromomethyl)biphenyl or 1,8-di(bromomethyl)naphthalene, respectively). The C(3)–C(2)–Br(1) angle is 113.1(2)° (similar to other similar angles of 112.4° [25] or 112.1° [26]). Molecules **5** and **6** are also monomers. Their thermal ellipsoid drawings are shown in Fig. 2 below.

Selected bond distances and angles in molecules **2**, **5** and **6** are given in Table 1. The carbon–iodine distances are 2.111(4) and 2.115(3) Å for **5** and **6**, respectively. Bond lengths in similarly crowded terphenyl iodides vary between 2.106(2) and 2.111(2) Å [27]. The slight elongation of the carbon–iodine bond in **5** and **6** may be attributable to both the inductive electron-donating effect of the methyl group in *para* position on the central ring and to the same effect of isopropyl groups on the flanking aryls. The angles C(1)–C(2)–C(8) in **5** and C(1)–C(2)–C(6) in **6** are 121.9(3)° and 122.55(2)°, being comparable to the angle in a similar terphenyl iodide species having the same structure as **5**, only lacking the *para* methyl on the central phenyl [28]. The angles C(2)–C(1)–I(1) in **5** and **6** are 118.7(3)° and 118.79(1)°, being also similar to other known angles in similar molecules [27].

The molecule **4** results from a head-to-tail dimerization reaction, probably via the mechanism shown in Scheme 2. Steric effects play a key role in the regiospecificity of the reaction and a 'face-to-face' dimerization is strongly disfavored by the steric pressure of the flanking aryl rings and their substituents. A thermal ellipsoid plot of the molecule is presented in Fig. 3. Selected bond distances and bond angles in molecule **4** are presented in Table 2. The two C–C bond distances that connect the central, benzylic carbon C(1) to the two rings are 1.515(3) Å to C(2) of an aryl ring and 1.551(3) Å to the aliphatic C(32). The slightly longer distance to the latter is due to its four coordinate nature and sp^3 character. The distances are well within the normal range for such compounds based on a study by Barnes and co-workers [29] of the structures of nine diphenylmethane molecules with various substituents who found that the C(aryl)–CH$_2$ distances spanned the range 1.497–1.60 Å. The C(2)C(1)C(32) angle in **4** is 115.58(2)°. This value is considerably wider than the normal tetrahedral value but it also falls in the known range 112.5°–119.2° for diphenylmethane derivatives mentioned above

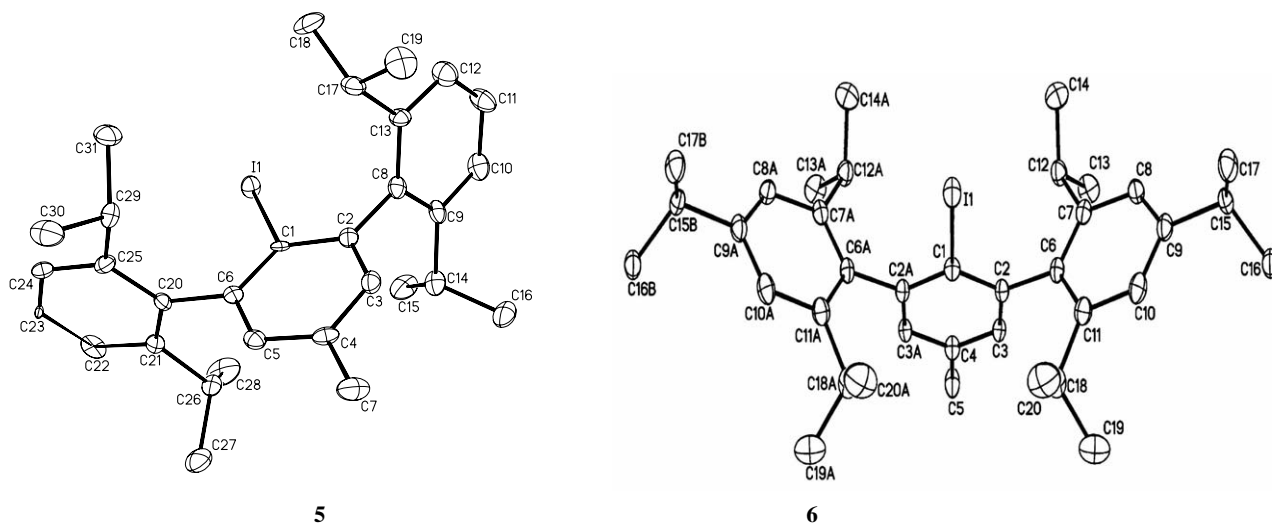**5**　　　　　　　　　　　　　　　　　　**6**

Fig. 2. Thermal ellipsoid plots for molecules **5** and **6**. Hydrogen atoms are not shown.

Table 1
Selected bond distances (Å) and angles (°) for **2**, **5** and **6**

Compound 2			
Br(1)–C(2)	1.975(3)	Br(1)–C(2)–C(3)	113.1(2)
C(2)–C(3)	1.500(4)	C(2)–C(3)–C(4)	119.9(2)
C(3)–C(4)	1.405(4)	C(2)–C(3)–C(8)	119.9(2)
C(3)–C(8)	1.407(4)	C(4)–C(3)–C(8)	120.1(2)
C(4)–C(5)	1.383(4)	C(3)–C(4)–C(9)	121.5(2)
Compound 5			
I(1)–C(1)	2.111(4)	C(2)–C(1)–I(1)	118.7(3)
C(1)–C(2)	1.414(5)	C(6)–C(1)–I(1)	119.5(3)
C(1)–C(6)	1.394(5)	C(1)–C(2)–C(8)	121.9(3)
C(2)–C(8)	1.496(5)	C(1)–C(6)–C(20)	121.3(3)
C(4)–C(7)	1.497(6)	C(3)–C(4)–C(7)	121.4(4)
Compound 6			
I(1)–C(1)	2.115(3)	C(2)–C(1)–I(1)	118.79(12)
C(1)–C(2)	1.398(2)	C(2A)–C(1)–I(1)	118.79(12)
C(1)–C(2A)	1.398(2)	C(2)–C(1)–C(2A)	122.3(2)
C(2)–C(6)	1.497(2)	C(1)–C(2)–C(6)	122.45(18)
C(4)–C(5)	1.515(4)	C(3)–C(4)–C(5)	121.19(12)

Table 2
Selected bond distances (Å) and angles (°) for compound **4**

| C(1)–C(2)	1.515(3)	C(34)–C(39)	1.500(3)
C(1)–C(32)	1.551(2)	C(36)–C(51)	1.499(3)
C(2)–C(3)	1.412(3)	C(35)–C(38)	1.346(3)
C(3)–C(4)	1.398(3)	C(2)–C(1)–C(32)	115.58(16)
C(4)–C(5)	1.382(3)	C(3)–C(2)–C(1)	121.15(17)
C(3)–C(8)	1.507(3)	C(7)–C(2)–C(1)	119.85(17)
C(7)–C(20)	1.509(3)	C(33)–C(32)–C(1)	112.99(15)
C(32)–C(33)	1.486(3)	C(37)–C(32)–C(1)	110.36(15)
C(32)–C(37)	1.501(3)	C(33)–C(34)–C(39)	121.75(17)
C(33)–C(34)	1.337(3)	C(35)–C(36)–C(51)	118.89(16)
C(34)–C(35)	1.483(3)	C(38)–C(35)–C(36)	121.70(18)
C(35)–C(36)	1.472(3)	C(38)–C(35)–C(34)	122.01(18)
C(36)–C(37)	1.330(3)	C(33)–C(32)–C(37)	111.81(16)
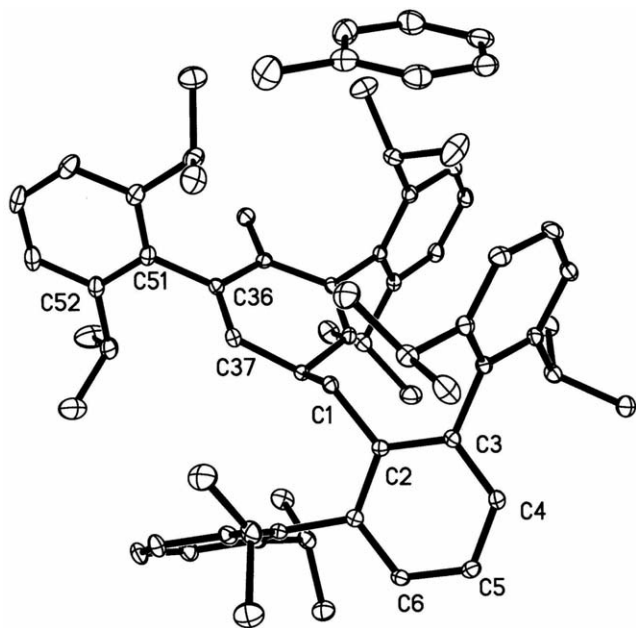
Fig. 3. Thermal ellipsoid plot (30%) of molecule **4**. H atoms are not shown.

[29]. Other structural parameters of **4** are also significant. The pyramidal coordination of C(32), where the sum of the inter-carbon bond angles is 335.2(2)°, implies the presence of a hydrogen attached to this carbon. The C–C distances in the C(32)–C(37) ring are also informative. The C(33)–C(34) and C(36)–C(37) bond lengths are 1.337(3) and 1.330(3) Å consistent with C–C double bonding, whereas the remaining four C–C distances within this ring are close to 1.49 Å which is consistent with single bonding between two sp² hybridized carbons. Most significantly perhaps, the C(35)–C(38) bond length is 1.346(3) Å consistent with a double bond between C(38) and the ring. In the ¹H NMR spectrum, the benzylic CH₂ group (C1) connecting the two terphenyl Ar′ and pseudoterphenyl

"Ar′ = CH₂" moieties appears as a doublet at 2.53 ppm, and is close to the value reported for toluene (2.51 ppm) [30] or 2.74 ppm in ethylbenzene [31]. The *exo*-methylene group (or C38) on pseudoterphenyl moiety was observed at 4.86 ppm, which is typical for unsubstituted alkene carbons [32]. For comparison, in the case of isobutylene the protons in the methylene group resonate at 4.73 ppm. In the ¹³C NMR, carbon C1 appears at 37.15 ppm, while C38 was observed at 112.56 ppm. This is in good agreement with chemical shifts of other *exo*-methylene groups, which are expected to resonate at higher field than ethylene, such as 107.7 and 113.3 ppm for isobutylene and 1-butene, respectively [33]. For C32 the signal appears at 40.07 ppm, which is a normal shift for a saturated allyl carbon [31].

Molecule **3**, which can be described as a terphenylmethyl formate, could not be crystallized well and it was only characterized by ¹H and ¹³C NMR spectroscopy. It displayed signals at the expected values for a formate derivative. Thus, the HCOO proton appeared as a singlet at 7.54 ppm, which slightly upfield from the corresponding proton in methyl formate, which resonates at 8.05 ppm [34]. The benzylic CH₂ group was observed as a singlet at 4.58 ppm, which is about 0.56 ppm downfield from the corresponding protons in terphenylmethyl bromide **2**. This is probably due to the stronger electron-withdrawing effect of the adjacent carboxyl group in comparison to bromine, which results in the downfield shift of the methylenic protons. In the ¹³C NMR spectrum the signal of CH₂ group appeared at 61.5 ppm, while that of HCOO group is at about 160 ppm. The latter value is similar to the carboxylic group in methyl formate which resonates at 160.9 ppm [34]. In the case of the two terphenyl lithium derivatives **7** and **8**, proton and carbon NMR spectra were recorded since, despite several attempts, X-ray quality crystals could not be isolated for structural analysis. In both cases, the NMR spectra displayed proton and carbon signals in the expected regions [35] and no particular characteristics were observed. The slight differences noted in chemical shifts of **7** and **8** when compared to the parent terphenyl iodides **5** and **6**, respectively, follow the same trend observed in other related examples of terphenyl iodides [27].

3. Conclusion

In the present paper, the synthesis and characterization of eight new terphenyl derivatives was presented. A possible reaction mechanism was proposed for the formation of an unusual head-to-tail dimer upon the attempted preparation of a terphenyl benzyl species. Two new terphenyl iodides were synthesized also, along with their corresponding lithium derivatives. The application of the newly synthesized molecules in the generation of new main-group and transition element multiply bonded species will be described in a future publication.

4. Experimental

All manipulations involving air and/or moisture sensitive compounds were carried out by using modified Schlenk techniques under an atmosphere of Ar or N_2. All solvents were distilled from molten Na/K alloy and degassed twice prior to use. Paraformaldehyde (Acros Organics, reagent 96%) was dried under reduced pressure for 2 h and used immediately in the reaction without further purification. Hydrobromic acid as well as formic acid were purchased from Acros Organics as ACS reagents of 48% and, respectively, 96% solutions. The bromide 2,4,6-triisopropyl bromobenzene used in the synthesis of **7** was purchased from Aldrich Chemicals. They were used in as received. The lithium compound Ar′Li was prepared as described previously [36]. The precursor used in the synthesis of terphenyl iodides **5** and **6**, 2,6-dibromo-4-methyl-iodobenzene, was obtained by following a reaction protocol originally described by Hart and co-workers [37] and detailed by Protasiewicz and co-workers [20]. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian 300 or 400 MHz spectrometer and referenced to known standards. Melting points were recorded in glass capillaries under N_2 and are uncorrected. The infrared spectrum for **1** was recorded as Nujol mull between CsI plates on a Perkin–Elmer 1430 spectrometer.

Selected crystallographic data for compounds **2**, **5** and **6** are presented in Table 3 below. The corresponding parameters for molecule **4** are shown in Table 4.

Following a procedure similar to the one previously described [20], we obtained 2,6-dibromo-4-methyl-iodobenzene as a white solid, melting point m.p. = 52–54 °C, after recrystallization from hexane. We report the molecule's ^{13}C NMR spectrum which had not been published previously. The ^{1}H NMR spectrum is in agreement with that previously reported [20]. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 2.25 (s, 3H, CH$_3$), 7.38 (s, 2H, *m*-Ph) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$, 25 °C): δ = 20.59 (CH$_3$), 105.02 (C–I), 130.88 (C–Br), 132.08 (C–H), 141.17 (C–Me) ppm.

4.1. 1-OHCH₂-2,6(C₆H₃-2′,6′-Pr$_2^i$)₂-C₆H₃ (1)

To a stirred and cooled (0 °C) solution of Ar′Li (2.2 g, ca. 5 mmol) in 80 mL THF, gaseous formaldehyde, gener-

Table 3
Selected crystallographic data for **2**, **5** and **6**

Compound	2	5	6
Formula	C$_{31}$H$_{37}$Br	C$_{31}$H$_{39}$I	C$_{37}$H$_{51}$I
Formula weight	491.54	538.52	622.68
Crystal color and habit	Colorless wedge	Needle, pale yellow	Colorless block
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$Pnma$
a (Å)	8.0458(8)	11.800(2)	8.0175(6)
b (Å)	21.227(2)	18.297(3)	25.5621(2)
c (Å)	15.9281(2)	12.696(2)	16.1975(1)
$α$ (°)	90	90	90
$β$ (°)	97.350(2)	98.604(3)	90
$γ$ (°)	90	90	90
V (Å)	2698.0(5)	2710.1(8)	3319.6(4)
Z	4	4	4
Crystal size (mm)	0.28 × 0.20 × 0.15	0.53 × 0.08 × 0.07	0.46 × 0.27 × 0.13
D_{calc} (g cm^{-3})	1.220	1.320	1.246
Absorption coefficient, $μ$ (mm^{-1})	1.540	1.197	0.987
No. of independent reflections	7142	4506	4942
No. of observed reflections	3924	3534	3923
R, observed reflections	0.1018	0.0568	0.0541
wR_2, all data	0.1511	0.1127	0.0846

Table 4
Selected crystallographic data for molecule **4**

Formula	C$_{69}$H$_{87}$
Formula weight	916.39
Crystal color and habit	Colorless block
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	13.676(2)
b (Å)	14.446(3)
c (Å)	15.043(3)
$α$ (°)	95.080(3)
$β$ (°)	104.269(4)
$γ$ (°)	94.577(4)
V (Å^3)	2853.1(8)
Z	2
Crystal size (mm)	0.21 × 0.18 × 0.15
D_{calc} (g cm^{-3})	1.067
Absorption coefficient, $μ$ (mm^{-1})	0.059
No. of independent reflections	13010
No. of observed reflections	6948
R, observed reflections	0.1125
wR_2, all data	0.1512

ated by heating 1.6 g of dried paraformaldehyde on an oil bath at 170–180 °C, was bubbled by means of a wide (8 mm) bent glass tube, under a slow stream of argon. The addition was complete in about 10 min and the reaction mixture was allowed to react for an additional 2 h, after which time it was quenched with a 10% HCl solution. Extraction with 2 × 50 mL diethyl ether followed by washing of the combined ethereal layers with brine, drying over

MgSO$_4$, filtration and evaporation of solvent afforded 2.1 g of a white powder. Recrystallization from hexane gave 1.93 g (ca. 4.5 mmol, yield 90%) product: m.p. = 199–203 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 0.92 (t, $^3J_{\text{H–H}}$ = 6.8 Hz, 1H, OH), 1.10 (d, $^3J_{\text{H–H}}$ = 6.4 Hz, 12H, o-CH(CH_3)$_2$), 1.13 (d, $^3J_{\text{H–H}}$ = 6.8 Hz, 12H, o'-CH(CH_3)$_2$), 2.60 (sept., $^3J_{\text{H–H}}$ = 6.8 Hz, 4H, o-CH(CH$_3$)$_2$), 4.07 (d, $^3J_{\text{H–H}}$ = 6.8 Hz, 2H, CH$_2$), 7.14 (d, $^3J_{\text{H–H}}$ = 7.2 Hz, 2H, m-C$_6$H$_3$), 7.23 (d, $^3J_{\text{H–H}}$ = 8 Hz, 4H, m-C$_6$H$_3'$), 7.37 (m, 3H, p-C$_6$H$_3$ + p-C$_6$H$_3'$) ppm. ^{13}C NMR (100.25 MHz, CDCl$_3$, 25 °C): δ = 23.04 (o-CH(CH_3)$_2$), 25.33 (o-CH(CH_3)$_2$), 30.81 (o-CH(CH$_3$)$_2$), 60.81 (CH$_2$–OH), 122.60 (p-C$_6$H$_3$), 123.02 (m-C$_6$H$_3'$), 127.23 (i-C$_6$H$_3'$), 128.40 (p-C$_6$H$_3'$), 129.41 (m-C$_6$H$_3$), 137.51 (o-C$_6$H$_3$), 140.51 (i-C$_6$H$_3$), 146.93 (o-C$_6$H$_3'$) ppm. IR (Nujol): v = 3560 cm^{-1} (v_{OH}, sharp).

4.2. 1-Br-CH$_2$-2,6(C$_6$H$_3$-2′,6′-Pr$_2^i$)$_2$-C$_6$H$_3$ (2)

The alcohol 1 (2.1 g, ca. 5 mmol) was placed in a 100 mL round-bottom flask provided with a reflux condenser and a magnetic stir bar. Then, 30 mL of concentrated HBr solution was added and the reaction mixture was heated to a gentle reflux for 3 h. After cooling the solution in an ice-bath, a white precipitate appeared. The supernatant liquid was carefully decanted off, the white solid was washed with 3 × 10 mL cold water and dried under reduced pressure. After crystallization from diethyl ether in a −20 °C freezer, 2.36 g (ca. 4.8 mmol, yield 96%) of 2 were obtained as colorless crystals, suitable for X-ray crystallographic analysis: m.p. = 154–155 °C. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 1.09 (d, $^3J_{\text{H–H}}$ = 6.6 Hz, 12H, CH(CH_3)$_2$), 1.24 (d, $^3J_{\text{H–H}}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 2.57 (sept., $^3J_{\text{H–H}}$ = 6.6 Hz, 4H, CH(CH$_3$)$_2$), 4.02 (s, 2H, CH$_2$), 7.17 (d, $^3J_{\text{H–H}}$ = 7.5 Hz, 2H, m-C$_6$H$_3$), 7.26 (d, $^3J_{\text{H–H}}$ = 7.5 Hz, 4H, m-C$_6$H$_3'$), 7.38 (t, $^3J_{\text{H–H}}$ = 7.8 Hz, 1H, p-C$_6$H$_3$), 7.40 (t, $^3J_{\text{H–H}}$ = 8.1 Hz, 2H, p-C$_6$H$_3$) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$, 25 °C): δ = 23.03 (CH(CH_3)$_2$), 25.86 (CH(CH_3)$_2$), 29.58 (CH$_2$), 30.75 (CH(CH_3)$_2$), 123.05 (m-C$_6$H$_3'$), 127.77 (p-C$_6$H$_3$), 128.56 (p-C$_6$H$_3'$), 130.12 (m-C$_6$H$_3$), 133.67 (o-C$_6$H$_3$), 136.74 (i-C$_6$H$_3'$), 141.25 (i-C$_6$H$_3$), 146.88 (o − C$_6$H$_3'$) ppm.

4.3. 1-HC(O)O-CH$_2$-2,6(C$_6$H$_3$-2′,6′-Pr$_2^i$)$_2$-C$_6$H$_3$ (3)

The bromide 2 (1.96 g, 4 mmol) was placed in a 50 mL round-bottom flask provided with a magnetic stir bar. Tetrahydrofuran (20 mL) was added to solubilize the halide, followed by the addition of 5 mL 96% formic acid (excess). The reaction mixture was stirred overnight at room temperature. The following day the solution was extracted with THF, washed with 2 × 30 mL portions of deionized water and dried over MgSO$_4$. Filtration, followed by evaporation of the solvent under reduced pressure, afforded 3 as a white powder. Yield: 1.6 g (3.5 mmol, 88%). m.p. = 150–152 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 1.09 (d, $^3J_{\text{H–H}}$ = 6.4 Hz, 12H, CH(CH_3)$_2$), 1.14 (d, $^3J_{\text{H–H}}$ = 6.4 Hz, 12H,

CH(CH_3)$_2$), 2.57 (sept., $^3J_{\text{H–H}}$ = 6.8 Hz, 4H, CH(CH$_3$)$_2$), 4.58 (s, 2H, CH$_2$), 7.19 (d, $^3J_{\text{H–H}}$ = 7.6 Hz, 2H, m-C$_6$H$_3$), 7.20 (d, $^3J_{\text{H–H}}$ = 7.6 Hz, 4H, m-C$_6$H$_3'$), 7.35 (t, $^3J_{\text{H–H}}$ = 7.6 Hz, 2H, p-C$_6$H$_3$), 7.45 (t, $^3J_{\text{H–H}}$ = 7.6 Hz, 1H, p-C$_6$H$_3$), 7.54 (s, 1H, HCOO) ppm. ^{13}C NMR (100.4 MHz, CDCl$_3$, 25 °C): δ = 23.02 (CH(CH_3)$_2$), 25.40 (CH(CH_3)$_2$), 30.78 (CH(CH_3)$_2$), 61.51 (CH$_2$), 122.82 (m-C$_6$H$_3'$), 128.36 (p-C$_6$H$_3'$), 128.46 (m-C$_6$H$_3$), 129.53 (p-C$_6$H$_3$), 131.22 (o-C$_6$H$_3$), 136.82 (i-C$_6$H$_3'$), 142.17 (i-C$_6$H$_3$), 146.69 (o-C$_6$H$_3'$), 159.93 (HCOO) ppm.

4.4. 2,6-(2′,6′-Pr$_2^i$C$_6$H$_3$)$_2$-4[2,6-(2‴,6‴-Pr$_2^i$C$_6$H$_3$)$_2$-C$_6$H$_3$-1-CH$_2$]-1-methylene-cyclohexa-2,5-diene (4)

The alcohol 1 (2.1 g, ca. 5 mmol) was placed in 50 mL two-necked round-bottom flask, provided with a reflux condenser and a magnetic stir bar, was changed with the bromide (0.49 g, ca. 1 mmol) dissolved in 20 mL dry and degassed THF, are 0.03 g (1.25 mmol) of magnesium turnings. The resulting solution was heated to reflux for 2 h, while it assumed a pale yellow color and almost all of the metal was consumed. Then, 10 mL methanol was syringed in. The pale yellow color disappeared and the solution became cloudy. It was extracted with 2 × 15 mL diethyl ether, and the combined organic layers were dried over MgSO$_4$ and subsequently filtered. The solvent was evaporated under reduced pressure and a white solid was obtained. Recrystallization from toluene afforded X-ray quality crystals of 4. Yield: 0.22 g (ca. 0.24 mmol, 45%); m.p. = 109–111 °C. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 0.73 (d, $^3J_{\text{H–H}}$ = 6.9 Hz, 6H, CH(CH_3)$_2$ on Ar′), 0.96 (d, $^3J_{\text{H–H}}$ = 6.9 Hz, 6H, CH(CH_3)$_2$ on Ar′), 1.04 (d, $^3J_{\text{H–H}}$ = 7.2 Hz, 24H, CH(CH_3)$_2$), 1.08 (d, $^3J_{\text{H–H}}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 2.53 (d, $^3J_{\text{H–H}}$ = 4.8 Hz, 2H, CH$_2$), 2.59 (sept., $^3J_{\text{H–H}}$ = 6.9 Hz, 6H, CH(CH$_3$)$_2$), 2.72–2.76 (m, 1H, C32-H), 2.83 (sept., $^3J_{\text{H–H}}$ = 6.9 Hz, 2H, CH(CH$_3$)$_2$ on Ar′), 4.86 (s, 2H, =CH$_2$), 7.03 (t, $^3J_{\text{H–H}}$ = 7.5 Hz, 1H, p-Ar′), 7.08 (d, $^3J_{\text{H–H}}$ = 6.9 Hz, 2H, m-Ar′), 7.13 (d, $^3J_{\text{H–H}}$ = 8.4 Hz, 8H, m-Dipp), 7.21 (t, $^3J_{\text{H–H}}$ = 7.8 Hz, 4H, p-Dipp), 7.25 (d, $^4J_{\text{H–H}}$ = 1.8 Hz, 2H, m-Ar′ = CH$_2$) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$, 25 °C): δ = 22.24 (CH(CH_3)$_2$), 23.06 (CH(CH_3)$_2$), 23.51 (CH(CH_3)$_2$), 24.19 (CH(CH_3)$_2$), 24.88 (CH(CH_3)$_2$), 24.95 (CH(CH_3)$_2$), 25.01 (CH(CH_3)$_2$), 26.18 (CH(CH_3)$_2$), 30.31 (CH(CH_3)$_2$), 30.39 (CH(CH_3)$_2$), 30.63 (CH(CH_3)$_2$), 30.87 (CH(CH_3)$_2$), 37.15 (CH$_2$), 40.07 (C32), 112.57 (=CH$_2$), 122.25 (m-Dipp (Ar′)), 122.43 (m-Dipp (Ar′ = CH$_2$)), 122.86 (p-Ph (Ar′)), 123.39 (m-Ph (Ar′ = CH$_2$)), 125.51 (o-Ph (Ar′)), 127.31 (p-Dipp (Ar′)), 128.30 (p-Dipp (Ar′ = CH$_2$)), 130.37 (m-Ph (Ar′)), 132.06 (i-Ph (Ar′)), 134.97 (o-Ph (Ar′ = CH$_2$)), 137.11 (i-Dipp (Ar′)), 138.36 (i-Dipp (Ar′ = CH$_2$)), 140.43 (i-Ph (Ar′ = CH$_2$)), 146.94 (o-Dipp (Ar′ = CH$_2$)), 147.12 (o-Dipp (Ar′)) ppm.

4.5. 1-I-2,6(C$_6$H$_3$-2′,6′-Pr$_2^i$)$_2$-4-CH$_3$-C$_6$H$_2$ (5)

Following the known [38] general synthetic protocols, 0.1 mol 2,6-dibromo-4 methyliodobenzene was dissolved in

ca. 400 mL THF, cooled to −78 °C and treated with 0.11 mol Bu^{n}Li. The solution became light brown and, after stirring at this temperature for an additional 20 min, a freshly prepared Grignard solution of 2,6-diisopropyl bromobenzene (0.25 mol, excess), was added slowly, via cannula. After the addition was complete, the reaction mixture was allowed to reach room temperature overnight. Next day it was refluxed for 2 h, cooled in an ice-bath, then iodine (0.15 mol, excess) was added in small portions and the solution stirred for 6 h. The excess iodine was quenched with a 10% solution of Na$_2$SO$_3$, the organic layer separated, dried over anhydrous MgSO$_4$. The solvent was pumped off and the solid residue was refluxed in ethanol overnight. The precipitate that had formed was filtered off, washed with cold methanol and dried. Crystallization from diethyl ether afforded crystals suitable for X-ray crystallographic analysis. Yield: 0.065 mol, 65%: m.p. = 188–190 °C. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ = 1.12 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, o-CH(CH_3)$_2$), 1.24 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, o-CH (CH_3)$_2$), 2.38 (s, 3H, p-CH$_3$), 2.57 (sept., $^3J_{H-H}$ = 6.9 Hz, 4H, CH(CH$_3$)$_2$), 7.00 (s, 2H, m-C$_6$H$_2$), 7.24 (d, $^3J_{H-H}$ = 7.8 Hz, 4H, m-C$_6$H$'_3$), 7.42 (t, $^3J_{H-H}$ = 8.1 Hz, 2H, p-C$_6$H$'_3$) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$, 25 °C): δ = 21.27 (p-CH$_3$), 23.45 (o-CH(CH$_3$)$_2$), 25.06 (o-CH(CH$_3$)$_2$), 30.94 (o-CH(CH$_3$)$_2$), 106.15 (i-C$_6$H$_2$), 122.92 (m-C$_6$H$'_3$), 128.41 (m-C$_6$H$_2$), 129.14 (p-C$_6$H$'_3$), 137.38 (p-C$_6$H$_2$), 142.79 (i-C$_6$H$'_3$), 146.20 (o-C$_6$H$'_3$), 146.27 (o-C$_6$H$_2$) ppm.

4.6. 1-I-2,6(C_6H_2-2′,4′,6′-Pr^i_3)$_2$-4-CH$_3$-C$_6$H$_2$ (6)

In a similar procedure as the one used for the synthesis of **5**, except that the Grignard reagent was generated from the reaction of Mg and TripBr, the terphenyliodide (**7**) was obtained as a white powder. Starting with 22.4 g (ca. 60 mmol) of the precursor 2,6-dibromo-4-methyliodobenzene, 13.7 g (22 mmol, 36.7%) **7** was obtained. After recrystallization from diethyl ether, X-ray quality crystals were obtained: m.p. = 201–203 °C. ^{1}H NMR (300 MHz, CDCl$_3$, 25°): δ = 1.11 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, o-CH(CH_3)$_2$), 1.23 (d, $^3J_{H-H}$ = 7.5 Hz, 12H, o-CH(CH_3)$_2$), 1.32 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, p-CH(CH_3)$_2$), 2.35 (s, 3H, p-CH$_3$), 2.56 (sept., $^3J_{H-H}$ = 6.9 Hz, 4H, o-CH(CH$_3$)$_2$), 2.97 (sept., $^3J_{H-H}$ = 6.9 Hz, 2H, p-CH(CH$_3$)$_2$), 6.99 (s, 2H, m-C$_6$H$_2$), 7.06 (s, 4H, m-C$_6$H$'_2$) ppm. ^{13}C NMR (75.4 MHz, CDCl$_3$, 25°): δ = 21.20 (p-CH$_3$), 23.55 (o-CH(CH$_3$)$_2$), 24.24 (o-CH(CH$_3$)$_2$), 25.09 (p-CH(CH$_3$)$_2$), 30.93 (o-CH(CH$_3$)$_2$), 34.33 (p-CH(CH$_3$)$_2$), 107.0 (i-C$_6$H$_2$), 120.82 (m-C$_6$H$'_2$), 129.28 (m-C$_6$H$_2$), 137.05 (p-C$_6$H$_2$), 140.46 (i-C$_6$H$'_2$), 145.72 (o-C$_6$H$'_2$), 146.50 (o-C$_6$H$_2$), 148.39 (p-C$_6$H$'_2$) ppm.

4.7. 1-Li-2,6(C_6H_3-2′,6′-Pr^i_2)$_2$-4-CH$_3$-C$_6$H$_2$ (7)

To a suspension of 2.7 g (5 mmol) **5** in 50 mL hexane, 3.2 mL of a 1.6 M solution of Bu^{n}Li in hexane was added by syringe, at 0 °C. The reaction mixture was then stirred at room temperature for 6 h, allowed to settle and the supernatant solution was decanted off. The white precipi-

tate was washed once with ca. 30 mL cold hexane and dried under reduced pressure. Yield: 1.97 g (4.8 mmol, 96%): m.p. = 168–169 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ = 1.07 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, o-CH(CH_3)$_2$), 1.09 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, o-CH(CH_3)$_2$), 1.95 (s, 3H, p-CH$_3$), 2.75 (sept., $^3J_{H-H}$ = 6.9 Hz, 4H, o-CH(CH$_3$)$_2$), 6.88 (s, 2H, m-C$_6$H$_2$), 7.17 (d, $^3J_{H-H}$ = 7.8 Hz, 4H, m-C$_6$H$_3$), 7.31 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, p-C$_6$H$'_3$) ppm. ^{13}C NMR (75.4 MHz, C$_6$D$_6$, 25 °C): δ = 20.85 (p-CH$_3$), 23.77 (o-CH(CH$_3$)$_2$), 25.11 (o-CH(CH$_3$)$_2$), 31.32 (o-CH(CH$_3$)$_2$), 123.31 (m-C$_6$H$_3$), 128.96 (m-C$_6$H$_2$), 129.47 (p-C$_6$H$_3$), 137.63 (p-C$_6$H$_2$), 143.02 (i-C$_6$H$'_3$), 146.22 (o-C$_6$H$'_3$), 147.12 (o-C$_6$H$_2$) ppm.

4.8. 1-Li-2,6(C_6H_2-2′,4′,6′-Pr^i_3)$_2$-4-CH$_3$-C$_6$H$_2$ (8)

To a suspension of 6.2 g (10 mmol) **7** in 120 mL hexane, 4.1 mL of a 2.5 M Bu^{n}Li solution in heptane was added dropwise, at 0 °C, via syringe. The reaction mixture was stirred at room temperature overnight. The supernatant solution was decanted off via cannula and the remaining solid was washed once with ca. 40 mL cold hexane. After decanting off the liquid, the white powder was dried under reduced pressure. Yield: 4.2 g (8.3 mmol, 83%): m.p. = 186–188 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, 25°): δ = 1.14 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, o-CH(CH_3)$_2$), 1.24 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, o-CH(CH_3)$_2$), 1.41 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, p-CH(CH_3)$_2$), 1.96 (s, 3H, p-CH$_3$), 2.82 (sept., $^3J_{H-H}$ = 6.9 Hz, 6H, o-CH(CH$_3$)$_2$ + p-CH(CH$_3$)$_2$), 6.90 (s, 2H, m-C$_6$H$_2$), 7.20 (s, 4H, m-C$_6$H$_2$) ppm. ^{13}C NMR (75.4 MHz, C$_6$D$_6$, 25°): δ = 20.68 (p-CH$_3$), 23.74 (o-CH(CH$_3$)$_2$), 24.27 (o-CH(CH$_3$)$_2$), 25.05 (p-CH(CH$_3$)$_2$), 31.25 (o-CH(CH$_3$)$_2$), 34.71 (p-CH(CH$_3$)$_2$), 121.0 (m-C$_6$H$'_2$), 129.47 (m-C$_6$H$_2$), 137.35 (p-C$_6$H$_2$), 140.86 (i-C$_6$H$'_2$), 146.0 (o-C$_6$H$'_2$), 147.14 (o-C$_6$H$_2$), 148.85 (p-C$_6$H$'_2$) ppm.

5. X-ray crystallographic studies

In all cases, a colorless crystal was selected and mounted on a Bruker Smart 1000 CCD system at 90 K. The initial unit cells were indexed by using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω-scans, 10 s/frame, and 25 frames/series that were well-distributed in reciprocal space. Mo Kα (λ = 0.71073 Å) radiation was used. Absorption corrections were applied using SADABS [39,40]. All crystallographic calculations were performed on a Personal computer (PC) provided with SHELXTL [41] program. The structures were determined by direct methods or by using the Patterson option in SHELXS [42] and were refined with SHELXL [42]. 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 presented in Tables 3 and 4 above, but further details can be found in the supporting information.

6. Supplementary information

CIF files for **1** and **3** may be obtained from the Cambridge Crystallographic Data Centre as supplementary publications CCDC 292610–292613 upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgement

References

[1] B.E. Eichler, P.P. Power, J. Am. Chem. Soc. 122 (36) (2000) 8785–8786.

[2] A.F. Richards, B.E. Eichler, M. Brynda, M.M. Olmstead, P.P. Power, Angew. Chem. Int. Ed. 44 (17) (2005) 2546–2549.

[3] A.F. Richards, M. Brynda, M.M. Olmstead, P.P. Power, Organometallics 23 (12) (2004) 2841–2844.

[4] R.J. Wright, A.D. Phillips, S. Hino, P.P. Power, J. Am. Chem. Soc. 127 (13) (2005) 4794–4799.

[5] A.F. Richards, H. Hope, P.P. Power, Angew. Chem., Int. Ed. 42 (34) (2003) 4071–4074.

[6] B.E. Eichler, P.P. Power, Angew. Chem., Int. Ed. 40 (4) (2001) 796–797.

[7] B.E. Eichler, N.J. Hardman, P.P. Power, Angew. Chem., Int. Ed. 39 (2) (2000) 383–385.

[8] M. Stender, A.D. Phillips, R.J. Wright, P.P. Power, Angew. Chem., Int. Ed. 41 (2002) 1785–1787.

[9] A.D. Phillips, R.J. Wright, M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 124 (2002) 5930–5931.

[10] L. Pu, B. Twamley, P.P. Power, J. Am. Chem. Soc. 122 (2000) 3524–3525.

[11] R.S. Simons, P.P. Power, J. Am. Chem. Soc. 118 (1996) 11966–11967.

[12] L. Pu, B. Twamley, S.T. Haubrich, M.M. Olmstead, B.V. Mork, R.S. Simons, P.P. Power, J. Am. Chem. Soc. 122 (2000) 650–656.

[13] P.P. Power, Chem. Rev. 103 (3) (2003) 789–809.

[14] C. Cui, M. Brynda, M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 126 (21) (2004) 6510–6511.

[15] M.M. Olmstead, L. Pu, R.S. Simons, P.P. Power, Chem. Commun. (1997) 1595–1596.

[16] M.M. Olmstead, R.S. Simons, P.P. Power, J. Am. Chem. Soc. 119 (1997) 11705–11706.

[17] C. Stanciu, M.M. Olmstead, A.D. Phillips, M. Stender, P.P. Power, Eur. J. Inorg. Chem. (2003) 3495–3500.

[18] T. Nguyen, A. Panda, M.M. Olmstead, Anne F. Richards, M. Stender, M. Brynda, P.P. Power, J. Am. Chem. Soc. 127 (2005) 8545–8552.

[19] E. Urnezius, J.D. Protasiewicz, Main Group Chemistry 1 (4) (1996) 369–372.

[20] S. Shah, S.C. Burdette, S. Swavey, Fred L. Urbach, J.D. Protasiewicz, Organometallics 16 (1997) 3395–3400.

[21] M. Schmid, R. Eberhardt, M. Klinga, M. Leskela, B. Rieger, Organometallics 20 (2001) 2321–2330.

[22] R.J. Wright, P.P. Power, unpublished results.

[23] (a) J.B. Lambert, H.F. Shurvell, D.A. Lightner, R.G. Cooks, Organic Structural Spectroscopy, Simon & Schuster, Prentice-Hall, Inc., 1998, p. 46;
(b) J.B. Lambert, H.F. Shurvell, D.A. Lightner, R.G. Cooks, Organic Structural Spectroscopy, Simon & Schuster, Prentice-Hall, Inc., 1998, p. 204.

[24] J. Trotter, in: S. Patai (Ed.), The Chemistry of the Carbon–Halogen Bond, Wiley, New York, 1973, pp. 49–62 (Part I).

[25] S.J. Obrey, S.G. Bott, A.R. Barron, J. Chem. Cryst. 32 (17) (2002) 205–207.

[26] J.-B. Robert, J.S. Sherfinski, R.E. Marsh, J.D. Roberts, J. Org. Chem. 39 (8) (1974) 1152–1156.

[27] C. Stanciu, A.F. Richards, J.C. Fettinger, M. Brynda, P.P. Power, J. Organomet. Chem. 2006, in press.

[28] A.D. Phillips, P.P. Power, unpublished results.

[29] J.C. Barnes, J.D. Paton, J.R. Damewood Jr., K. Mislow, J. Org. Chem. 46 (24) (1981) 4975–4979.

[30] J.B. Lambert, H.F. Shurvell, D.A. Lightner, R.G. Cooks, Organic Structural Spectroscopy, Simon & Schuster, Prentice-Hall, Inc., 1998, p. 55.

[31] Sadtler Standard NMR Spectra, Sadtler Research Laboratories, Inc., 3314 Spring Garden Street, Philadelphia, PA, 19104.

[32] J.B. Lambert, H.F. Shurvell, D.A. Lightner, R.G. Cooks, Organic Structural Spectroscopy, Simon & Schuster, Prentice-Hall, Inc., 1998, p. 43.

[33] J.B. Lambert, H.F. Shurvell, D.A. Lightner, R.G. Cooks, Organic Structural Spectroscopy, Simon & Schuster, Prentice-Hall, Inc., 1998, p. 53.

[34] J.B. Lambert, H.F. Shurvell, D.A. Lightner, R.G. Cooks, Organic Structural Spectroscopy, Simon & Schuster, Prentice-Hall, Inc., 1998, p. 57.

[35] B. Schiemenz, P.P. Power, Organometallics 15 (1996) 958–964.

[36] B. Schiemenz, P.P. Power, Angew. Chem., Int. Ed. 35 (1996) 2150.

[37] C.J.F. Du, H. Hart, K.-K.D. Ng, J. Org. Chem. 51 (1986) 3162–3165.

[38] (a) A. Saednya, H. Hart, Synthesis. 12 (1996) 1455–1458;
(b) M. Niemeyer, S.T. Haubrich, R.S. Simons, B.V. Mork, P.P. Power, Main Group Chemistry 2 (1998) 275.

[39] An Empirical Correction for Absorption Anisotropy, R.H. Blessing, Acta Cryst. A 51 (1995) 33–38.

[40] G.M. Sheldrick, SADABS, Version 2.10, Siemens Area Detector Absorption Correction, Universität, Göttingen, Göttingen, Germany, 2003.

[41] G.M. Sheldrick, SHELXTL Version 6.1, Bruker AXS Inc., Madison, WI, USA, 2002.

[42] G.M. Sheldrick, SHELXS 97 and SHELXL 97, Universität Göttingen, Göttingen, Germany, 1997.