

Reduction of azobenzene by neodymium(II), dysprosium(II), and thulium(II) diiodides

Marina A. Katkova, Georgy K. Fukin, Anatolii A. Fagin, Mikhail N. Bochkarev*

Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Tropinina 49, 603950 Nizhny Novgorod, Russia

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Abstract

The diiodides of divalent neodymium (**1**), dysprosium (**2**), and thulium (**3**) LnI_2 readily reduce azobenzene under ambient conditions to give binuclear complexes $[\text{LnI}(\text{THF})_2]_2(\text{N}_2\text{Ph}_2)_2$ ($\text{Ln} = \text{Nd}$ (**4**), Dy (**5**), Tm (**6**)). Magnetic measurements and X-ray structural analyses of **5** and **6** revealed that the bridging N_2Ph_2 ligands are dianions bounded to the trivalent lanthanoid. The complexes displayed photochromic properties. Ytterbium iodide $\text{YbI}_2(\text{THF})_2$ reacts with N_2Ph_2 at 80°C yielding the known $[\text{YbI}(\text{THF})_3]_2(\text{N}_2\text{Ph}_2)_2$ (**7**).

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Keywords: Lanthanoid complexes; Azobenzene; Diiodides; Dysprosium; Neodymium; Thulium

1. Introduction

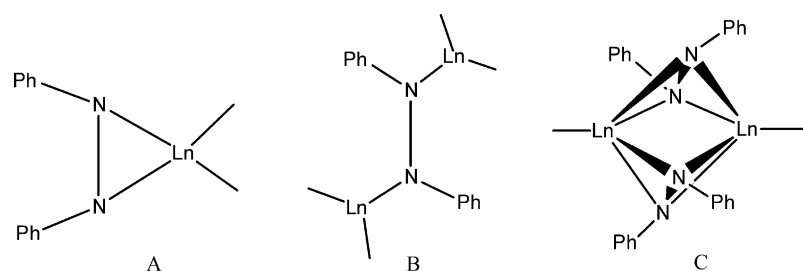
It has previously been shown that divalent neodymium (**1**), dysprosium (**2**), and thulium (**3**) diiodides are powerful reducing agents [1]. Addition of alkyl halides to ketones in the presence of **2** and **3** proceeds faster and more easily than with SmI_2 [1a,1b]. Oxidative addition to **3** was observed in the reactions with 3,6-di(*tert*-butyl)catecholate, 3,6-di(*tert*-butyl)benzoquinone-1,2, [1c], cyclooctatetraene, acenaphthylene [1d] and calix[4]arene [1e]. Dysprosium diiodide **2** adds to naphthalene and diphenylacetylene [1a]. Interaction of **2** or **3** with acetonitrile is accompanied by C–C coupling and formation of novel bis(imine)amine complexes $[(\text{HN}=\text{CMe})_2\text{MeCNH}_2]\text{Ln}(\text{MeCN})_6\text{I}_3$ [1f]. In most reactions the triiodides $\text{LnI}_3(\text{solvent})_x$ were isolated as the second product in high yield indicative of disproportionation of the starting LnI_2 or initially formed products of the type RLnI_2 . The data obtained in the reactions of **1** and **2** with benzene and other aromatic compounds in THF solutions support the first mechanism [1g].

In continuation of these investigations we have studied the reactions of the indicated iodides with azobenzene. In the past, azobenzene was involved in the reactions with $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$, $\text{Cp}_2\text{Yb}(\text{THF})_2$, the samarium pyrazolylborate complex Tp_2Sm ($\text{Tp} = \text{hydrotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate}$) [3], a mixture of Ln and I_2 ($\text{Ln} = \text{Sm}, \text{Yb}$) [4], and naphthalene complexes of samarium and ytterbium $\text{C}_{10}\text{H}_8\text{Ln}(\text{THF})_3$ [5]. In the reactions with metallocenes the complexes of the type $(\text{Cp}_2\text{Ln})_2\text{N}_2\text{Ph}_2$, $\text{Cp}_2\text{LnN}_2\text{Ph}_2$ or $(\text{CpLn})_2(\text{N}_2\text{Ph}_2)_2$ were isolated depending on a reagents ratio. The products revealed different arrangement of Ln -azobenzene fragments: **A**, **B**, or **C**, respectively.

The samarium pyrazolylborate complex afforded the product $(\text{Tp})_2\text{Sm}(\text{N}_2\text{Ph}_2)$ with the **A** type of central fragment whereas a mixture of lanthanoid metals and iodine gave the binuclear complex $[\text{SmI}(\text{THF})_3]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-trans-N}_2\text{Ph}_2)_2$ of **C** type. In all the cases azobenzene was subjected to one- or two-electron reduction. Quite different tetranuclear clusters $[\text{Ln}_4(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-Ph-N=N})_4(\mu_3\text{-PhN})_2(\text{THF})_x]$ were obtained in the lanthanoid naphthalenide reactions, which were accompanied by combined two- and four-electron reduction. It seemed interesting to study the reduction of Ph_2N_2 by divalent iodides of neodymium, dysprosium and thulium whose reduction power is much higher than that of

* Corresponding author. Tel.: +7-831-266-6795; fax: +7-831-266-1497.

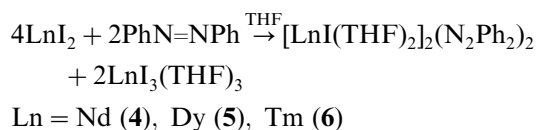
E-mail address: mboch@imoc.sinn.ru (M.N. Bochkarev).



cyclopentadienyl, pyrazolylborate and iodide compounds of Sm(II) or Yb(II) but probably is comparable with the potential of naphthalenelanthanoids.

2. Results and discussion

It was found that all three diiodides **1**, **2**, and **3** react easily with azobenzene in THF solution to give, immediately after mixing under ambient conditions, yellowish solutions. After several days a mixture of the triiodide and the product $[\text{LnI}(\text{THF})_2]_2(\text{N}_2\text{Ph}_2)_2$ ($\text{Ln} = \text{Nd}$ (**4**), Dy (**5**), Tm (**6**)) precipitated from the solution, respectively.



Extraction of the solid mixture with warm THF allows separation of the azobenzene derivatives from LnI_3 , the former being isolated as greenish-yellow solids in 78–82% yield after removal of a solvent from the extract. Their composition was confirmed by elemental analysis, IR spectroscopy and hydrolysis, which afforded quantitatively diphenylhydrazine. The molecular iodide $\text{TmI}_2(\text{THF})_5$ reacts with azobenzene similarly to diiodide **3** affording **6** in 81% yield.

Recrystallization of the obtained complexes from THF does not give good crystals, however the single crystals of **5** and **6** suitable for X-ray analysis were obtained directly from the reaction mixture when the reactions were carried out in dilute solutions. It was found that the dysprosium compound **5** is isostructural

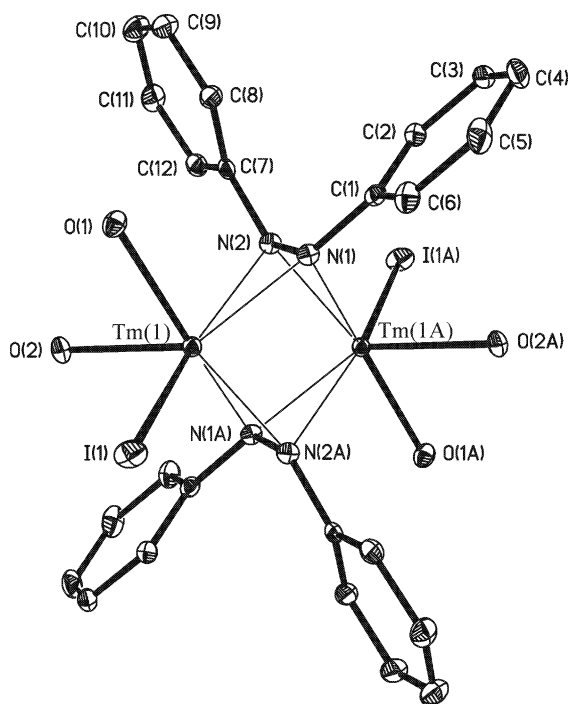


Fig. 1. ORTEP view of the structure of the complex **6** with atom numbering scheme (thermal ellipsoids at 40% probability level).

Table 1
Selected bond lengths (Å) and angles (°) for $[\text{TmI}(\text{THF})_2]_2(\text{N}_2\text{Ph}_2)_2$ (**6**)

Bond lengths	
Tm–I	2.986(1)
Tm(1)–N(1)	2.219(2)
Tm(1)–N(2)	2.460(2)
Tm(1)–N(1A)	2.489(2)
Tm(1)–N(2A)	2.227(2)
N(1)–N(2)	1.471(3)
N(1)–C(1)	1.393(3)
N(2)–C(7)	1.398(3)
Bond angles	
C(1)N(1)N(2)	119.2(2)
C(1)N(1)Tm(1)	156.99(18)
N(2)N(1)Tm(1)	80.88(13)
C(1)N(1)Tm(1A)	110.76(16)
N(2)N(1)Tm(1A)	62.32(12)
Tm(1)N(1)Tm(1A)	87.93(8)
C(7)N(2)N(1)	119.9(2)
C(7)N(2)Tm(1A)	152.39(18)
N(1)N(2)Tm(1A)	81.87(13)
C(7)N(2)Tm(1)	115.81(16)
N(1)N(2)Tm(1)	62.94(11)
Tm(1A)N(2)Tm(1)	88.48(8)

with its thulium analogue **6**, but the poor quality of the data for the former prevented a detailed discussion of its structural features. The molecular structure of **6**, including the atom numbering scheme, is shown in Fig. 1. The most relevant bond distances and angles are collected in Table 1. Complex **6** consists of two TmI(THF)₂ units joined by two bridging N₂Ph₂ ligands. The Tm atoms have a trigonal-bipyramidal coordination. The I atom and one η²-N₂Ph₂ ligand occupy the apical positions but oxygen atoms of two THF molecules and the second η²-N₂Ph₂ ligand are located in the equatorial positions. The structural feature of **6** is quite similar to that of [SmI(THF)₃]₂(μ-η²:η²-*trans*-N₂Ph₂)₂ (**6a**) [4], [(C₅Me₅)(THF)Sm]₂(μ-η²:η²-*trans*-N₂Ph₂)₂ (**6b**) [2], [(C₅H₅)(THF)Yb]₂(μ-η²:η²-*trans*-N₂Ph₂)₂ (**6c**) [2].

The dihedral angle in η²-N₂Ph₂ unit between the planes of the phenyl rings is 68.6° for **6** (76° for **6b**, 45.7° for **6c**). The N(1)–N(2) distance is 1.471(3) Å which is nearly equal to the similar distances in **6a** (1.477(12) Å), **6b** (1.44(1) Å) and **6c** (1.470(6) Å). These distances are much closer to the N–N single bond distance in hydrazine (1.45 Å [6]) than to that of the N=N bond in azobenzene (1.25 Å [6]). The geometry around each nitrogen atom is consistent with an sp³ center. Therefore we can assume the presence of the N₂Ph₂²⁻ ligand. The same situation was found for **6a–6c**.

The Tm(1)–N(1), Tm(1)–N(2) distances are 2.219(2) Å, 2.460(2) Å respectively and a little bit shorter than the Tm(1)–N(1A) (2.489(2) Å) and Tm(1)–N(2A) (2.227(2) Å) distances. It should be noted that the difference between the Tm–N distances in **6** and Sm–N in **6a** is bigger than the difference in ionic radii of the Tm and Sm [7]. Note, the relative Ln–N distances in the compounds **6–6b** are close. A significant difference in the same distances was found only in **6c**. The distances from the Yb atom in **6c** up to the first N₂Ph₂ unit are 2.206(5) and 2.188(5) Å and up to the second N₂Ph₂ unit are 2.487(5) and 2.572(5) Å.

All these data clearly show a trivalent state of Tm in **6** that is confirmed also by magnetic measurements (μ_{eff} = 7.4μ_B).

Our attempts to prepare single crystals of the neodymium complex **4** for X-ray diffraction investigations failed but the data from elemental analysis, hydrolysis and comparison of its IR spectrum with those of **5** and **6** strictly confirm a similarity of molecular structure of all these compounds.

It is well known that azobenzene derivatives are one of the representative photochromic compounds and are used for preparation of various dyes and photo-switching molecular devices [8]. The same feature was found for the complexes **4**, **5** and **6**. Irradiation by sunlight of the yellowish reaction solutions formed immediately after mixing of initial reagents for several minutes caused the color change to green. This property is the

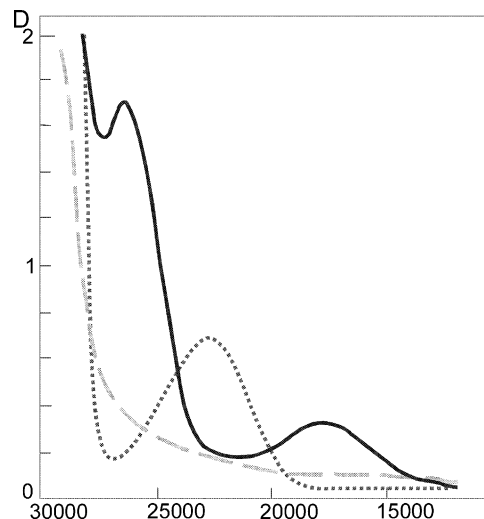


Fig. 2. Electronic spectra of azobenzene (dotted line), reaction solution of **6** freshly prepared (broken line) and after irradiation by sunlight (full line) in THF.

most characteristic for the thulium compound **6**, a solution of which in 20–30 min under sunlight turned deep green and then deep blue. In 5–8 h at ambient temperature the blue solution irreversibly changes color to light brown. UV–vis spectroscopic monitoring of the reaction in THF solution (Fig. 2) revealed that in a few minutes after mixing of reagents the initial absorption band of azobenzene at 447 nm disappeared, which can be assigned to formation of a short-living intermediate in which the azobenzene ligand has lost its initial *trans* configuration. The initial absorption bands of TmI₂ at 420, 581 and 650 nm also are absent in these spectra. After sunlight irradiation two new bands at 383 and 568 nm occur. It should be noted that the green color is typical of Tm(II) compounds but the magnetic measurements of the reaction solution on the green and blue stage indicated the trivalent state of the metal (μ_{eff} = 7.4μ_B). We believe that the intermediate colors could be attributed to metal-to-ligand charge-transfer (MLCT) transitions involving the azobenzene π*(N=N) orbital as was suggested in a photochemical study of dark-green Pt-azobenzene complexes (432 and 592 nm), in which *cis*-azobenzene binds two platinum fragments [9]. Unfortunately our attempts to isolate the green or blue product (which are probably intermediate complexes with non-reduced azobenzene ligand) in crystalline form for X-ray analysis failed.

The reduction potential of divalent ytterbium (–1.15 V) is much lower than that of Tm(II) (–2.22 V [10]) therefore the reaction of YbI₂(THF)₂ with azobenzene proceeds under more drastic conditions (80 °C, 15 h) but yields a product of similar composition: [YbI(THF)₃]₂(N₂Ph₂)₂ (**7**). A structure of the same compound, obtained by the reaction of N₂Ph₂ with ytterbium metal and iodine was established previously

[4]. Interestingly, the reaction solution of the complex **7** in contrast to the **4**, **5** and **6** analogues does not display any color change under sunlight irradiation.

Thus, in spite of high reduction potentials the diiodides of neodymium(II), dysprosium(II) and thulium(II) do not reduce azobenzene to the imido ligand. Under given conditions only two-electron reduction takes place in all the cases. From two possible routes of the reactions (via disproportionation of starting LnI_2 or initially generated $[(\text{LnI}_2)_2(\text{N}_2\text{Ph}_2)]$) the latter seems more plausible since **4**, **5**, and **6** are formed in high yield. A similar scheme has been proposed before for the reactions of azobenzene with $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ and $\text{Cp}_2\text{Yb}(\text{THF})$ [2]. If the reaction would include the disproportionation of LnI_2 , inevitable side reactions of the generated monovalent species LnI with solvent would greatly decrease the yield of the obtained complexes.

3. Experimental

All manipulations were carried under vacuum using Schlenk techniques. Azobenzene was purchased from Aldrich and recrystallized from hexane. NdI_2 (**1**), DyI_2 (**2**) and TmI_2 (**3**) were prepared by modified procedures [11] as described below. $\text{TmI}_2(\text{THF})_5$ and $\text{YbI}_2(\text{THF})_2$ were synthesized according to Refs. [12] and [13], respectively. THF was refluxed continuously over molten alkali metals and collected immediately prior to use. Melting points were taken in sealed capillaries and are uncorrected. IR spectra were obtained on a Perkin–Elmer 577 spectrometer and recorded from 4000 to 450 cm^{-1} as a Nujol mull on KBr plates. Magnetic measurements of solid samples were carried out at room temperature as described previously [14], and magnetic

measurements of solutions were carried out on a Bruker DPX 200 instrument by Evans' NMR method [15].

3.1. Preparation of NdI_2 (**1**)

A mixture of neodymium shavings (100–150 mesh) 3.06 g (21.2 mmol) and 3.63 g (14.3 mmol) of powdered iodine was placed in an ampoule **A** connected via rubber tube **C** to a Pyrex ampoule **B** ($20 \times 70\text{ mm}$), containing a few shavings of Nd (Fig. 3). The system was evacuated, vacuum line was disconnected and the bottom of ampoule **B** was heated by gas-burner up to 200–300 °C. Heating was stopped and a portion of 0.1–0.2 g of Nd/I mixture from ampoule **A** was added to ampoule **B**. From a hot bottom of ampoule **B** the mixture ignited and burned for 2–3 s. At the end of the burning an additional portion of 0.1–0.2 g of the mixture was added to ampoule **B**. The operation was repeated until all Nd/I mixture was transferred to ampoule **B** and burned. The formed black solid was heated for 3–5 min at 400–500 °C under vacuum and allowed to cool. Gentle tapping of ampoule **B** allowed crushing of the black solid to a powder, which was transferred in vacuum a line to another ampoule. Most of the excess neodymium was left in the ampoule **B** as frozen drops. According to the data of complexometry (Found: Nd, 49.99) and hydrolysis the obtained black powder (6.12 g) consisted of NdI_2 (4.8 g, 78%) and Nd metal (1.32 g, 22%). This mixture without additional purification was used in the reaction with azobenzene.

The iodides **2** and **3** were prepared and analyzed similarly.

3.2. Synthesis of $[\text{NdI}(\text{THF})_2]_2(\text{N}_2\text{Ph}_2)_2$ (**4**)

To a Nd/ NdI_2 mixture containing 390 mg (0.98 mmol) of NdI_2 was added with stirring at ambient temperature a solution of azobenzene (89 mg, 0.49 mmol) in 20 ml of THF. The mixture immediately turned pale brown. After 5 min the mixture was filtered through a glass filter and placed in a freezer (–20 °C) for 2 days. The formed mixture of crystals of **4** and $\text{NdI}_3(\text{THF})_3$ were separated from the solution by decantation and washed by hexane. The obtained solid mixture was extracted with warm THF ($2 \times 10\text{ ml}$). Removal of the solvent from the extract in vacuum gave **4** (241 mg, 82%) as yellowish crystals; m.p. > 181 (dec.). Anal. Calc. for $\text{C}_{40}\text{H}_{52}\text{I}_2\text{N}_4\text{Nd}_2\text{O}_4$: C, 40.20; H, 4.39; Nd, 24.14. Found: C, 40.09; H, 4.47; Nd, 24.17%. IR bands (cm^{-1}) 1580 (s), 1295 (m), 1210 (s), 1170 (s), 1075 (m), 1020 (s), 930 (w), 870 (s), 845 (w), 790 (m), 750 (s), 705 (m), 670 (w), 605 (w), 520 (w).

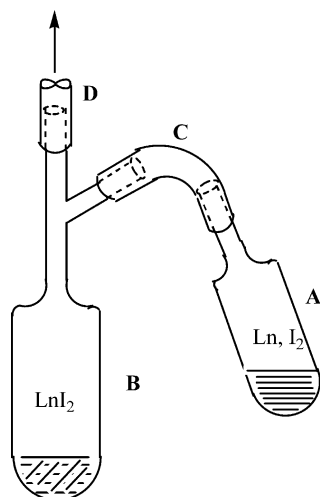


Fig. 3. Diagram of the solid-state apparatus: (A), (B) pyrex ampoules; (C) connecting rubber tube; (D) rubber tube to vacuum line.

3.3. Synthesis of $[DyI(THF)_2]_2(N_2Ph_2)_2$ (**5**)

The compound was prepared similarly to **4** from 400 mg (0.96 mmol) of DyI_2 and 87 mg (0.48 mmol) of azobenzene. Yield of **5**: 231 mg, 78%; m.p. > 182 (dec.). Anal. Calc. for $C_{40}H_{52}Dy_2I_2N_4O_4$: C, 39.01; H, 4.26; Dy, 26.39. Found: C, 38.91; H, 4.41; Dy, 26.43%. IR bands (cm^{-1}) 1600 (s), 1310 (m), 1250 (s), 1160 (m), 1070 (s), 1020 (m), 920 (w), 890 (m), 860 (m), 750 (s), 695 (s), 645 (w), 515 (m).

3.4. Synthesis of $[TmI(THF)_2]_2(N_2Ph_2)_2$ (**6**)

To a solution of $TmI_2(THF)_5$ (478 mg, 0.61 mmol) in THF (10 ml) a solution of azobenzene (55 mg, 0.30 mmol) in THF (10 ml) was added with stirring at ambient temperature. The green color of the solution immediately turned to yellowish upon addition of azobenzene. The solution was placed in a freezer ($-20^\circ C$) for 2 days. The precipitated mixture of greenish-yellow crystals of **6** and colorless crystals of $TmI_3(THF)_3$ was separated by filtration and washed with hexane. To separate **6** and $TmI_3(THF)_3$ the mixture was extracted with warm THF (2×10 ml). Removal of the solvent from the extract gave **6** as a yellow microcrystalline solid. Yield 152 mg (80%); m.p. > 185 (dec.). Anal. Calc. for $C_{40}H_{52}I_2N_4O_4Tm_2$: C, 38.60; H, 4.21; Tm, 27.15. Found: C, 38.52; H, 4.31; Tm, 27.19%. IR bands (cm^{-1}) 1605 (m), 1515 (w), 1330 (m), 1280 (w), 1210 (m), 1170 (m), 1040 (m), 1000 (ws), 920 (s), 830 (ws), 670 (m), 570 (w). $\mu_{eff} = 7.4\mu_B$.

3.5. Synthesis of $[YbI(THF)_3]_2(N_2Ph_2)_2$ (**7**)

To a solution of $YbI_2(THF)_2$ (452 mg, 0.79 mmol) in THF (10 ml) was added a solution of azobenzene (71 mg, 0.39 mmol) in THF (10 ml) with stirring. After stirring the mixture for 15 h at $80^\circ C$ dark red crystals of **7** had formed and settled out of the solution. Yield of **7**: 102 mg, 37%; m.p. > 191 (dec.). Anal. Calc. for $C_{48}H_{68}I_2N_4O_6Yb_2$: C, 41.27; H, 4.91; Yb, 24.77. Found: C, 40.09; H, 5.12; Yb, 24.75%. IR bands (cm^{-1}) 1600 (s), 1300 (m), 1220 (m), 1170 (m), 1070 (s), 1020 (m), 920 (m), 880 (m), 860 (m), 650 (w), 580 (s). $\mu_{eff} = 4.3\mu_B$.

3.6. X-ray crystallography of $[TmI(THF)_2]_2(N_2Ph_2)_2$ (**6**)

Intensity data were collected at 100 K temperature on a Smart Apex diffractometer with graphite monochromated Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$) in the $\varphi-\omega$ scan mode ($\omega = 0.3^\circ$, 10 s on each frame). $[TmI(THF)_2]_2(N_2Ph_2)_2 \cdot 2THF$, empirical formula: $C_{48}H_{68}I_2N_4O_6Tm_2$, $M = 1390.72$, orthorhombic, space group $Pbcn$, $a = 17.744(1)$, $b = 13.2641(8)$, $c = 21.3756(12) \text{ \AA}$, $V = 5030.9(5) \text{ \AA}^3$, $Z = 4$, $\rho_{calc} = 1.833 \text{ g}$

cm^{-3} , $\mu = 4.781 \text{ mm}^{-1}$, crystal size $0.15 \times 0.10 \times 0.06 \text{ mm}$, $1.91 \leq \theta \leq 29.03^\circ$, 29 793 reflections collected of which 6626 were independent [$R_{int} = 0.0374$]. The structure was solved by direct method and refined on F^2 by full-matrix least-squares calculations with SHELX 97 [16]. The phenyl H atoms was found from Fourier synthesis and refined isotropically. A riding model was applied to H atoms of THF molecules, placed at calculated position with C-H = 0.99 Å and isotropic $U = 1.2U_{eq}$ of attached atoms. Final R indices $R_1 = 0.0294$, $wR_2 = 0.0627$ [$I > 2\sigma(I)$].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 207634 for compound **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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