Synthesis of Arylcalcium Halides – General Procedure, Scope and Limitations

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Abstract: A general procedure for the synthesis of a wide variety of arylcalcium halides by activation of the alkaline earth metal as well as bromo- or iodoarenes is reported. Chloro- and fluoroarenes are not suitable substrates for an insertion of calcium into the carbon–halogen bond. Furthermore, *ortho*-fluoro substitution prevents the formation of the corresponding heavy calcium organometallics. The *ipso*-carbon atoms show a strong low-field shift in the ^{13}C NMR spectra. The arylcalcium iodides crystallize monomeric as tetrakis(THF) complexes. Naphthylcalcium iodide shows a Ca–C bond length of 255.2(6) pm which lies in the characteristic region.

Keywords: Grignard reaction, arylcalcium halides, direct synthesis, calcium, metal activation

The organic chemistry of the alkali metals has a long tradition and is well established.[1] Especially the organolithium chemistry has found a wide spectrum of applications.[2] The interest in the organic chemistry of the alkaline earth metals was mainly limited to magnesium.[3] Due to the toxicity of beryllium[4] and the difficulties during the formation of metal–carbon bonds of the heavy alkaline earth metals,[5] only the direct synthesis of alkyl- and arylmagnesium halides by insertion of magnesium into a carbon–halogen bond gained tremendous importance. Even though several review articles on the organic chemistry of calcium, strontium and barium appeared approximately 30 years ago,[6] these compounds remained poorly characterized or were deduced solely from derivatization reactions. In contrast to this lack of knowledge, the metallocenes of the heavy alkaline earth metals represent an exception and are easily accessible in good yields.[7]

The main challenge of the organic chemistry of the heavy alkaline earth metals stems from the discrepancy of the low reactivity of the calcium metal and the extreme high reactivity of the organocalcium compounds with the tendency to cleave ethers. Due to this fact, low temperatures have to be maintained throughout the synthesis, which affords an activation of the alkaline earth metal prior to use. In addition, shielding of the Ca–C bonds by coordinating co-ligands such as ethers or bulky groups at the periphery is advantageous. This concept allowed the isolation and structure determinations of $(diox)_2Ca[CH(SiMe_3)_2]_2$[8] (prepared via co-condensation of calcium vapor and organic substrate) and solvent-free $Ca[C(SiMe_3)_3]_2$ (from the metathesis reaction of $KC(SiMe_3)_3$ with CaI_2).[9]

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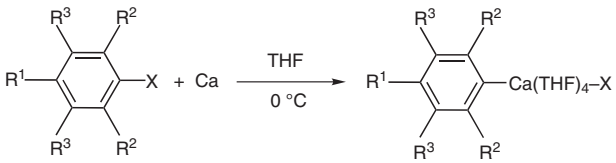
Due to the difficulties in performing the direct synthesis, the metathesis reaction of organic potassium compounds with calcium diiodide represents the standard procedure for the synthesis of organocalcium compounds.[5] An additional stabilization can be achieved via an α-substitution with phenyl and trialkylsilyl groups in order to stabilize the anionic charge.[10] However, the calcium atom tends to bind to the π-system of the benzyl anion rather than forming a Ca–C σ-bond.

General Remarks: The preparation of 2,4,6-trimethylphenylcalcium iodide (mesitylcalcium iodide),[11] phenylcalcium iodide and *p*-tolylcalcium iodide[12] showed the suitability of insertion of calcium into a carbon–halogen bond according to Equation 1. The decomposition via ether cleavage reactions occurred already at temperatures below –35 °C. Therefore, a variety of arylcalcium halides were prepared and a general procedure was developed.



Equation 1

Activation of Calcium: Due to the low reactivity of calcium metal, activation prior to use is necessary. Distillation of calcium affords pure metal. However, the metal surface of these calcium crystals is rather small and long reaction periods and activation methods such as ultrasound have to be applied which also promote side reactions. Therefore, activation via dissolution in liquid ammonia proved to be advantageous. In order to prevent amide formation, the ammonia should be removed immediately from these solutions. The remaining calcium powder is dried in vacuo and then a suspension in THF is formed. Instead of a stirring bar, glass balls in a shaken flask proved to be advantageous for grinding the metal powder during the reaction with aryl halides.

General Procedure: In order to evaluate the scope of the direct synthesis of arylcalcium halides, the metal-bound halogen atom and the substitution pattern of the aryl group were varied (see Table 1). The highest yields were obtained for aryl iodides whereas the aryl chlorides and fluorides show nearly no reactivity towards activated calcium. The fluorine substitution of the aryl group also spoils the isolation of the arylcalcium iodides **10** and **11**. Whereas 1-bromo-3,4,5-triflourobenzene was not at-

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Table 1 Arylcalcium Halides Prepared According to Equation 1[a]

Compound	R^1	R^2	R^3	X	Yield (%)	Remarks
1a	H	H	H	I	93[b]	Schlenk equilibrium in Et_2O, solubility in THF at r.t.: 0.25 mol·L^{-1} (133 g·L^{-1})
1b	H	H	H	Br	71[c]	–
1c	H	H	H	Cl	<5	No reaction
2	Me	H	H	I	60	See ref.[12]
3	I	H	H	I	95	No formation of ICa-C_6H_4-CaI
4	Cl	H	H	I	81	No Wurtz-type coupling
5	F	H	H	I	75	No formation of CaF_2
6	OMe	H	H	I	89	Schlenk equilibrium in THF[d]
7	NMe_2	H	H	I	91	Schlenk equilibrium in THF[d]
8	H	OMe	H	I	56	Schlenk equilibrium in THF
9a	Me	Me	H	I	52	Schlenk equilibrium in THF
9b	Me	Me	H	Br	–	No reaction
10	F	H	F	Br	–	No reaction
11a	F	F	F	I	–	Fast decomposition, $Ca(F/I)_2$ formation
11b	F	F	F	Br	–	Fast decomposition, $Ca(F/Br)_2$ formation
12	1-naphthyl			I	68	Solubility in THF at r.t.: 0.1 mol·L^{-1} (58 g·L^{-1})
13	Ph	H	H	I	–	Fast decomposition, ether cleavage

[a] The numbering of the substituents R^1 (*para* position), R^2 (*ortho* position) and R^3 (*meta* position) is also shown in this equation.
[b] Crystalline $PhCa(THF)_4I$ can be isolated in a yield of 63%; in 70% yield after 3 h at 0 °C with 0.7 equiv of iodobenzene.[12]
[c] Yield is 50% after 3 h at r.t. with 0.7 equiv of bromobenzene.[12]
[d] Schlenk equilibrium shows a temperature dependency.

tacked by calcium, bromopentafluorobenzene reacted with calcium. However, the immediate formation of calcium dihalide $Ca(F/Br)_2$ was observed. The isolation of pentafluorophenylcalcium units affords bulky shielding groups as was shown by Niemeyer and co-workers.[13]

The THF solutions of the arylcalcium halides **6** to **9** showed two resonance sets in the ^{13}C NMR spectra, which can be addressed to a Schlenk equilibrium. On cooling, these solutions led to the precipitation of $(THF)_4CaI_2$. In contrast to this observation, no Schlenk equilibrium was operative for phenylcalcium iodide in THF. Therefore, the isolation of crystalline arylcalcium iodide succeeded after cooling the reaction mixtures. However, a solvent change to diethyl ether led to a dismutation reaction and diphenylcalcium decomposed immediately under these reaction conditions via ether cleavage reactions.

NMR Spectroscopy: The $^{13}C\{^1H\}$ NMR parameters are summarized in Table 2. The *ipso*-carbon atoms are low-field shifted as one would expect for ionic compounds. For phenyllithium and phenylmagnesium bromide δ values of 186.6 and 164.3,[14] respectively, were observed and are comparable to those of the arylcalcium halides. The chemical shifts of the other carbon atoms strongly depend on the substitution pattern of the aryl groups. The iodine atom leads to an enormous high-field shift of the ^{13}C resonance due to a heavy atom effect. Therefore, the chemical shifts of the *para*-carbon atoms of **3** (R^1 = I), **4** (R^1 = Cl) and **5** (R^1 = F) relate to the δ values of 94.4, 134.8 and 163.3 of the corresponding halogenobenzenes.[14]

*Molecular Structure of (THF)$_4$Ca(Naph)I (**12**)*: The molecular structure of the THF complex of naphthylcalcium iodide (**12**) is shown in Figure 1. The disorder of the THF ligand with O2 is not drawn. The Ca atom is in an octahedral environment with a C1–Ca–I angle of 177.7(2)°. The Ca–C1 bond lengths of 255.2(6) and the Ca–I distance of 318.7(1) lie in characteristic regions. The endocyclic C2–C1–C10 angle of 113.5(6)° is rather narrow. This fact can be addressed to the repulsion forces between the anionic lone pair and the C1–C2 as well as C1–C10 bonds. Due to steric reasons, the coordination of the naphthyl group to the calcium atom leads to different Ca–C1–C2/C10 angles of 116.7(5)° and 129.8(5)°, respectively. The hindrance between the C9-H moiety and the neighboring THF molecules leads to the enhancement of the appropriate Ca–

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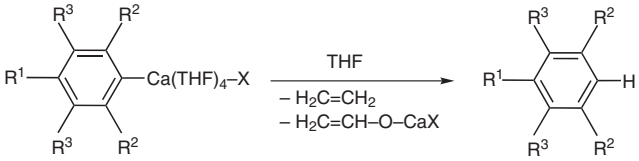
Table 2 $^{13}C\{^1H\}$ NMR Parameters of the THF Complexes of Arylcalcium Halides

Compound	δ (*i*-C)	δ (*o*-C)	δ (*m*-C)	δ (*p*-C)	δ (R^1, R^2, R^3)
1a	190.3	141.1	125.3	122.5	–
1b	190.0	142.1	128.9	123.3	–
2	185.3	141.3	126.2	130.4	21.8 (*p*-Me)[12]
3	188.9	143.5	133.9	89.7	–
4	187.8	142.5	125.0	129.0	–
5	186.6	141.4	111.6	161.3	–
6	178.0	141.5	111.6	157.3	54.4 (OMe)[a]
7	173.6	140.8	111.8	147.4	40.7 [NMe_2][a]
8	152.0	167.6	103.9	127.5	56.8 (OMe)
9a	182.5	147.1	124.2	131.0	21.6 (*p*-Me), 27.7 (*o*-Me)[11]
12	122.2, 122.9, 123.1, 124.6, 128.8, 134.1, 136.9, 138.0, 146.2, 195.4[b]				

[a] The resonances of 4-$MeOC_6H_4CaI$ and 4-$Me_2NC_6H_4CaI$, respectively, are summarized in this Table; the data for $[4\text{-}MeOC_6H_4]_2Ca$ and $[4\text{-}Me_2NC_6H_4]_2Ca$ are given in the experimental section.
[b] The data are listed without any assignments.

C1–C10 angle whereas on the opposite side the THF ligands can move more freely which causes disordering.

Stability: Arylcalcium halides are highly reactive and tend to cleave ethers. Due to the formation of cage compounds such as $[\{(THF)_2CaPhI\}_3\cdot(THF)CaO]$,[15] a manifold amount of heavy Grignard reagent is bound to the finally resulting oxide. As a representative example, the decomposition of 4-chlorophenylcalcium iodide (**4**) in THF was investigated. The first reaction step is the α-deprotonation of a THF molecule, followed by the formation of arene, ethenolate and ethene according to Equation 2. All arylcalcium halides can be prepared at 0 °C and separated from the decomposition products; only the mesityl derivatives have to be handled at lower temperatures.



Equation 2

As a representative example, the decomposition reaction of **4** in THF was followed by means of ^1H NMR spectroscopy in a sealed NMR tube. Selected spectra are displayed in Figure 2 and show the formation of the decomposition products, which consist mainly of chlorobenzene. The first spectrum was recorded overnight directly after the synthesis, whereas the other spectra were observed after 10, 30, and 50 days. For comparison reasons, the lowest spectrum shows the resonances of pure chlorobenzene. It is obvious that the major product of the decomposition is C_6H_5Cl which stems from the ether cleavage reaction.

These reactions offer two perspectives in comparison to the aryllithium and arylmagnesium chemistry. Due to the low reactivity of the calcium metal, 1,4-diiodobenzene reacts only once with activated calcium to yield **3** even in the presence of excess of calcium powder, whereas it is able to react twice with magnesium shavings[16] or lithium reagents.[17] On the other hand, the reactivity of the arylcalcium halides seems to be enhanced compared to the magnesium derivatives. This fact can be utilized for a wide field of applications such as metalation, metathesis and addition reactions, which are under investigation in our research group.

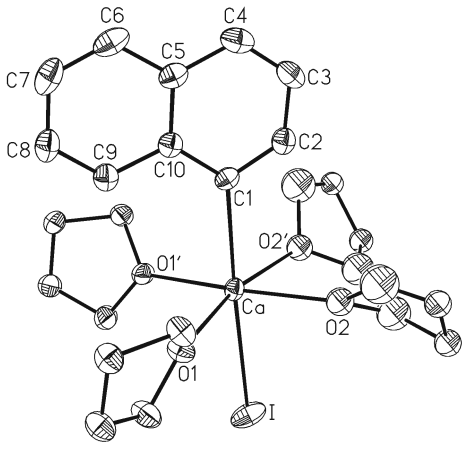


Figure 1 Molecular structure of $(THF)_4Ca(Naph)I$ (**12**). The ellipsoids represent a probability of 40%. The H atoms are neglected for clarity. Symmetry-related atoms (x, –y + 0.5, z) are marked with an apostrophe. The disordering of the THF ligands is not shown.

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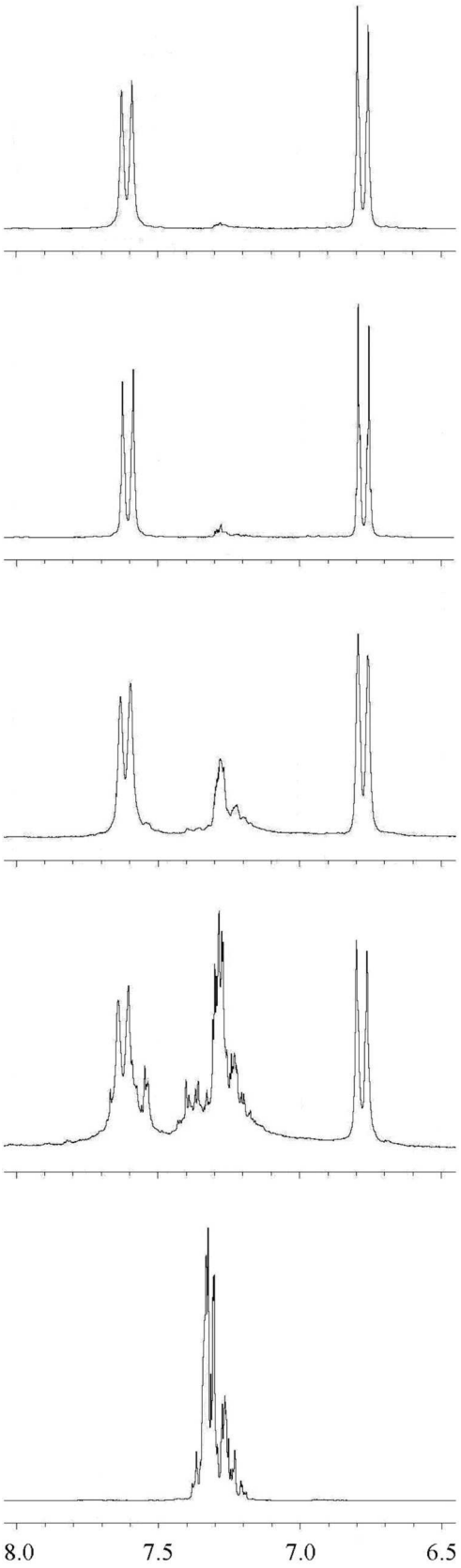

Figure 2 ^{1}H NMR spectroscopic follow-up of the decomposition reaction of 4-chlorophenylcalcium iodide (**4**) in THF (δ scale, r.t.); from the top to the bottom: 12 h, 10 d, 30 d, 50 d after direct synthesis; bottom spectrum shows C_6H_5Cl for comparison).

^{1}H and ^{13}C NMR spectra were recorded at r.t. on a Bruker AC 200 MHz spectrometer. All spectra were referenced to deuterated solvent (THF-d_8) as an internal standard.

All reactions were carried out by using standard Schlenk techniques under argon. Prior to use, THF was dried (KOH) and distilled (Na/benzophenone). Calcium (granules, 99%), distilled calcium (dendritic pieces, 99.5%), iodobenzene, bromobenzene, chlorobenzene, 1,4-diiodobenzene, 4-iodoanisole, 4-chloro-1-iodobenzene, bromopentafluorobenzene, iodopentafluorobenzene, 2-bromomesitylene, 4-iodotoluene, 5-bromo-1,2,3-trifluorobenzene, 1-iodonaphthalene, 2-iodomesitylene were used as purchased without further purification. 4-Fluoro-1-iodobenzene and 4-iodo-*N*,*N*-dimethylaniline were prepared from the corresponding Grignard compounds, obtained from magnesium and 4-fluoro-1-bromobenzene and 4-bromo-*N*,*N*-dimethylaniline, respectively, and then cleaved with iodine. 1-Iodo-2,6-dimethoxybenzene was prepared from 1,3-dimethoxybenzene, *n*-butyllithium and iodine.[18] Acid-base titrations to determine the metal content were conducted with HCl (0.1 mol·L^{-1}) using phenolphthalein as an indicator.

Activation of Calcium Metal

A Schlenk flask was equipped with calcium granules and glass balls (5 mm diameter, ca. 2 g per 1 mmol Ca) and cooled to –60 °C. Then a stream of gaseous ammonia was bubbled through the flask to form liquid ammonia, which dissolves the calcium metal. After all calcium had dissolved, the ammonia was removed at r.t. in vacuo. During this process, the dark blue solution gave a gold-colored solid, which lost further ammonia to yield activated calcium as a grey, pyrophoric powder. This activated calcium was dried in vacuo for at least 5 h prior to use for the direct synthesis.

Arylcalcium Halides; General Procedure

A Schlenk flask with activated calcium and glass balls was filled with THF and cooled to 0 °C. Then, half of a stoichiometric equivalent of the aryl halide was slowly added. Thereafter, the flask was shaken at 0 °C for 1 h and for additional 6 h at r.t. The obtained, brownish suspension was filtered through a Schlenk frit, covered with diatomaceous earth and the residue was washed with THF (2 × 5 mL). The conversion was determined by acidic consumption of a hydrolyzed aliquot of the filtrate. By cooling this solution to –90 °C, the precipitation of the appropriate arylcalcium halide resulted within one day, which was isolated at this temperature and dried in vacuo. The THF content was determined by titration of a definite mass of each compound.

The particular size of the procedures as well as the ^{1}H NMR data are summarized in Table 3, yields are given in Table 2. NMR data of the diarylcalcium derivatives which can be seen in the Schlenk equilibrium are given below.

4-Methoxyphenylcalcium Iodide (6)

4-$MeOC_6H_4CaI$/(4-$MeOC_6H_4)_2Ca$ in a ratio of 77:23 (25 °C) and 91:9 (–50 °C); CaR_2:

^{1}H NMR: δ = 3.72 (s, 3 H, CH_3O), 6.68 (BB′, *J* = 7.2 Hz, 2 H, H-3 + H-5), 8,08 (AA′, *J* = 7.2 Hz, 2 H, H-2 + H-6).

^{13}C{^{1}H} NMR: δ = 55.2 (1 C, CH_3O), 112.5 (2 C, C-3 + C-5), 143.9 (2 C, C-2 + C-6), 159.6 (1 C, C-4), 173.9 (1 C, C-1).

4-Dimethylaminophenylcalcium Iodide (7)

4-$Me_2NC_6H_4CaI$/(4-$Me_2NC_6H_4)_2Ca$ in a ratio of 74:26 (25 °C) and 69:31 (–50 °C); CaR_2:

^{1}H NMR: δ = 2.78 [s, 6 H, $(CH_3)_2N$], 6.64 (BB′, ^3J = 8.0 Hz, 2 H, H-3 + H-5), 8.06 (AA′, *J* = 7.6 Hz, 2 H, H-2 + H-6).

^{13}C{^{1}H} NMR: δ = 39.6 [1 C, $(CH_3)_2N$], 112.2 (2 C, C-3 + C-5), 142.8 (2 C, C-2 + C-6), 149.5 (1 C, C-4), 169.5 (1 C, C-1).

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Table 3 Experimental Details for the Direct Synthesis of Arylcalcium Halides Aryl-Ca(THF)$_n$X and THF Content n and ^{1}H NMR Data

Compound	Amount of Ca	Amount of Aryl-X	n	^{1}H NMR (THF-d_8), δ, *J* (Hz)
1a	2.25 g/56.1 mmol	5.73 g/28.1 mmol	4	6.62 (*p*-H), 6.75 (*m*-H), 7.60 (*o*-H)
1b	0.55 g/13.7 mmol	1.08 g/6.86 mmol	4	6.7 (*p*-H), 6.81 (*m*-H), 7.80 (*o*-H)
2	0.66 g/16.5 mmol	2.60 g/11.9 mmol	4	2.06 (*p*-Me), 6.60 (*m*-H), 7.50 (*o*-H)
3	1.14 g/28.4 mmol	4.69 g/14.2 mmol	6	7.12 (*m*-H), 7.44 (*o*-H) (^3J = 7.4)
4	2.00 g/49.9 mmol	5.95 g/25.0 mmol	4	6.78 (*m*-H), 7.61 (*o*-H) (^3J = 7.6)
5	1.63 g/40.7 mmol	4.51 g/20.3 mmol	5	6.52 (*m*-H), 7.57 (*o*-H) (^3J = 7.8)[a]
6	1.08 g/26.9 mmol	3.15 g/13.5 mmol	4	3.69 (OMe), 6.45 (*m*-H), 7.53 (*o*-H)
7	1.09 g/27.2 mmol	3.36 g/13.6 mmol	5	2.69 [NMe_2], 6.41 (*m*-H), 7.53 (*o*-H)
8	1.50 g/37.4 mmol	4.94 g/18.7 mmol	2.5	3.69 (OMe), 6.39 (*m*-H), 6.91 (*p*-H)
12	1.78 g/44.4 mmol	5.64 g/22.2 mmol	4	–[b]

[a] $^3J_{H,F}$ = 11.6 Hz, $^4J_{H,F}$ = 8.8 Hz.
[b] ^{1}H NMR: δ = 7.04 (dd, ^3J = 6.0 Hz, ^3J = 8.0 Hz, 1 H, H-3), 7.12 (dt, ^4J = 1.6 Hz, ^3J = 6.8 Hz, 1 H, H-6 or H-7), 7.16 (dt, ^4J = 1.6 Hz, ^3J = 6.8 Hz, 1 H, H-7 or H-6), 7.28 (d, ^3J = 8.0 Hz, 1 H, H-4), 7.54 (dd, ^4J = 1.6 Hz, ^3J = 7.6 Hz, 1 H, H-5), 7.87 (d, ^3J = 5.2 Hz, 1 H, H-8), 7.94 (d, ^3J = 8.0 Hz, 1 H, H-2).

Crystal Structure Determination of 12

Cooling of a solution of **12** in THF to 0 °C led to the formation of single crystals suitable for an X-ray structure determination. The intensity data for the compounds were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz, polarization effects and for absorption effects.[19–21] The structure was solved by direct methods (SHELXS)[22] and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97).[23] The hydrogen atoms were included at calculated positions with fixed thermal parameters. Without the disordered THF molecule all non-hydrogen atoms were refined anisotropically.[23] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data of 12[24]

$C_{26}H_{39}CaIO_4$, M = 582.55 g mol^{-1}, colorless prism, size 0.09 × 0.09 × 0.04 mm^3, orthorhombic, space group *Pnma*, *a* = 23.5829(9), *b* = 13.4343(5), *c* = 8.7749(2) Å, V = 2780.06(16) Å^3, T = –90 °C, Z = 4, ρ_{calcd} = 1.392 gcm^{-3}, μ (Mo-K_α) = 13.63 cm^{-1}, multiscan, $trans_{min}$: 0.7456, $trans_{max}$: 0.9600, F(000) = 1200, 16108 reflections in h(–30/30), k(–17/12), l(–11/9), measured in the range 2.30° ≤ Θ ≤ 27.47°, completeness Θ_{max} = 99.5%, 3312 independent reflections, R_{int} = 0.0635, 2284 reflections with $F_o > 4\sigma(F_o)$, 158 parameters, 0 restraints, $R1_{obs}$ = 0.0602, $wR2_{obs}$ = 0.1564, $R1_{all}$ = 0.0928, $wR2_{all}$ = 0.1777, GOOF = 1.042, largest difference peak and hole: 1.288/–1.869 e Å^{-3}.

Acknowledgment

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(24) CCDC-627216 contains the supplementary crystallographic data for compound **12**. These 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, UK; fax: +44(1223)336 033; or deposit@ccdc.cam.ac.uk).

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