ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

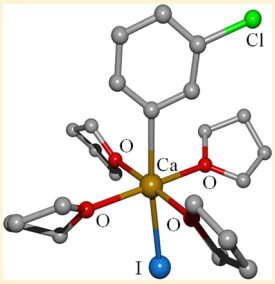
Synthesis and Molecular Structures of Meta-Substituted Arylcalcium Iodides

Mathias Köhler, Jens Langer, Helmar Görls, and Matthias Westerhausen*

Institute of Inorganic and Analytical Chemistry, Friedrich Schiller University Jena, Humboldtstrasse 8, D-07743 Jena, Germany

Supporting Information

ABSTRACT: The reduction of *meta*-methyl-substituted iodobenzene with activated calcium in tetrahydrofuran (THF) yields $[(3\text{-}MeC_6H_4)CaI(thf)_4]$ (**1**) and $[(3,5\text{-}Me_2C_6H_3)CaI(thf)_4]$ (**2**). The reaction of 3-halo-1-iodobenzene with calcium powder leads to the formation of the corresponding post-Grignard reagents $[(3\text{-}XC_6H_4)CaI(thf)_4]$ [X = F (**3**), Cl (**4**), Br (**5**), and I (**6**)]. The synthesis of the thf adducts of 3-methoxyphenylcalcium iodide (**7**) and *β*-naphthylcalcium iodide (**8**) follows the same strategy. All post-Grignard reagents show a characteristic low-field shift for the calcium-bound carbon atoms in ^{13}C NMR spectra. The molecular structures of **1**, **2**, **4**, and **8** show distorted octahedral environments for the calcium centers with the aryl and halide anions in a trans arrangement.



INTRODUCTION

Grignard reagents represent widely used organomagnesium compounds that were introduced into preparative organic and organometallic chemistry more than a century ago.[1−3] Because of the importance of these reagents, Grignard was honored with the Nobel Prize in 1912. Despite the fact that early attempts to prepare arylcalcium halides also date back more than a 100 years,[4] the first structurally characterized arylcalcium complexes consisted of oxygen-centered oligonuclear arylcalcium clusters.[5,6] Nevertheless, this success of isolation of arylcalcium derivatives intensified the efforts to also isolate and characterize arylcalcium halides that can be considered as post-Grignard reagents with mesitylcalcium iodide being the first structurally characterized representative[7] and entering the textbooks shortly thereafter.[8] Knowing the requirements to isolate crystalline arylcalcium complexes, many of such derivatives were prepared and investigated spectroscopically as well as via derivatization reactions. Several recent review articles summarize this vastly growing arylcalcium (post-Grignard) chemistry.[9−12]

The synthesis of arylcalcium complexes succeeds with high yields if iodoarenes are reduced with activated calcium in Lewis basic solvents, such as ethers.[9−12] Amines were also used to stabilize arylcalcium complexes.[13] As also observed for classical Grignard reagents, a Schlenk-type equilibrium converts arylcalcium halides into homoleptic diarylcalcium and calcium dihalides depending mainly on solvent and temperature. Substitution of iodide by an alkoxide shifts this equilibrium quantitatively to the side of the homoleptic complexes.[14] Because of the high reactivity of the arylcalcium complexes, degradation of ethers often was observed,[7,15,16] as is also known for organyllithium[17] and, in minor extent, for Grignard reagents,[18] justifying to consider these organometallics as superbases.[19] On the basis of similar electronegativities of lithium and calcium, a comparable reactivity can be envisioned that should be higher than that of Grignard reagents due to a larger ionic character of the metal−carbon bonds.

Despite the vastly growing knowledge of post-Grignard reagents, the influence of the substitution pattern on reactivity and molecular structures is mainly limited to ortho and para substituents.[12] Ortho-positioned halogen substituents drastically reduce the stability and durability of arylcalcium reagents in solution.[16] Fluoro functionalities in ortho positions require special stabilization strategies in order to avoid formation of intermediate arynes and precipitation of calcium dihalide. Niemeyer and co-workers[20] kinetically shielded the reactive pentafluorophenylcalcium unit by *π*-bonding encapsulation between bulky aryl groups, thus enabling the crystal structure determination of this complex [Ca−C 249.9(11) pm]. Also, methyl groups can be attacked, yielding benzylcalcium derivatives.[7] In addition, *ortho-tert*-butyl groups are also involved in degradation reactions, finally yielding 2,5-dimethyl-2,5-bis[3,5-di(*tert*-butyl)phenyl]hexane.[10−12] In para positions, many more functional groups are tolerated, such as halo,[15,16] dimethylamino,[16] and silyl groups.[21] Astonishingly, *para*-phenyl-substituted arylhalides as substrates did not yield the expected arylcalcium halides,[22,23] whereas derivatives with phenyl groups in ortho positions are easily accessible, probably due to effective steric shielding of the formed Ca−C bond.[23]

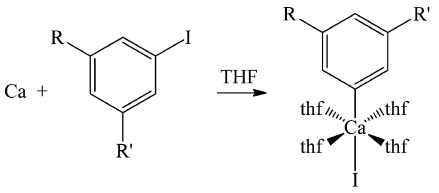
It is likely that both the regioselectivity and the speed of subsequent reactions of these calcium-substituted arenes will be affected by the other substituents already attached to the benzene ring. Since ortho- and para-functionalized derivatives often show similar effects, for instance, in electrophilic aromatic substitution reactions, the accessibility of hitherto unexplored meta-functionalized arylcalcium compounds is highly desirable for comparison reasons. Therefore, we investigated the meta-substituted arylcalcium reagents to fill the knowledge gap with respect to these post-Grignard derivatives.

Received: November 13, 2012
Published: November 30, 2012

dx.doi.org/10.1021/om301087e | *Organometallics* 2012, 31, 8647−8653

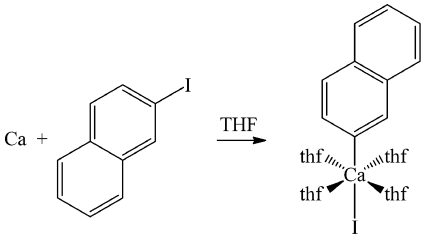
RESULTS AND DISCUSSION

Synthesis. In a general procedure, finely divided calcium powder (prepared via dissolution in liquid ammonia and immediate complete removal of NH_3 in vacuum) was reacted with the respective iodoarene in THF solution at −20 °C. During continuous shaking, the reaction mixture was warmed stepwise to 0 °C and then to ambient temperature. The solid material was removed by filtration, and the filtrate was stored at low temperatures, yielding crystalline arylcalcium iodides according to eq 1. These calcium-based organometallics were



R/R' = H/Me (**1**), Me/Me (**2**), R = H, R' = F (**3**), Cl (**4**), Br (**5**), I (**6**), OMe (**7**) (1)

collected on a cooled frit and dried in vacuo. They could be recrystallized by cooling of a THF solution, saturated at ambient temperature, to −40 °C. A solvent change and the use of tetrahydropyran neither enhanced the yield nor improved the crystallization behavior of these meta-substituted complexes significantly. The thf adduct of *β*-naphthylcalcium iodide, [(*β*-naphthyl)CaI(thf)$_4$] (**8**), was synthesized in a similar manner (eq 2).



8 (2)

The yields of the reduction of meta- and para-substituted arenes are compared in Table 1. The conversion was determined by titration of an aliquot of the reaction solution after removal of all solids (such as excess of calcium). In all cases, the conversion was above 50%, in many cases above 70%. In comparison to the para-substituted congeners, the conversion rates were only slightly lower. Attempts to isolate crystalline material were successful, but the yields were significantly lower. Recrystallization of *meta*-fluoro- and *meta*-chlorophenylcalcium iodides was extremely challenging. The fluoro-substituted post-Grignard reagent was extremely soluble, and also, the chloro-substituted derivative showed poor crystallization behavior. The isolation of literature-known mesitylcalcium iodide was challenging for another reason because the synthesis of this highly soluble post-Grignard reagent is accompanied by ether degradation reactions, thus yielding benzylcalcium derivatives and lowering the yield of isolated crystalline material.[7]

Table 1. Yields (%) of [(3-RC$_6$H$_4$)CaI(thf)$_4$] and [(4-RC$_6$H$_4$)CaI(thf)$_4$] Determined via Titration of an Aliquot of the Solution and Yields (%) of Isolated Crystalline Material Depending on Meta or Para Substitution

	[(*meta*-aryl)CaI(thf)$_4$]		[(*para*-aryl)CaI(thf)$_4$]		
aryl	titrated	crystalline	titrated	crystalline	ref
C_6H_5			93	70	16, 24
Me-C_6H_4	60	44	60	38	16, 24
$Me_2C_6H_3$	81	39	86[a]	12[a]	7
F-C_6H_4	51	4.9	75		16
Cl-C_6H_4	74	3.6	81		16
Br-C_6H_4	67	25.5	60.7[b]	18.3[b]	15
I-C_6H_4	66	27.9	95		16
MeO-C_6H_4	75		89		15

[a]Aryl = 2,4,6-$Me_3C_6H_2$ (mesityl). [b]Solvent: tetrahydropyran (thp). Isolated complex: [(4-BrC$_6$H$_4$)CaI(thp)$_4$].

NMR Investigations. The NMR parameters of the aryl groups of these post-Grignard reagents strongly depend on the meta substituent (Table 2); an assignment is in agreement with the increment method of these substituents and was unambiguous on the basis of 2D NMR experiments. Nevertheless, all arylcalcium organometallics show low-field shifted resonances for the calcium-bound *ipso*-carbon atoms of approximately δ = 190. A similar chemical shift of δ = 189.1 was also detected for *β*-naphthylcalcium iodide in a [D$_8$]THF solution. Another obvious trend pertains to the halogen-bound carbon atoms; due to the heavy atom effect, these carbon atoms show a strong high-field shift with increasing mass of the halogen. Expectedly, the degree of electron-withdrawing nature of the halogen also influences the other resonances, leading to a low-field shift of the other resonances with increasing size of the halogen atom.

Molecular Structures. Despite the fact that these meta-substituted arylcalcium organometallics can be recrystallized and purified, crystal structure determinations failed for most of the derivatives. The thf adduct of *meta*-fluorophenylcalcium iodide (**3**) was extremely soluble in ethereal solvents, and the complex crystallized in flimsy needles that agglomerated, looking like wool. The chlorine-substituted derivative [(3-ClC$_6$H$_4$)CaI(thf)$_4$] (**4**) precipitated as a microcrystalline substance. Nevertheless, we were able to determine the molecular structure at a very tiny crystal. The single crystals of [(3-BrC$_6$H$_4$)CaI(thf)$_4$] (**5**) exhibited extremely poor diffraction properties, and we were unable to obtain a reasonable data set. The data set of crystalline [(3-IC$_6$H$_4$)CaI(thf)$_4$] (**6**) gave no meaningful solution with direct and heavy atom methods. The crystal quality of [(3-MeOC$_6$H$_4$)CaI(thf)$_4$] (**7**) did not allow an X-ray crystal structure determination. In THF solution, this complex forms a tetrakis(thf) adduct, whereas in the solid state, the high calcium content hints toward a tris(thf) complex, probably suggesting that the 3-methoxy group kicks out a thf ligand on an adjacent calcium ion to form a dimer. The ability of methoxy groups to act as a donor ligand in competition to thf was already observed in dinuclear [{2,6-(MeO)$_2$C$_6$H$_3$}$_3$Ca$_2$(thf)$_3$I].[25]

The molecular structures and numbering schemes of *meta*-alkylated 3-methylphenyl- and 3,3′-dimethylphenylcalcium derivatives **1** and **2** are depicted in Figures 1 and 2. The molecular structures of phenyl-,[24] 4-methylphenyl-[24] and 2,4,6-trimethylphenyl- (mesityl) calcium iodide[7] are dominated by the enhanced steric strain, induced by the *ortho*-methyl substituents, and are included in Table 3 for comparison reasons. All of these molecular structures have a hexacoordinate calcium atom in distorted octahedral environments in common. The anionic ligands are trans-arranged due to electrostatic

dx.doi.org/10.1021/om301087e | *Organometallics* 2012, 31, 8647−8653

Table 2. $^{13}C\{^1H\}$ NMR Data of Meta-Substituted Arylcalcium Iodides (Chemical Shifts δ of Exclusively Aryl Carbon Atoms)

compound	C1	C2	C3	C4	C5	C6
$[(3\text{-}MeC_6H_4)CaI(thf)_4]$	189.7	142.1	132.5	123.5	125.0	138.1
$[(3,5\text{-}Me_2C_6H_3)CaI(thf)_4]$	189.7	139.2	132.2	124.6	132.2	139.2
$[(3\text{-}FC_6H_4)CaI(thf)_4]$	195.6	125.9	162.6	108.8	125.3	136.1
$[(3\text{-}ClC_6H_4)CaI(thf)_4]$	194.8	139.8	133.2	122.5	126.7	138.7
$[(3\text{-}BrC_6H_4)CaI(thf)_4]$	196.3	142.6	124.5	125.4	127.5	139.0
$[(3\text{-}IC_6H_4)CaI(thf)_4]$	197.1	149.0	101.0	131.4	128.4	139.0
$[(3\text{-}MeOC_6H_4)CaI(thf)_4]$	191.3	125.0	156.8	106.5	124.4	132.5

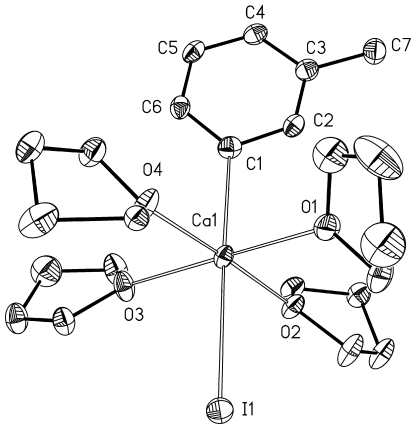


Figure 1. Molecular structure and numbering scheme of $[(3\text{-}MeC_6H_4)CaI(thf)_4]$ (**1**). Ellipsoids represent a probability of 40%, and H atoms are omitted for the sake of clarity. Selected bond lengths (Å): Ca1–C1 2.522(6), Ca1–I1 3.1425(12), Ca1–O1 2.396(4), Ca1–O2 2.382(4), Ca1–O3 2.365(4), Ca1–O4 2.400(5). Angles (deg): C1–Ca1–I1 176.89(15), C1–Ca1–O1 92.45(17), C1–Ca1–O2 90.38(18), C1–Ca1–O3 91.45(17), C1–Ca1–O4 92.43(19), I1–Ca1–O1 88.09(11), I1–Ca1–O2 86.55(10), I1–Ca1–O3 88.27(11), I1–Ca1–O4 90.65(13).

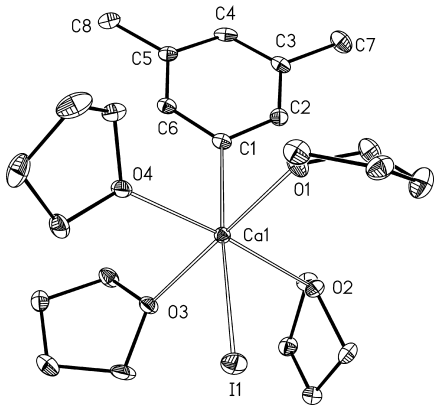


Figure 2. Molecular structure and numbering scheme of $[(3,5\text{-}Me_2C_6H_3)CaI(thf)_4]$ (**2**). Ellipsoids represent a probability of 40%, and H atoms are not drawn. Selected bond lengths (Å): Ca1–C1 2.540(3), Ca1–I1 3.1912(6), Ca1–O1 2.382(2), Ca1–O2 2.4178(19), Ca1–O3 2.3974(19), Ca1–O4 2.351(2). Angles (deg): C1–Ca1–I1 175.28(6), C1–Ca1–O1 89.10(8), C1–Ca1–O2 91.92(8), C1–Ca1–O3 95.71(8), C1–Ca1–O4 92.02(8), I1–Ca1–O1 86.30(5), I1–Ca1–O2 87.40(5), I1–Ca1–O3 88.94(5), I1–Ca1–O4 88.89(5).

reasons. Selected structural data of substituted phenylcalcium iodides are compared in Table 3. Obviously, methyl groups in meta positions do not induce much intramolecular strain, and the Ca–C bonds of **1** and **2** are very short, even shorter than those in the thf adducts of phenylcalcium and *para*-tolylcalcium iodide.[24] The situation is much more complex for the Ca–I distances because the large iodide ion is very soft and highly polarizable. This fact leads to a flat energy surface with respect to the variation of the Ca–I distance. Harvey and Hanusa[27] demonstrated that a difference of 0.15 Å for the Ca–I bond length in $[CaI_2(thf)_4]$ only requires 7.1 kJ mol^{-1}. Because of this flat energy potential, packing effects and intermolecular forces in the crystalline state gain on importance and overcompensate small intramolecular effects. In light of this consideration, the Ca–I bond length difference of 5 pm between **1** and **2** becomes understandable. Intramolecular strain as observed for mesitylcalcium iodide additionally enhances the Ca–I distance.[7]

The *meta*-methyl-functionalized phenyl substituents of **1** and **2** show rather narrow endocyclic C2–C1–C6 bond angles of 114.5(5)° and 113.4(2)°, respectively. These small values result from electrostatic repulsion between the anionic charge (sp^2 hybrid orbital at C1) and the C1–C2/6 bonds and represent a common feature for aryl groups coordinated at very electropositive metals, such as calcium. The Ca1–C1–C2/6 bond angles in $[(3,5\text{-}Me_2C_6H_3)CaI(thf)_4]$ (**2**) are very similar [Ca1–C1–C2 122.15(19)°; Ca1–C1–C6 123.70(19)°], whereas large differences between proximal [Ca1–C1–C2 115.3(4)°] and distal angles [Ca1–C1–C6 130.1(5)°] are observed for $[(3\text{-}MeC_6H_4)CaI(thf)_4]$ (**1**). However, an obvious dependency of these flexible angles on the coligand (thf or thp) or the size and substitution pattern of the aryl group cannot be recognized (Table 3), thus supporting again the influence of packing effects in the solid state.

The molecular structure and numbering scheme of $[(3\text{-}ClC_6H_4)CaI(thf)_4]$ (**4**) is shown in Figure 3. The data set was collected at a very tiny crystal, and therefore, rather large estimated standard deviations limit the discussion of this data. The rather similar size of methyl and chloro substitutents leads to comparable distortions, especially with respect to the proximal and distal Ca1–C1–C2/6 angles (Table 3), despite the fact that the arylcalcium iodides **1** and **4** crystallize in different space groups.

The molecular structure and numbering scheme of the thf adduct of β-naphthylcalcium iodide is depicted in Figure 4. Expectedly, the hexacoordinate calcium center exhibits a similar environment as in meta-substituted phenylcalcium iodides. The Ca–I distance is rather large; nevertheless, Ca–I and Ca–C bond lengths fall in the common range. The rather large β-naphthyl group leads to a slight bending of the C1–Ca1–I1 bond angle [173.08(11)°]. Intramolecular steric repulsion leads to significantly different proximal and distal angles at the *ipso*-carbon atom [Ca1–C1–C10 110.2(3)°, Ca1–C1–C2 136.9(4)°; see also Table 3].

dx.doi.org/10.1021/om301087e | *Organometallics* 2012, 31, 8647–8653

Table 3. Comparison of Selected Structural Parameters of Arylcalcium Iodide of the Type $[(Aryl)CaI(L)_4]$ with Hexacoordinate Calcium Atoms in Distorted Octahedral Environments (Bond Lengths [Å] and Angles [deg])

aryl	L[b]	Ca−C	Ca−I	C_{ipso}−Ca−I	Ca−C_{ipso}−$C_{proximal}$	Ca−C_{ipso}−C_{distal}	C−C_{ipso}−C	ref
Ph	thf	2.574(7)	3.178(3)	177.4(2)	117.5(5)	121.9(5)	120[a]	24
Ph	thp	2.510(6)	3.121(1)	171.8(1)	123.5(4)	124.5(4)	111.6(6)	26
4-MeC_6H_4	thf	2.556(5)	3.173(1)	174.6(1)	118.4(4)	128.4(4)	113.2(5)	24
4-MeC_6H_4	thp	2.647(5)	3.1571(9)	176.4(1)	112.6(3)	129.5(3)	117.6(4)	15
3-MeC_6H_4	thf	2.522(6)	3.143(1)	176.9(2)	115.3(4)	130.1(5)	114.5(5)	this work
3,5-$Me_2C_6H_3$	thf	2.540(3)	3.1912(6)	175.28(6)	122.2(2)	123.7(2)	113.4(2)	this work
2,4,6-$Me_3C_6H_2$	thf	2.574(4)	3.2084(9)	177.4(1)	121.3(3)	124.5(3)	114.2(4)	7
4-$MeOC_6H_4$	thp	2.550(4)	3.1560(8)	176.3(1)	122.3(3)	125.1(3)	112.5(4)	15
4-ClC_6H_4	thp	2.643(9)	3.136(2)	175.0(2)	115.3(6)	126.4(6)	118.3(9)	15
3-ClC_6H_4	thf	2.573(13)	3.158(3)	174.1(3)	115.6(10)	128.7(9)	115.6(12)	this work
4-BrC_6H_4	thp	2.605(9)	3.060(2)	174.5(2)	116.5(6)	129.1(6)	114.3(8)	15
4-IC_6H_4	thp	2.565(4)	3.1512(8)	176.3(1)	117.1(3)	130.0(3)	112.5(4)	15
α-naphthyl	thf	2.552(6)	3.187(1)	177.7(2)	116.7(5)	129.8(5)	113.5(6)	16
β-naphthyl	thf	2.528(5)	3.1932(8)	173.1(1)	110.2(3)	136.9(4)	112.9(5)	this work
β-naphthyl	thp	2.565(4)	3.1512(8)	176.3(1)	117.1(4)	129.0(4)	113.8(5)	15

[a]The phenyl ring was restrained to a regular hexagon with equal C−C bond lengths. [b]Tetrahydrofuran, thf; tetrahydropyran, thp.

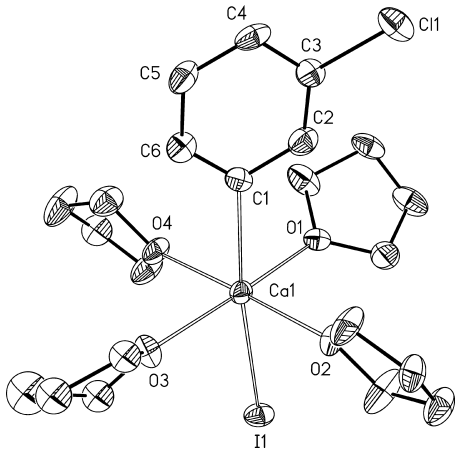


Figure 3. Molecular structure and numbering scheme of $[(3\text{-}ClC_6H_4)CaI(thf)_4]$ (4). Ellipsoids represent a probability of 40%, and H atoms are neglected for the sake of clarity. Selected bond lengths (Å): Ca1−C1 2.573(13), Ca1−I1 3.158(3), Ca1−O1 2.344(9), Ca1−O2 2.398(10), Ca1−O3 2.371(10), Ca1−O4 2.365(9). Angles (deg): C1−Ca1−I1 174.1(3), C1−Ca1−O1 88.6(3), C1−Ca1−O2 87.8(4), C1−Ca1−O3 94.6(4), C1−Ca1−O4 91.8(4), I1−Ca1−O1 87.2(2), I1−Ca1−O2 88.3(2), I1−Ca1−O3 90.2(3), I1−Ca1−O4 92.3(2).

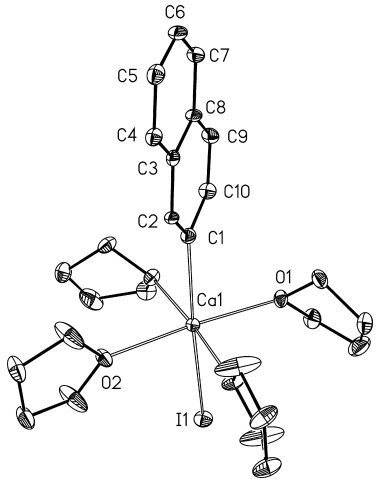


Figure 4. Molecular structure and numbering scheme of $[(\beta\text{-naphthyl})CaI(thf)_4]$ (8). Ellipsoids represent a probability of 40%, and H atoms are omitted for clarity reasons. Symmetry-related atoms (x, $-y-1$, z) are marked with the letter "A". Selected bond lengths (Å): Ca1−C1 2.528(5), Ca1−I1 3.1932(8), Ca1−O1 2.386(2), Ca1−O2 2.384(2). Angles (deg): C1−Ca1−I1 173.08(11), C1−Ca1−O1 87.87(9), C1−Ca1−O2 94.50(9), I1−Ca1−O1 87.42(5), I1−Ca1−O2 90.51(5).

CONCLUSION

The direct synthesis of meta-substituted phenylcalcium iodides via the reduction of iodoarenes with activated calcium succeeds in moderate to good yields; however, isolation of pure crystalline substances often proved to be challenging. Functional groups, such as halogens or methoxy substituents, are tolerated in para and meta positions as well. The reduction of 3-halo-1-iodobenzene selectively gave the 3-halophenylcalcium iodides in crystalline form; a second reduction step at the other halogen functionality was not observed, even when 1,3-diiodobenzene was employed. Contrary to this finding, magnesium reacts twice with 1,3-diiodobenzene, yielding $[C_6H_4\text{-}1,3\text{-}(MgI)_2]$.[28] This reaction was recently rediscovered, and in the presence of lithium chloride, 1,5-diiodo-2,4-dimethoxybenzene was reacted with a large excess of magnesium turnings to prepare the 2-fold magnesiated derivative $[2,4\text{-}(MeO)_2C_6H_2\text{-}1,5\text{-}(MgI\cdot LiCl)_2]$.[29]

The arylcalcium complexes show a characteristic strong low-field shift of the *ipso*-carbon atom in ^{13}C NMR spectra regardless of the substitution pattern. 2D NMR methods allow an unambiguous assignment of the aryl resonances that is in agreement with the increment method. In addition, it is well-known that the heavy atom effect leads to a significant high-field shift of the halogen-bound carbon atom with increasing mass of the halogen.

The thf adducts of arylcalcium iodides crystallize as monomeric molecules with hexacoordinate calcium centers in distorted octahedral environments regardless of meta and para substituents. The aryl groups and iodide ions prefer a trans arrangement due to electrostatic reasons. Softness and polarizability of the large iodide ion lead to variable Ca−I bond lengths between 314 and 321 pm depending largely on

dx.doi.org/10.1021/om301087e | Organometallics 2012, 31, 8647−8653

packing effects and intermolecular forces in the solid state. For the same reason, the molecules often also show severe differences between proximal and distal Ca−C_{ipso}−C_{ortho} bond angles. In these mainly ionic organometallics with very electropositive metals, tilting of the aryl group is provoked by intermolecular forces and packing effects in the solid state.

These investigations establish a large group tolerance during the reduction of substituted iodobenzene with activated calcium. The maintenance of reaction temperatures at and below ambient temperature allows the high-yield synthesis of post-Grignard reagents with a wide variety of functional groups, a precondition for fruitful and intense use of calcium-based organometallics in organic and organometallic chemistry.

EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out under an inert argon atmosphere using standard Schlenk techniques. THF was dried over KOH and distilled over sodium/benzophenone in an argon atmosphere; deuterated THF was dried over sodium, degassed, and saturated with argon. The yields given are not optimized. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker AC 200, AC 400, or AC 600 spectrometers. Chemical shifts are reported in parts per million relative to Me_4Si as an external standard. The residual signals of [D_8]THF were used as an internal standard. Calcium was activated by dissolution in liquid NH_3 and subsequent reduction of the deep blue solution to dryness, resulting in finely divided calcium powders.

The calcium content of the products was determined by complexometric titration of a hydrolyzed aliquot with 0.05 M EDTA using Eriochrome BlackT as an indicator.[30]

Synthesis of [(3-MeC_6H_4)CaI(thf)$_4$] (1). A suspension of finely divided calcium metal (1.2 g, 30 mmol) in THF (40 mL) was cooled to −20 °C. 3-Iodotoluene (5.45 g, 25 mmol) was added at this temperature, and the resulting mixture was allowed to warm to 0 °C while shaking. Shaking was continued for 1 h at 0 °C and for an additional 5 h at ambient temperature. The resulting brown suspension was filtered. The solid residue was extracted with THF (20 mL) and discarded afterward. The combined THF solutions (60% yield of organocalcium compounds, determined by acid consumption by a hydrolyzed aliquot) were stored at −90 °C for 5 days. Afterward, the precipitated crystalline solid was collected on a cooled Schlenk frit and dried in vacuo. Yield: 6.01 g of an off-white solid (crude product). Suitable crystals of the composition [(*m*-tolyl)CaI(thf)$_4$]·0.5thf for X-ray diffraction experiments were obtained by cooling of a saturated solution in THF from ambient temperature to −40 °C. Those crystals were also used for NMR measurements. Elemental analysis ($C_{23}H_{39}CaIO_4$, 546.55): calcd, Ca 7.33; found, Ca 7.03. ^{1}H NMR ([D_8]THF, 600 MHz): δ 1.78 (m, 16H, CH_2 thf), 2.15 (br, 3H, CH_3 tolyl), 3.64 (m, 16H, OCH_2 thf), 6.55 (br, 1H, *p*-CH tolyl), 6.72 (br, 1H, *m*-CH tolyl), 7.45 (br, 1H, *o*-CH tolyl), 7.52 (br, 1H, *o*-CH′ tolyl). Besides this signal set, another one of low intensity (*) was observed: δ 2.19 (s, CH_3 * tolyl), 6.67 (pseudo-d, *p*-CH * tolyl), 6.84 (pseudo-t, *m*-CH * tolyl), 8.29 (pseudo-d, *o*-CH * tolyl), 8.45 (s, *o*-CH′ * tolyl). Additionally, three intensive and very broad signals were observed: δ 2.1−2.3, 6.6−7.0, 7.7−8.2. ^{13}C{1H}NMR ([D_8]THF, 600 MHz): δ 21.8 (1C, CH_3 * tolyl), 22.2 (1C, CH_3 tolyl), 26.3 (8C, CH_2 thf), 68.2 (8C, OCH_2 thf), 123.5 (1C, C4), 125.0 (1C, C5), 126.1 (1C, C4 *), 126.6 (1C, C5 *), 132.5 (1C, C3), 134.2 (1C, C3 *), 138.1 (1C, C6), 141.0 (1C, C6 *), 142.1 (1C, C2), 144.9 (1C, C2 *), 185.3 (1C, C1 *), 189.7 (1C, C1). Again, additional broad signals were obtained: δ 125−127, 139.4−140.4, 143.5−144.5.

Synthesis of [(3,5-$Me_2C_6H_3$)CaI(thf)$_4$] (2). A suspension of finely divided calcium metal (1.2 g, 29.9 mmol) in THF (40 mL) was cooled to −20 °C. 1-Iodo-3,5-dimethylbenzene (5.80 g, 25 mmol) was added at this temperature, and the resulting mixture was allowed to warm to 0 °C while shaking. Shaking was continued for 1 h at 0 °C and for an additional 4 h at ambient temperature. The resulting violet suspension was filtered, and the solid residue was discarded. The THF solution (81% yield of organocalcium compounds, determined by acid consumption by a hydrolyzed aliquot) was stored at −40 °C for 2 days. Afterward, the formed crystalline solid was collected on a cooled Schlenk frit and dried in vacuo (4.50 g). A second crop of the product (0.95 g) was obtained from the mother liquor at −90 °C. Combined yield: 5.45 g (9.72 mmol, 39%) of needle-shaped crystals. Suitable crystals of the composition [(3,5-$Me_2C_6H_3$)CaI(thf)$_4$] for X-ray diffraction experiments were obtained by cooling a saturated solution in THF from ambient temperature to −40 °C. Elemental analysis ($C_{24}H_{41}CaIO_4$, 560.57): calcd, Ca 7.15; found, Ca 7.39%. ^{1}H NMR ([D_8]THF, 600 MHz): δ 1.78 (m, 16 H, CH_2 thf), 2.12 (br, 6H, CH_3 tolyl), 3.63 (m, 16H, OCH_2 thf), 6.38 (br, 1H, *p*-CH tolyl), 7.29 (br, 2H, *o*-CH tolyl). ^{13}C{^{1}H} NMR ([D_8]THF, 150.9 MHz): δ 22.1 (2C, CH_3 tolyl), 26.3 (8C, CH_2 thf), 68.2 (8C, OCH_2 thf), 124.6 (1C, C4), 132.2 (2C, C3 and C5), 139.2 (2C, C2 and C6), 189.7 (1C, C1).

Synthesis of [(3-FC_6H_4)CaI(thf)$_4$] (3). Finely divided calcium metal (1.2 g, 29.9 mmol) was suspended in THF (40 mL) and cooled to −20 °C. 1-Iodo-3-fluorobenzene (5.55 g, 25 mmol) was added at this temperature, and the resulting mixture was allowed to warm to 0 °C while shaking. Shaking was continued for 1 h at 0 °C and for an additional 4 h at ambient temperature. The resulting brown suspension was filtered, and the solid residue was discarded. The THF solution (51% yield of organocalcium compounds, determined by acid consumption by a hydrolyzed aliquot) was stored at −90 °C for 3 days. Afterward, the formed crystalline solid was collected on a cooled Schlenk frit and dried in vacuo. Yield: 0.67 g (1.22 mmol, 4.9%) of a violet solid (crude product). ^{1}H NMR ([D_8]THF, 200 MHz): δ 1.73 (m, 16 H, CH_2 thf), 3.60 (m, 16H, OCH_2 thf), 6.33 (m, *p*-CH phenyl), 6.79 (m, 1H, *m*-CH phenyl), 7.33 (m, 2H, *o*-CH and *o*-CH′ phenyl). ^{13}C{^{1}H} NMR ([D_8]THF, 50.6 MHz): δ 26.4 (8C, CH_2 thf), 68.3 (8C, OCH_2 thf), 108.8 (d, J_{CF} = 21,0 Hz, 1C, C4), 125.3 (d, J_{CF} = 5,0 Hz, 1C, C5), 125.9 (d, J_{CF} = 2,9 Hz, 1C, C2), 136.1 (s, 1C, C6), 162.6 (d, J_{CF} = 251.9 Hz, 1C, C3), 195.6 (s, 1C, C1). ^{19}F{^{1}H} NMR ([D_8]THF, 188.3 MHz): δ −120.3 (s, 1F).

Synthesis of [(3-ClC_6H_4)CaI(thf)$_4$] (4). 1-Iodo-3-chlorobenzene (5.96 g, 25 mmol) was added to a suspension of finely dispersed calcium metal (1.2 g, 29.9 mmol) in THF (40 mL) at −20 °C. The resulting mixture was shaken for 1 h at 0 °C and for an additional 4 h without cooling. The unreacted calcium was removed by filtration through a Schlenk frit and covered with diatomaceous earth, and the residue on the filter was dried in vacuo, suspended in THF (40 mL), and stirred for 2 h at ambient temperature. After filtration, the obtained solution was combined with the mother liquor. An overall conversion of 74% was determined by acidimetric consumption of an aliquot. The purple solution was stored for 1 day at −40 °C, and the formed precipitate was collected on a cooled Schlenk frit and dried in vacuo. Yield: 1.93 g (3.40 mmol, 13.6%). Suitable crystals of the composition [(3-ClC_6H_4)CaI(thf)$_4$] for X-ray diffraction experiments were obtained by cooling a saturated solution in THF from ambient temperature to −40 °C. Elemental analysis ($C_{22}H_{36}CaIClO_4$, 566.96): calcd, Ca 7.07; found, Ca 7.52%. ^{1}H NMR ([D_8]THF, 200 MHz): δ 1.73 (m, 16H, CH_2 thf), 3.60 (m, 16H, OCH_2 thf), 6.65 (m, 1H, *p*-CH phenyl), 6.75 (m, 1H, *m*-CH phenyl), 7.48 (m, 1H, *o*-CH′ phenyl), 7.56 (m, 1H, *o*-CH phenyl). ^{13}C{^{1}H} NMR ([D_8]THF, 100.6 MHz): δ 25.3 (8C, CH_2 thf), 67.5 (8C, OCH_2 thf), 122.5 (1C, C4), 126.7 (1C, C5), 133.2 (1C, C3), 138.7 (1C, C6), 139.8 (1C, C2), 194.8 (1C, C1).

Synthesis of [(3-BrC_6H_4)CaI(thf)$_4$] (5). Activated calcium metal (1.2 g, 29.9 mmol) was suspended in THF (40 mL), and 1-iodo-3-bromobenzene (7.07 g, 25 mmol) was added slowly at −20 °C. The suspension was shaken for 1 h at 0 °C and for an additional 4 h without cooling. The formed precipitate was removed by filtration through a Schlenk frit and covered with diatomaceous earth, and the residue on the filter was dried in vacuo, suspended in THF (40 mL), and stirred for 2 h at ambient temperature. After filtration, the obtained solution was combined with the mother liquor. By acidimetric consumption of an aliquot of the combined solutions, a conversion of 67% was determined. After 4 days of storage of the brown solution at −40 °C, the formed precipitate was finally collected on a Schlenk frit and dried in vacuo. Yield: 3.90 g (6.38 mmol, 25.5%) of a brown solid (crude product). Elemental analysis ($C_{22}H_{36}CaIBrO_4$,

dx.doi.org/10.1021/om301087e | *Organometallics* 2012, 31, 8647−8653

611.41): calcd, Ca 6.56; found, Ca 6.80%. ^{1}H NMR ([D$_8$]THF, 200 MHz): δ 1.73 (m, 16H, CH$_2$ thf), 3.60 (m, 16H, OCH$_2$ thf), 6,72 (m, 1H, *m*-CH phenyl), 6.82 (m, 1H, *p*-CH phenyl), 7.54 (m, 1H, *o*-CH′ phenyl), 7.73 (m, 1H, *o*-CH phenyl). ^{13}C{^{1}H} NMR ([D$_8$]THF, 100.6 MHz): δ 25.3 (8C, CH$_2$ thf), 67.6 (8C, OCH$_2$ thf), 124.5 (1C, C3), 125.4 (1C, C4), 127.5 (1C, C5), 139.0 (1C, C6), 142.6 (1C, C2), 196.3 (1C, C1).

Synthesis of [(3-IC$_6$H$_4$)CaI(thf)$_4$] (6). Finely dispersed calcium metal (1.2 g, 29.9 mmol) was suspended in THF (80 mL) and cooled to −20 °C. 1,3-Diiodobenzene (8.25 g, 25 mmol) was added at this temperature, and the resulting mixture was allowed to warm to 0 °C while shaking. Shaking was continued for 1 h at 0 °C and for an additional 4 h at ambient temperature. The resulting brown suspension was filtered, and the solid residue was dried in vacuo. The residue was twice extracted with THF (40 mL), and the filtrates were combined. The combined solutions (66% yield of organocalcium compounds, determined by acid consumption by a hydrolyzed aliquot) were stored at −40 °C for 4 days. Afterward, the formed crystalline solid was collected on a cooled Schlenk frit and dried in vacuo. Yield: 4.59 g (6.97 mmol, 27.9%) of a pale yellow solid. Elemental analysis (C$_{22}$H$_{36}$CaI$_2$O$_4$, 658.42): calcd, Ca 6.09; found, Ca 6.34%. ^{1}H NMR ([D$_8$]THF, 400 MHz): δ 1.73 (m, 16H, CH$_2$ thf), 3.58 (m, 16H, OCH$_2$ thf), 6.63 (m, *m*-CH phenyl), 7.05 (m, 1H, *p*-CH phenyl), 7.56 (m, 1H, *o*-CH′ phenyl), 7.96 (m, 1H, *o*-CH phenyl). ^{13}C{^{1}H} NMR ([D$_8$]THF, 100.6 MHz): δ 25.3 (8C, CH$_2$ thf), 67.2 (8C, OCH$_2$ thf), 101.0 (1C, C3), 128.4 (1C, C5), 131.4 (1C, C4), 139.0 (1C, C6), 149.0 (1C, C2), 197.1 (1C, C1).

Synthesis of [(3-MeOC$_6$H$_4$)CaI(thf)$_n$] (7). 3-Iodo-anisole (5.85 g, 25 mmol) was added to a suspension of finely divided calcium metal (1.2 g, 29.9 mmol) in THF (40 mL) at −20 °C. The resulting brown mixture was allowed to warm to 0 °C while shaking. Shaking was continued for 1 h at 0 °C and for an additional 4 h at ambient temperature. The suspension was filtered, and the solid residue was discarded. The THF solution (75% yield of organocalcium compounds, determined by acid consumption by a hydrolyzed aliquot) was stored at −90 °C for 1 week. Afterward, the formed crystalline solid was collected on a cooled Schlenk frit and dried in vacuo. Yield: 4.43 g of a pale yellow solid. Elemental analysis (tetrakis(thf) adduct: C$_{23}$H$_{39}$CaIO$_5$, 562.54): calcd, Ca 7.12; (tris(thf) complex: C$_{19}$H$_{31}$CaIO$_4$, 490.44): calcd, Ca 8.17; found, Ca 8.69%. ^{1}H NMR ([D$_8$]THF, 400 MHz): δ 1.73 (m, 16H, CH$_2$ thf), 3.58 (m, 19H, CH$_2$ thf and OCH$_3$ phenyl), 6.24 (m, 1H, *p*-CH phenyl), 6.72 (m, 1H, *m*-CH phenyl); 7,19 (m, 2H, *o*-CH and *o*-CH′ phenyl). ^{13}C{^{1}H} NMR ([D$_8$]THF, 100.6 MHz): δ 25.3 (8C, CH$_2$ thf), 67.2 (8C, OCH$_2$ thf), 53.2 (1C, OCH$_3$ phenyl), 106.5 (1C, C4), 124.4 (1C, C5), 125.0 (1C, C2), 132.5 (1C, C6), 156.8 (1C, C3), 191.3 (1C, C1).

Synthesis of [(*β*-Naphthyl)CaI(thf)$_4$] (8). A suspension of finely divided calcium metal (1.2 g, 30 mmol) in THF (60 mL) was cooled to −20 °C. *β*-Iodonaphthalene (5.00 g, 19.7 mmol) was added at this temperature, and the resulting mixture was allowed to warm to 0 °C while shaking. Shaking was continued for 1 h at 0 °C and for an additional 5 h at ambient temperature. During this time, the color of the suspension turned from dark green to violet. The resulting violet suspension was filtered. The solid residue was extracted with THF (140 mL) and discarded afterward. The combined THF solutions (84% yield of organocalcium compounds, determined by acid consumption by a hydrolyzed aliquot) were stored at −40 °C for 4 days. Afterward, the formed crystalline solid was collected on a cooled Schlenk frit and dried in vacuo. Yield: 3.26 g (5.60 mmol, 22.4%) of a colorless solid. Suitable crystals of the composition [(*β*-naphthyl)CaI(thf)$_4$] for X-ray diffraction experiments were obtained by cooling of a saturated solution in THF from ambient temperature to −10 °C. Those crystals were used for NMR measurements. Elemental analysis (C$_{26}$H$_{39}$CaIO$_4$, 582.55): calcd, Ca 6.88; found, Ca 6.89%. ^{1}H NMR ([D$_8$]THF, 600 MHz): δ 1.73 (m, 16H, CH$_2$ thf), 3.59 (m, 16H, OCH$_2$ thf), 7.02 (m, 1H), 7.10 (m, 1H), 7.28 (m, 1H), 7.47 (m, 2H), 7.90 (m, 1H), 8.10 (m, 1H). ^{13}C{^{1}H} NMR ([D$_8$]THF, 100.6 MHz): δ 25.3 (8C, CH$_2$ thf), 67.5 (8C, OCH$_2$ thf), 122.3 (1C), 122.5 (1C), 123.5 (1C), 127.5 (1C), 128.2 (1C), 132.9 (1C), 134.0 (1C), 139.5 (1C), 140.8 (1C), 189.1 (1C, C−Ca).

X-ray Crystal Structure Determination. The intensity data were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects, but not for absorption.[31,32]

The structures were solved by direct methods (SHELXS[33]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[33]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All nondisordered, non-hydrogen atoms were refined anisotropically.[33] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for **1**. C$_{23}$H$_{39}$CaIO$_4$, 0.5 C$_4$H$_8$O; M_r = 582.57 g mol^{-1}; colorless prism, size 0.06 × 0.06 × 0.06 mm^3; monoclinic; space group *C*2/*c*; *a* = 17.5880(3) Å, *b* = 18.9070(4) Å, *c* = 16.7740(3) Å, β = 90.123(3)°; *V* = 5577.95(18) Å^3; *T* = −140 °C; *Z* = 8; ρ_{calcd} = 1.387 g cm^{-3}; μ (Mo Kα) = 13.6 cm^{-1}; *F*(000) = 2416; 5317 reflections in *h*(−22/22), *k*(−24/24), *l*(0/21); measured in the range 3.16° ≤ Θ ≤ 27.48°; completeness Θ_{max} = 86.8%; 5319 independent reflections; R_{int} = 0.0422; 4857 reflections with $F_o > 4\sigma(F_o)$; 285 parameters, 0 restraints; $R1_{obs}$ = 0.0483, wR^2_{obs} = 0.1074, $R1_{all}$ = 0.0552, wR^2_{all} = 0.1131; GOF = 1.138; largest difference peak and hole = 1.087/−0.813 e Å^{-3}.

Crystal Data for **2**. C$_{24}$H$_{41}$CaIO$_4$; M_r = 560.55 g mol^{-1}; colorless prism, size 0.56 × 0.55 × 0.53 mm^3; monoclinic; space group $P2_1/c$; *a* = 13.3143(9) Å, *b* = 12.0557(9) Å, *c* = 16.2773(12) Å, β = 91.975(3)°; *V* = 2611.2(3) Å^3; *T* = 23 °C; *Z* = 4; $\rho_{calcd.}$ = 1.426 g cm^{-3}; μ (Mo Kα) = 14.48 cm^{-1}; *F*(000) = 1160; 5180 reflections in *h*(−16/16), *k*(0/14), *l*(0/20); measured in the range 3.02° ≤ Θ ≤ 27.58°; completeness Θ_{max} = 99.7%; 5184 independent reflections; R_{int} = 0.0677; 4592 reflections with $F_o > 4\sigma(F_o)$; 274 parameters, 0 restraints; $R1_{obs}$ = 0.0296, wR^2_{obs} = 0.0656, $R1_{all}$ = 0.0383, wR^2_{all} = 0.0690; GOF = 0.992; largest difference peak and hole = 1.299/−0.578 e Å^{-3}.

Crystal Data for **4**. C$_{22}$H$_{36}$CaClIO$_4$; M_r = 566.94 g mol^{-1}; colorless prism; size 0.05 × 0.05 × 0.05 mm^3; orthorhombic; space group $P2_12_12_1$; *a* = 7.9202(5) Å, *b* = 10.2280(7) Å, *c* = 31.556(2) Å; *V* = 2556.3(3) Å^3; *T* = −140 °C; *Z* = 4; $\rho_{calcd.}$ = 1.473 g cm^{-3}; μ (Mo Kα) = 15.81 cm^{-1}; *F*(000) = 1160; 9019 reflections in *h*(−9/9), *k*(−12/8), *l*(−37/37); measured in the range 2.58° ≤ Θ ≤ 25.02°; completeness Θ_{max} = 94.7%; 3970 independent reflections; R_{int} = 0.0542; 3240 reflections with $F_o > 4\sigma(F_o)$; 253 parameters, 0 restraints; $R1_{obs}$ = 0.0739, wR^2_{obs} = 0.1185, $R1_{all}$ = 0.1001, wR^2_{all} = 0.1291; GOF = 1.291; Flack parameter = 0.09(6); largest difference peak and hole = 0.563/−0.524 e Å^{-3}.

Crystal Data for **8**. C$_{26}$H$_{39}$CaIO$_4$; M_r = 582.55 g mol^{-1}; colorless prism; size 0.06 × 0.05 × 0.05 mm^3; monoclinic; space group *Cm*; *a* = 12.1149(4) Å, *b* = 13.5272(3) Å, *c* = 8.3474(3) Å, β = 99.737(1)°; *V* = 1348.27(7) Å^3; *T* = −140 °C; *Z* = 2; $\rho_{calcd.}$ = 1.435 g cm^{-3}; μ (Mo Kα) = 14.05 cm^{-1}; *F*(000) = 600; 4152 reflections in *h*(−15/11), *k*(−17/17), *l*(−8/10); measured in the range 3.01° ≤ Θ ≤ 27.51°; completeness Θ_{max} = 99.3%; 2419 independent reflections; R_{int} = 0.0195; 2397 reflections with $F_o > 4\sigma(F_o)$; 166 parameters, 2 restraints; $R1_{obs}$ = 0.0219, wR^2_{obs} = 0.0484, $R1_{all}$ = 0.0223, wR^2_{all} = 0.0486; GOF = 1.036; Flack parameter = −0.028(17); largest difference peak and hole = 0.309/−0.424 e Å^{-3}.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data deposited at the Cambridge Crystallographic Data Centre under CCDC-909485 for **1**, CCDC-909486 for **2**, CCDC-910006 for **4**, and CCDC-866605 for **8** contain the supplementary crystallographic data, excluding structure factors; this data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; Fax: (+44) 1223−336−033; or deposit@ccdc.cam.ac.uk).

AUTHOR INFORMATION

Corresponding Author

*Fax: +49 (0) 3641 948132. E-mail: m.we@uni-jena.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the German Research Foundation (DFG, Bonn-Bad Godesberg, Germany) and the Fonds der Chemischen Industrie (VCI/FCI, Frankfurt/Main, Germany) for financial support. M.K. is grateful to the Fonds der Chemischen Industrie (VCI, Frankfurt/Main, Germany) for a generous Ph.D. stipend. We also acknowledge support by the Friedrich Schiller University Jena and the European Fonds for Regional Development (EFRE).

REFERENCES

(1) Bickelhaupt, F. *J. Organomet. Chem.* **1994**, *475*, 1−14.
(2) Seyferth, D. *Organometallics* **2009**, *28*, 1598−1605.
(3) (a) Westerhausen, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2975−2977;(b) *Angew. Chem.* **2001**, *113*, 3063−3065.
(4) Beckmann, E. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 904−906.
(5) Fischer, R.; Görls, H.; Westerhausen, M. *Inorg. Chem. Commun.* **2005**, *8*, 1159−1161.
(6) Ruspic, C.; Harder, S. *Organometallics* **2005**, *24*, 5506−5508.
(7) (a) Fischer, R.; Gärtner, M.; Görls, H.; Westerhausen, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 609−612;(b) *Angew. Chem.* **2006**, *118*, 624−627.
(8) Holleman, A. F.; Wiberg, E.; Wiberg, N. *Lehrbuch der Anorganischen Chemie*, 102nd ed.; W. de Gruyter: Berlin, 2007; p 1255.
(9) (a) Westerhausen, M.; Gärtner, M.; Fischer, R.; Langer, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 1950−1956;(b) *Angew. Chem.* **2007**, *119*, 1994−2001.
(10) Westerhausen, M.; Gärtner, M.; Fischer, R.; Langer, J.; Yu, L.; Reiher, M. *Chem.—Eur. J.* **2007**, *13*, 6292−6306.
(11) Westerhausen, M. *Z. Anorg. Allg. Chem.* **2009**, *635*, 13−32.
(12) Westerhausen, M.; Langer, J.; Krieck, S.; Fischer, R.; Görls, H.; Köhler, M. *Top. Organomet. Chem.* **2012**, in press.
(13) Langer, J.; Görls, H.; Westerhausen, M. *Organometallics* **2010**, *29*, 2034−2039.
(14) (a) Langer, J.; Krieck, S.; Görls, H.; Westerhausen, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 5741−5744;(b) *Angew. Chem.* **2009**, *121*, 5851−5854.
(15) Langer, J.; Köhler, M.; Fischer, R.; Dündar, F.; Görls, H.; Westerhausen, M. *Organometallics* **2012**, *31*, 6172−6182.
(16) Gärtner, M.; Görls, H.; Westerhausen, M. *Synthesis* **2007**, *5*, 725−730.
(17) (a) Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 972−989;(b) *Angew. Chem.* **1987**, *99*, 1002−1019.
(18) Langer, J.; Krieck, S.; Fischer, R.; Görls, H.; Walther, D.; Westerhausen, M. *Organometallics* **2009**, *28*, 5814−5820.
(19) Westerhausen, M.; Langer, J.; Krieck, S.; Glock, C. *Rev. Inorg. Chem.* **2011**, *31*, 143−184.
(20) (a) Hauber, S.-O.; Lissner, F.; Deacon, G. B.; Niemeyer, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 5871−5875;(b) *Angew. Chem.* **2005**, *117*, 6021−6025.
(21) Langer, J.; Görls, H.; Westerhausen, M. *Inorg. Chem. Commun.* **2007**, *10*, 853−855.
(22) Krieck, S.; Görls, H.; Yu, L.; Reiher, M.; Westerhausen, M. *J. Am. Chem. Soc.* **2009**, *131*, 2977−2985.
(23) Krieck, S.; Görls, H.; Westerhausen, M. *J. Am. Chem. Soc.* **2010**, *132*, 12492−12501.
(24) Fischer, R.; Gärtner, M.; Görls, H.; Westerhausen, M. *Organometallics* **2006**, *25*, 3496−3500.
(25) Fischer, R.; Gärtner, M.; Görls, H.; Yu, L.; Reiher, M.; Westerhausen, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1618−1623.
(26) Langer, J.; Krieck, S.; Fischer, R.; Görls, H.; Westerhausen, M. *Z. Anorg. Allg. Chem.* **2010**, *636*, 1190−1198.
(27) Harvey, M. J.; Hanusa, T. P. *Organometallics* **2000**, *19*, 1556−1566.
(28) Bruhat, G.; Thomas, V. *C. R. Acad. Sci.* **1926**, *183*, 297−299.
(29) (a) Piller, F. M.; Appukkuttan, P.; Gavryushin, A.; Helm, M.; Knochel, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 6802−6806;(b) *Angew. Chem.* **2008**, *120*, 6907−6911.
(30) Jander, G.; Jahr, K. F.; Schulze, G.; Simon, J. *Massanalyse*; Walter de Gruyter: Berlin, Germany, 1989.
(31) *COLLECT: Data Collection Software*; Nonius B.V.: Delft, The Netherlands, 1998.
(32) Otwinowski, Z.; Minor, W. Processing of X-Ray Diffraction Data Collected in Oscillation Mode. In *Macromolecular Crystallography. Part A*; Carter, C. W., Sweet, R. M., Eds.; Methods in Enzymology; Academic Press: San Diego, CA, 1997; Vol. *276*, pp 307−326.
(33) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.