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Arylcalcium halides as substrates in Kumada-type cross-coupling reactions

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ABSTRACT

A precondition of a Kumada-type cross-coupling reaction with arylcalcium halides is the easy availability of these organometallics. Arylcalcium halides are accessible with high yields via reduction of arylhalides with activated calcium in ethers such as tetrahydrofuran. In order to demonstrate the generality of this Grignard-type reduction of haloarenes, [(4-BrC_6H_4)CaI(thf)$_4$] (**1**) and [(β-naphthyl)CaBr(thf)$_4$] (**2**) are prepared. First investigations regarding arylcalcium halides as substrates in cross-coupling reactions are undertaken choosing [(C_6H_5)CaI(thf)$_4$] (**3**) and [(4-$CH_3C_6H_4$)CaI(thf)$_4$] (**4**) as the organometallic substrate in a cross-coupling with chlorobenzene and 4-chlorotoluene. The nickel-mediated conversion of arylcalcium iodides and chloroarenes to (substituted) biphenyls proceeds with moderate yields and significant amounts of homo-coupling products are observed.

1. Introduction

Calcium-based organometallics are currently gaining importance due to many factors [1]. First of all, suitable minerals for the calcium production are widespread and available in enormous quantities; guaranteeing its worldwide accessibility at low prices. Furthermore, the calcium cation is considered non-toxic regardless of its concentration [2], making calcium-based reagents and catalysts an interesting choice for the synthesis of drugs and other compounds with potential medical applications, since residual calcium contents in the products do not add health risks and therefore do not have to be removed. Consequently, calcium-based catalysis attracted much attention and led to the development of calcium-mediated hydroamination, hydrosilylation, hydrophosphanylation, and other catalytic processes in recent years [3].

The attractiveness of organocalcium reagents is also based on the low electronegativity (comparable to lithium leading to very heteropolar Ca–C bonds with a high reactivity) and the possibility of d-orbital participation (comparable to early transition metals with catalytic activity). In case of arylcalcium derivatives, improvements of the direct Grignard-type synthesis and refined protocols for subsequent derivatizations led to a tremendous development of their organocalcium chemistry [4].

In contrast to the related benzylcalcium and allylcalcium derivatives [5], the potential of arylcalcium reagents in organic syntheses remained almost uninvestigated. Only one example of a directed ortho-metalation reaction [6] and one of an oligomerization reaction of nitriles involving arylcalcium compounds have been briefly mentioned [7]. Here we investigate if arylcalcium halides can serve as substrates in nickel-catalyzed Kumada-type cross-coupling reactions. In general nickel-mediated cross-coupling reactions represent a powerful tool for the formation of C–C bonds involving sp^2- and also sp^3-hybridized carbon atoms [8,9]. Typically, in the presence of catalytic amounts of Ni^0 (or Pd^0) complexes the reaction of the Grignard reagent R-Mg-X with R′-X yields R–R′. The reaction mechanism of this Kumada-type coupling is discussed in detail in several general text books and reviews [10,11].

2. Results and discussion

2.1. Availability of arylcalcium halides

The use of arylcalcium halides as substrates in organic synthesis requires a straight forward approach to these calcium-based reagents. Although the synthesis of first derivatives via a Grignard-analogous reaction dates back to the beginning of the 20th century [12], reliable and easily applicable protocols based on those early results were just developed within the last decade [13] and recently refined to overcome existing limitations e.g. in case of halosubstituted polycyclic aromatic carbons as substrates [14].

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Finely divided calcium powders, generated by dissolution of the bulk metal in ammonia and subsequent reduction of the resulting solution to dryness, are nowadays commonly used and allow the synthesis of a variety of arylcalcium iodides and bromides [4]. Doubly metalated derivates are also accessible [15]. Chloroarenes are not suitable as substrates for Grignard-type reactions with activated calcium, in contrast to magnesium. THF and THP are the most commonly used solvents. In order to demonstrate the generality of this Grignard-type reduction of haloarenes, we prepared [(4-BrC_6H_4)CaI(thf)$_4$] (**1**) and [(β-naphthyl)CaBr(thf)$_4$] (**2**) showing that even halogeno-substituted arylcalcium halides are accessible by this procedure (Scheme 1).

The molecular structures and numbering schemes of [(4-BrC_6H_4)CaI(thf)$_4$]·0.5 THF (**1**) and [(β-naphthyl)CaBr(thf)$_4$] (**2**) are depicted in Figs. 1 and 2. In contrast to the closely related derivatives [(α-naphthyl)Ca(μ-Br)(thf)$_3$]$_2$ [16] and [(phenanthryl)Ca(μ-Br)(thf)$_3$]$_2$ [14b], compound **2** is monomeric in solid state as it was also observed for [(C_6H_5)CaBr(thf)$_4$] [17] and [(phenanthryl)CaBr(thp)$_4$] [14b]. In **1** and **2**, the aryl group and the halide ion are trans-arranged due to electrostatic reasons. The structure of **2** contains a crystallographic mirror plane containing the naphthylcalcium-bromide fragment. The Ca–C bond lengths of 257.2 (6) and 256.9 (5) pm lie in the expected region [4].

For our first investigations regarding arylcalcium halides as substrates in cross-coupling reactions we have chosen [(C_6H_5)CaI(thf)$_4$] (3) [17] and [(4-$CH_3C_6H_4$)CaI(thf)$_4$] (**4**) [17] in order to limit side-reactions caused by any functional groups.

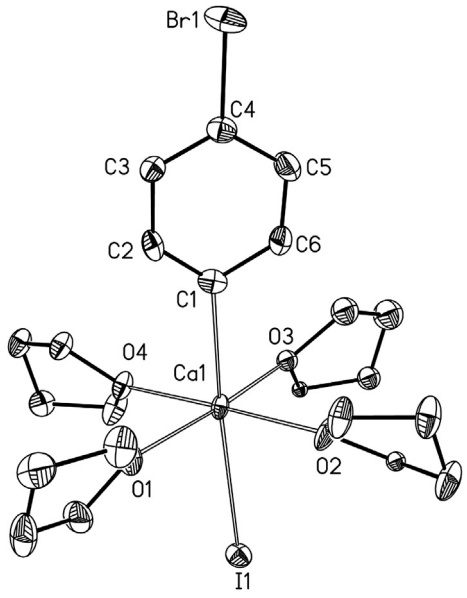


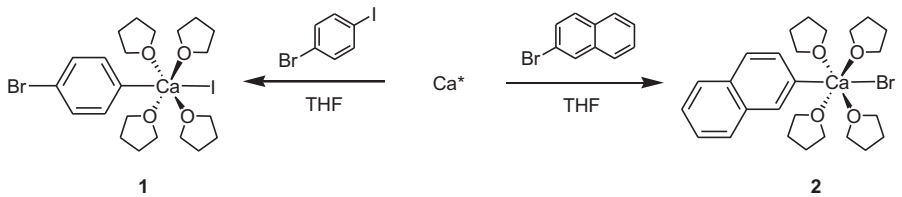
Fig. 1. Molecular structure and numbering scheme of [(4-BrC_6H_4)CaI(thf)$_4$]·0.5 THF (**1**). The ellipsoids represent a probability of 40%, H atoms are omitted for clarity reasons. In addition, the THF molecule in the gap between the calcium-based organometallics is neglected. Selected bond lengths (pm): Ca1–C1 257.2(6), Ca1–I1 311.81(12), Ca1–O1 238.2(4), Ca1–O2 235.0(4), Ca1–O3 243.3(9), Ca1–O4 239.7(4), Br1–C4 194.8(7); angle (deg.): C1–Ca1–I1 173.59(14).

2.2. Nickel-mediated cross-coupling reaction with arylcalcium iodides

In absence of a suitable nickel- or palladium-based catalyst, [(C_6H_5)CaI(thf)$_4$] (3) does not react with chlorobenzene to form biphenyl in a Wurtz-type reaction (Table 1, entry 1). The corresponding experiment with iodobenzene (Table 1, entry 2) did not result in biphenyl formation either [18], although biphenyl was observed as a by-product in the synthesis of **3** in an earlier investigation [19]. In order to confirm this fact, the mother liquor of the synthesis of **3** was hydrolyzed, extracted with chloroform and analyzed by gas chromatography. Biphenyl and unreacted iodobenzene are the only high boiling by-products observed. Together with the above mentioned experiment, it can be concluded that this biphenyl formation is rather the result of a reaction of metallic calcium and iodobenzene than of a reaction between phenylcalcium iodide and iodobenzene. It is likely that its formation is closely related to the radical conditions of the Grignard-type reaction.

The catalytic coupling experiments were performed in 0.1M solution of the arylcalcium iodides [(C_6H_5)CaI(thf)$_4$] (**3**) or [(4-$CH_3C_6H_4$)CaI(thf)$_4$] (**4**) in THF with equimolar amounts of either chlorobenzene or 4-chlorotoluene. [(dppp)$NiCl_2$] [dppp = 1,3-bis(diphenylphosphanyl)-propane] was employed as the pre-catalyst (see Scheme 2 and Table 1).

Using 5 mol% of [(dppp)$NiCl_2$], the nickel-mediated homo-coupling of phenylcalcium iodide with chlorobenzene as well as of 4-tolylcalcium iodide with 4-chlorotoluene gave conversion rates of 62% and 67% of the haloarenes after 24 h and yielded the corresponding symmetric products biphenyl and 4,4′-dimethylbiphenyl in yields of 56% and 52%, respectively. Although complete conversion of the halobenzenes was not anticipated because 10% of the arylcalcium reagent is expected to be consumed in the activation process of the precatalyst, the observed conversion is significantly lower than the achievable mark of 90%. A possible explanation is the known instability of arylcalcium reagents in THF at ambient temperature. It was reported that around 15% of tolylcalcium iodide decomposes within 24 h in THF at room temperature via solvent degradation reactions [14a]. The performed cross-coupling experiments of phenylcalcium iodide **3** with 4-chlorotoluene led to the formation of all possible biphenyl derivatives, namely biphenyl, 4-methylbiphenyl, and 4,4′-dimethylbiphenyl with a ratio of 23:23:5. In a complementary experiment, using **4** and chlorobenzene (see Table 1, entry 5), the three products were detected in a ratio of 7:32:21. In both cases, the desired product 4-methylbiphenyl is accompanied by large amounts of the homo-coupling product derived from the arylcalcium component of the reaction. Part of these homo-coupling products stems from the activation of the precatalyst [(dppp)$NiCl_2$] by arylcalcium iodide yielding [(dppp)Ni(Ar)$_2$] followed by the reductive elimination of biphenyls and formation of catalytically active Ni^0 species. The contribution of this activation reaction to the overall formation of homo-coupling products can be minimized by reduction of the catalyst loading. However, the



Scheme 1. Syntheses of **1** and **2**.

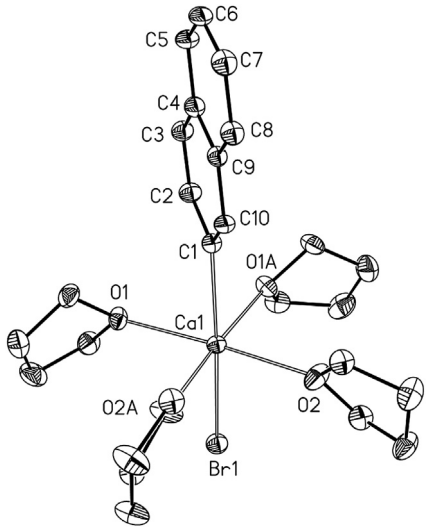


Fig. 2. Molecular structure and numbering scheme of [(β-naphthyl)CaBr(thf)$_4$] (**2**). The ellipsoids represent a probability of 40%, H atoms are not shown for the sake of clarity. The molecule contains a mirror plane (×, -y, z) and symmetry-related atoms are marked with the letter "A". Selected bond lengths (pm): Ca1–C1 256.9(5), Ca1–Br1 298.96(8), Ca1–O1 238.8(2), Ca1–O2 237.1(2); angle (deg.): C1–Ca1–Br1 173.56 (12).

employment of only 0.5 mol% catalyst just halves the overall product yield with an insignificant improvement of the selectivity of the system (Table 1, entry 7).

In order to gain further information on the catalysis, the reaction mixture of run 6 was investigated after 24 h by ^{31}P{H} NMR measurement. Surprisingly, only one phosphorus containing species was detected. The observed singlet at δ 11.8 (THF/d$_8$-THF) was assigned to [(dppp)$_2$Ni] in agreement with the literature value [20]. This assignment was further confirmed by comparison with an authentic sample, independently prepared from [(cod)$_2$Ni] (cod = 1,5-cyclooctadiene) and two equivalents of dppp.

Due to the rather large difference in electronegativity between strongly electropositive calcium (Allred–Rochow electronegativity EN: 1.04 [21]) and nickel (EN: 1.75 [21]), the observed lacking selectivity of the catalytic system and the detection of [(dppp)$_2$Ni], it can be assumed that the investigated catalysis does not proceed via the commonly accepted mechanism. Instead of neutral nickel(II) and nickel(0) compounds, we propose the formation of calcium nickelates as key intermediates of the system according to Scheme 3.

Similar compounds of other s-block metals e.g. [{(thf)$_2$Li}$_2${(μ-Ph)$_4$Ni}] are well documented [22]. Furthermore, this lithium complex is known to undergo reductive elimination of biphenyl in presence of phenyllithium [23] and it was shown that it is an active but rather unselective catalyst in Kumada-type cross-coupling reactions even in absence of supporting neutral phosphane ligands [22b]. Arylcalcium iodides have properties and reactivities similar to their lithium congeners and the ability of arylcalcium iodides to transfer aryl groups to transition metals is well documented [24].

3. Conclusion and perspective

Arylcalcium halides are easily accessible substrates for catalytic coupling reactions. These organometallics can be prepared via the reduction of iodoarenes in THF; even bromo substituents and fused aromatic systems represent useful substrates in this Grignard-type reaction. Thus, [(4-BrC$_6$H$_4$)CaI(thf)$_4$] (**1**) and [(β-naphthyl)CaBr(thf)$_4$] (**2**) were prepared by this procedure.

[(C$_6$H$_5$)CaI(thf)$_4$] (3) and [(4-CH$_3$C$_6$H$_4$)CaI(thf)$_4$] (**4**) were chosen for initial testing of the suitability of these substrates in Kumada-type homo- and cross-coupling reactions with chlorobenzene and 4-chlorotoluene. In all catalytic cross-coupling reactions all possible products biphenyl, 4-methylbiphenyl and 4,4′-dimethylbiphenyl were detected. This finding was ascribed to the intermediate formation of tetraarylnickelate anions.

Summarizing the catalytic nickel-mediated Kumada-type cross coupling with arylcalcium iodides and chloroarenes being the substrates the following conclusions can be drawn:

1. Without nickel-mediated catalysis arylcalcium iodides do not react with chloroarenes or iodoarenes in a Wurtz-type coupling reaction.
2. The nickel-mediated conversion of arylcalcium iodides and chloroarenes to (substituted) biphenyls proceeds with moderate yields.
3. The selectivity of the cross-coupling is rather poor and significant amounts of homo-coupling products are found.

4. Experimental

4.1. General comments

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$_4$Si as an external standard. The residual signals of [D$_8$]THF were used as an internal standard. Data are reported as follows: s = singlet; m = multiplet; br = broad.

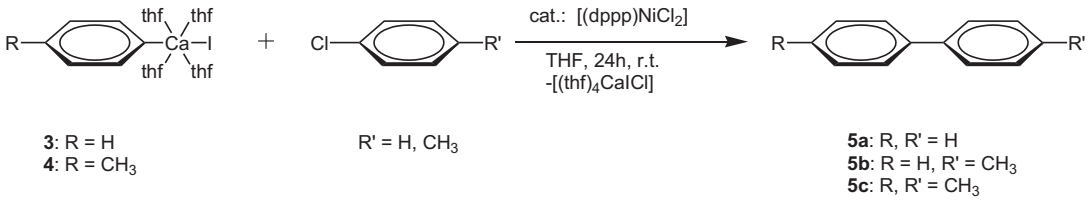
Gas chromatographic investigation was performed on a Varian CP-3800 gas chromatograph equipped with a Varian CP8410 autoinjector and a FactorFour Capillary Column VF-1 ms, 15 m × 0.25 mm ID.

Calcium was activated by dissolution in liquid NH$_3$ and subsequent reduction of the deep blue solution to dryness, resulting in

Table 1
Coupling experiments of arylcalcium iodides and haloarenes.

Entry	Arylcalcium iodide	Substrate	Catalyst [mol %]	Conversion of haloarene	Yield [%][a] 5a	Yield [%][a] 5b	Yield [%][a] 5c
1	**3**	PhCl	0	<1	–	–	–
2	**3**	PhI	0	<5	–	–	–
3	**3**	PhCl	5	62	56	–	–
4	**4**	TolCl[b]	5	67	–	–	52
5	**4**	PhCl	5	70	7	32	21
6	**3**	TolCl[b]	5	56	23	23	5
7	**3**	TolCl[b]	0.5	30	10	12	3

[a] GC yields using mesitylene as an internal standard.
[b] TolCl = 4-chlorotoluene.



Scheme 2. Cross-coupling reaction of arylcalcium iodides and chloroarenes.

finely divided calcium powders. The complexes $[(C_6H_5)CaI(thf)_4]$ (3) and $[(4\text{-}CH_3C_6H_4)CaI(thf)_4]$ (**4**) were prepared according to known procedures [17] and recrystallized from THF before use. The precatalyst $[(dppp)NiCl_2]$ was prepared as reported previously [25]. Chlorobenzene and 4-chlorotoluene were obtained from commercial sources, dried over calcium hydride and distilled before use.

The calcium content of the products was determined by complexometric titration of a hydrolyzed aliquot with 0.05 M EDTA using Eriochrome BlackT as the indicator [26].

4.2. Synthesis of $[(4\text{-}BrC_6H_4)CaI(thf)_4]$ (1)

Activated calcium (1.20 g, 29.9 mmol) was suspended in tetrahydrofuran (32 mL) and 4-bromo-iodobenzene (7.07 g, 25.0 mmol) was added at −20 °C. The resulting suspension was shaken for 1 h at 0 °C, warmed to ambient temperature and shaken for additional 4 h at this temperature. Thereafter, residual calcium was removed by filtration using a Schlenk frit covered with diatomaceous earth. The conversion (66.0%) was determined by acidimetric titration of an aliquot of the resulting brown solution. The mother liquor was stored at −40 °C for 4 days. The formed colorless crystals were isolated by filtration and were dried in vacuo. Yield of **1**: 2.89 g (4.73 mmol, 18.9%). Anal. Calcd. for $C_{22}H_{36}CaIBrO_4$ (611.41 g mol^{-1}): Ca 6.56%; found: Ca 6.90%. ^1H NMR ([D8]THF, 600 MHz): δ 1.77 (m, 16H, CH_2 thf), 3.63 (m, 16H, OCH_2 thf), 6.96 (AA′ part of an AA′BB′ spin system, 2H, CH), 7.61 (BB′ part of an AA′BB′ spin system, 2H, CH). $^{13}C\{^1H\}$ NMR ([D8]THF, 150.9 MHz): δ 26.3 (8C, CH_2 thf), 68.2 (8C, OCH_2 thf), 117.9 (1C, C–Br), 127.8 (2C, CH), 143.0 (2C, CH), 188.5 (1C, C–Ca). Suitable crystals for X-ray diffraction experiments of the composition $[(4\text{-}Br\text{-}C_6H_4)Ca(I)(thf)_4] \cdot 0.5$ THF were obtained by recrystallization from THF at −40 °C.

4.3. Synthesis of $[(\beta\text{-naphthyl})CaBr(thf)_4]$ (2)

Finely divided calcium (0.58 g, 14.5 mmol) was suspended in 20 mL of THF and the suspension was cooled to −20 °C. At this temperature 2.40 g (11.6 mmol) of β-bromonaphthalene and 0.21 g (0.81 mmol) of iodine were added and the mixture was warmed to 0 °C while shaking. After 1 h at 0 °C the reaction mixture was shaken for additional 5 h at ambient temperature. The resulting dark violet mixture was filtered through a Schlenk frit covered with diatomaceous earth. The solid residue was extracted with THF (40 mL) and discarded afterward. The combined THF solutions (67.4% yield of organocalcium compounds, determined by acid consumption by a hydrolyzed aliquot) were stored at −40 °C for 2 days. The precipitated crystalline solid was collected on a cooled Schlenk frit and dried in vacuo. Yield of **2**: 1.10 g (2.07 mmol, 17.9%) crude product, containing a very small amount of a dark violet impurity. Anal. Calcd. for $C_{26}H_{39}CaBrO_4$ (535.58 g mol^{-1}): Ca 7.48%; found: Ca 7.15%. ^1H NMR ([D8]THF, 400 MHz): δ 1.77 (m, 12H, CH_2 thf), 3.62 (m, 12H, OCH_2 thf), 7.05 (m, 1H, CH), 7.12 (m, 1H, CH), 7.31 (m, 1H, CH), 7.51 (m, 2H, CH), 7.99 (m, 1H, CH), 8.19 (br, 1H, CH). ^{13}C NMR ([D8]THF, 100.6 MHz): δ 26.3 (8C, CH_2 thf), 68.1 (8C, OCH_2 thf), 122.1 (1C, CH), 122.2 (1C, CH), 123.3 (1C, CH), 127.4 (1C, CH), 127.8 (1C, CH), 132.8 (1C, C), 133.8 (1C, C), 139.7 (1C, CH), 141.1 (1C, CH), 189.7 (1C, C–Ca). Suitable colorless crystals for X-ray diffraction experiments of the composition $[(\beta\text{-Naph})Ca(Br)(thf)_4]$ were obtained by recrystallization from THF at −40 °C.

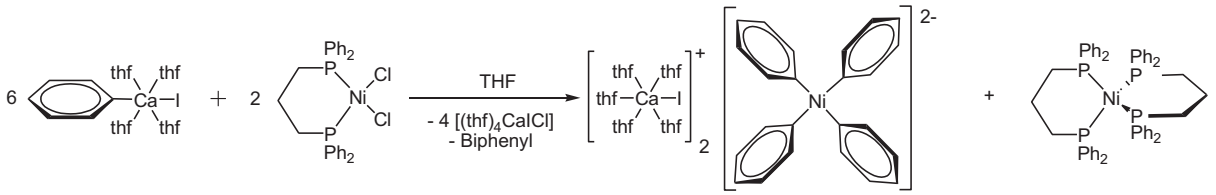
4.4. Coupling reaction (typical procedure)

The arylcalcium iodide (2 mmol) was dissolved in THF (20 mL). Afterward, the chlorosubstituted arene (2 mmol), solid $[(dppp)NiCl_2]$ (0.1 mmol) as catalyst and mesitylene (100 μL) as internal standard were added to the solution in that order. The resulting reaction mixture was stirred for 24 h at ambient temperature. Thereafter, a sample of the solution was hydrolyzed with 2 M hydrochloric acid (2 mL) and extracted with *n*-heptane (1 mL). The organic phase was analyzed by gas chromatography.

4.5. Crystal structure determinations

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data was corrected for Lorentz and polarization effects but not for absorption effects [27,28].

The structures were solved by direct methods (SHELXS [29]) and refined by full-matrix least squares techniques against F_0^2 (SHELXL-97 [29]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically [29]. Crystallographic data as well as structure solution and refinement details are summarized in Table 2. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.



Scheme 3. Proposed formation of calcium nickelates.

Table 2
Crystal data and refinement details for the X-ray structure determinations of [(4-BrC_6H_4)CaI(thf)$_4$]·0.5 THF (**1**) and [(β-naphthyl)CaBr(thf)$_4$] (**2**).

Compound	**1**	**2**
Formula	$C_{22}H_{36}BrCaIO_4{}^*$ 0.5C_4H_8O	$C_{26}H_{39}BrCaO_4$
fw (g mol^{-1})	647.45	535.56
T/°C	−140 (2)	−140 (2)
Crystal system	Triclinic	Monoclinic
Space group	P $\bar{1}$	C m
a/Å	9.4871 (3)	12.1895 (5)
b/Å	11.7654 (3)	13.4158 (4)
c/Å	12.6768 (3)	8.3097 (3)
α/°	91.907 (2)	90
β/°	97.181 (1)	100.350 (2)
γ/°	96.539 (1)	90
V/Å^3	1393.13 (7)	1336.79 (8)
Z	2	2
ρ (g cm^{-3})	1.543	1.331
μ (cm^{-1})	27.95	17.57
Measured data	9075	3774
Data with I > 2σ(I)	5434	2450
Unique data/R_{int}	6260/0.0228	2494/0.0203
wR_2 (all data, on F^2)[a]	0.1658	0.0752
R_1 ($I > 2\sigma(I)$)[a]	0.0657	0.0275
s[b]	1.070	1.121
Res. dens./e Å^{-3}	2.367/−1.326	0.351/−0.490
CCDC No.	942049	942050

[a] Definition of the R indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \mathrm{Max}(F_o^2)]/3$.
[b] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

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Appendix A. Supplementary material

CCDC 942049 and 942050 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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