

Easy access to uranium nucleophilic carbene complexes†

Jean-Christophe Tourneux,^a Jean-Claude Berthet,^{*a} Pierre Thuéry,^a Nicolas Mézailles,^{*b} Pascal Le Floch^b and Michel Ephritikhine^{*a}

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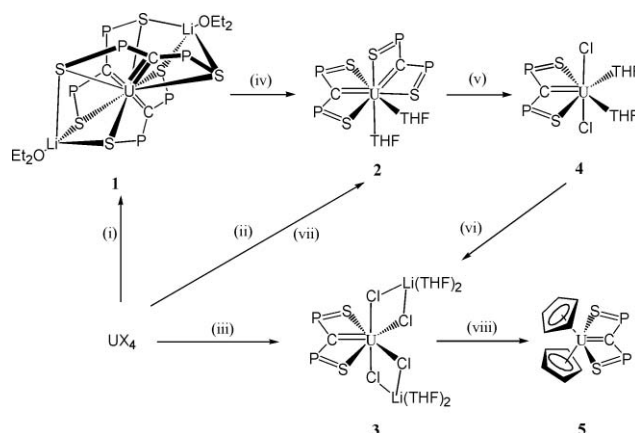
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Metathesis reactions of UCl_4 with $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$ in Et_2O only afforded the tris-carbene complex $[\{\text{Li}(\text{OEt}_2)\}_2\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}_3]$ (**1**), while the bis- and mono-carbene compounds $[\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}_2(\text{THF})_2]$ (**2**) and $[\{\text{Li}(\text{THF})_2\}_2\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}\text{Cl}_4]$ (**3**) were obtained by treatment of UCl_4 with $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$ in a mixture of THF and toluene. The bis-carbene complex **2** was also obtained either from the comproportionation reaction of **1** and UCl_4 or protonolysis reaction of $\text{U}(\text{NEt}_2)_4$ with $\text{H}_2\text{C}(\text{Ph}_2\text{PS})_2$ and was transformed into the mono-carbene complex $[\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}\text{Cl}_2(\text{THF})_2]$ (**4**) by further reaction with UCl_4 . The utility of these complexes as precursors is illustrated by the synthesis of the biscyclopentadienyl derivative $[\text{Cp}_2\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}]$ (**5**) by treatment of **3** with TiCp . The crystal structures of $[\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}_2(\text{py})_2] \cdot 1.5\text{py} \cdot 0.5\text{THF}$ and **5**·toluene are reported.

Actinide carbene complexes with significant metal–carbon multiple bond character are very rare. These were limited to the tris(cyclopentadienyl) uranium phosphoylide compounds $[\text{Cp}_3\text{U}=\text{CHP}(\text{Me})\text{RR}']$ ($\text{Cp} = \eta\text{-C}_5\text{H}_5$), discovered by Gilje *et al.* in 1981 and prepared by treatment of $[\text{Cp}_3\text{UCl}]$ with $\text{Li}(\text{CH}_2)(\text{CH}_2)\text{PRR}'$,¹ until we recently reported on the synthesis of the bis(thiophosphinoyl)methanediide complexes $[\text{M}_2\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}_3]$ [$\text{M} = \text{U}(\text{BH}_4)_3$ or $\text{Li}(\text{OEt}_2)$] and $[\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}(\text{BH}_4)_2(\text{THF})_2]$.² These nucleophilic carbene complexes were isolated from $\text{U}(\text{BH}_4)_4$ and the geminal dianionic reagent $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$. However, this synthetic route suffers from a major drawback, that is the use of the uranium borohydride as the starting material, whose preparation by the solvent-free reaction of finely powdered UCl_4 and LiBH_4 in a vacuum vibration ball mill, followed by sublimation, is somewhat tedious and skill-demanding.³ As such, these uranium carbene complexes have a limited utility and more practical precursors for the development of this class of compounds were clearly desirable. Here we report on (a) the easy and efficient syntheses of the tris-, bis- and mono-carbene complexes $[\{\text{Li}(\text{OEt}_2)\}_2\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}_3]$ (**1**), $[\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}_2(\text{L})_2]$ ($\text{L} = \text{THF}$, **2** or $\text{L} = \text{py}$, **2'**), $[\{\text{Li}(\text{THF})_2\}_2\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}\text{Cl}_4]$ (**3**) and $[\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}\text{Cl}_2(\text{THF})_2]$ (**4**) from UCl_4 , the most familiar

starting material in uranium chemistry, (b) the utility of these complexes as precursors with the synthesis of $[\text{Cp}_2\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}]$ (**5**), (c) the crystal structures of solvates of **2'** and **5**, first examples of uranium bis-carbene and bis(cyclopentadienyl) uranium carbene compounds, and (d) the reaction of $\text{U}(\text{NEt}_2)_4$ and $\text{H}_2\text{C}(\text{Ph}_2\text{PS})_2$ which afforded a mixture of **2** and the mono-carbene complex $[\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}(\text{NEt}_2)_2]$ (**6**).

The syntheses are summarized in Scheme 1.† The geminal dianionic reagent $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$ was so far used in diethyl ether or toluene, but not in THF where it is converted into the corresponding monoanion $[\text{HC}(\text{Ph}_2\text{PS})_2]^-$.⁴ Despite its poor solubility in Et_2O , the green solid of UCl_4 was reacted with 3 mol equivalents of $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$ and after stirring for 2 days at 20 °C, was transformed into the yellow powder of **1**.² After evaporation of the solvent, extraction with toluene in which it is more soluble, complex **1** was isolated in 84% yield. Mono- and bis-carbene complexes were not obtained by treating UCl_4 with 1 or 2 mol equivalents of $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$ in Et_2O as these reactions led to the sole formation of **1**. However, the desired mono- and bis-carbene compounds could be synthesized by addition of a toluene solution of $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$ to a concentrated solution of UCl_4 in THF, in a volume ratio of 5 : 1. Under these conditions, the reactions were immediate and much faster than the detrimental conversion of $[\text{C}(\text{Ph}_2\text{PS})_2]^{2-}$ into $[\text{HC}(\text{Ph}_2\text{PS})_2]^-$. Thus, the bis-carbene complex **2** was readily synthesized from UCl_4 and $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$ in the molar ratio of 1 : 2; following usual work-up, the dark orange powder of **2** was obtained in 95% yield. Similar treatment of UCl_4 with 1 mol equivalent of $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$ afforded a unique



Scheme 1 Synthesis of the complexes: (i) 3 $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$, Et_2O ; (ii) 2 $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$, THF–toluene 1 : 5; (iii) 1 $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$, THF–toluene 1 : 5; (iv) 0.5 UCl_4 , THF; (v) 1 UCl_4 , THF; (vi) 2 LiCl , THF; (vii) 2 $\text{H}_2\text{C}(\text{Ph}_2\text{PS})_2$, THF; (viii) 2 TiCp , THF. X = Cl except for (vii) X = NEt_2 . The phenyl rings on the phosphorus atoms are omitted.

^aCEA, IRAMIS, SIS2M, CNRS UMR 3299, 91191, Gif-sur-Yvette, France. E-mail: jean-claude.berthet@cea.fr; michel.ephritikhine@cea.fr; Fax: +33 169 08 66 40; Tel: +33 169 08 60 42

^bLaboratoire "Hétéroéléments et Coordination", Ecole Polytechnique, CNRS, 91128, Palaiseau Cédex, France. E-mail: nicolas.mezailles@polytechnique.edu; Fax: +33 169 33 44 40; Tel: +33 169 33 44 02

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brown compound which was formulated as the mono-carbene “ate” complex **3** because of the failure to eliminate LiCl and in view of the reactions described hereafter.

The bis-carbene complex **2** was also obtained from a 1:2 mixture of UCl_4 and **1** in THF; after 4 h at 20 °C, the solvent was evaporated off and **2** was separated from LiCl by extraction in toluene; the yield was almost quantitative. Under the same conditions, the comproportionation reaction between **2** and UCl_4 in the 1:1 molar ratio quantitatively yielded the mono-carbene compound **4** which was isolated as an orange powder after evaporation of THF. Complex **4** was readily transformed into the “ate” derivative **3** upon addition of 2 mol equivalents of LiCl (NMR experiment). The structure of **4** is likely to be similar to that of the borohydride analogue;² a plausible structure of **3** is presented in Scheme 1.

An alternative preparation of **2** was attempted with the reaction of the tetraamide precursor $\text{U}(\text{NEt}_2)_4$ ⁵ with 2 mol equivalents of $\text{H}_2\text{C}(\text{Ph}_2\text{PS})_2$ in THF. Such synthetic route involving protonolysis of $[\text{U}]\text{-NR}_2$ bonds with an acidic proton molecule would be similar to that employed for the preparation of $[\text{Hf}\{\text{C}(\text{Ph}_2\text{PNSiMe}_3)_2\}\text{Cl}_2]$ ⁶ and $[\text{Sm}\{\text{C}(\text{Ph}_2\text{PNSiMe}_3)_2\}(\text{NCy}_2)(\text{THF})]$.⁷ This reaction afforded after 5 h at 60 °C a mixture of **2** and the mono-carbene derivative $[\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}(\text{NEt}_2)]$ (**6**) in relative proportions of 73:27 (NMR experiments). Although this procedure cannot be considered as a convenient synthesis of **2**, efforts are currently being made to isolate **6** in a pure form.

Single crystals of $\text{2} \cdot 1.5\text{py} \cdot 0.5\text{THF}$ were formed by crystallization of **2** from a mixture of pyridine and THF. A view of **2'** is presented in Fig. 1 together with selected bond distances and angles. The eight-coordinate uranium atom is in a slightly distorted square antiprismatic environment, the square bases defined by the N1–S2–N2–S4 and C1–S1–C26–S3 atoms (rms deviations 0.435 and 0.511 Å) forming a dihedral angle of 2.80(5)°. The line passing through the metal centre and perpendicular to the square bases is a two-fold axis of pseudo-symmetry. The U–C distances of 2.399(7) and 2.390(8) Å are intermediate between

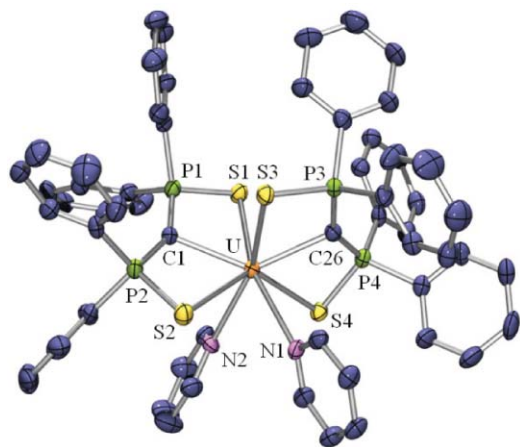


Fig. 1 View of $[\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}_2(\text{py})_2]$ (**2'**) with displacement ellipsoids drawn at the 40% probability level. The hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (°): U–S1 2.892(2), U–S2 2.940(2), U–C1 2.399(7), U–S3 2.876(2), U–S4 2.951(2), U–C26 2.390(8), U–N1 2.670(7), U–N2 2.683(6), S1–U–C1 66.44(18), S2–U–C1 66.49(19), S3–U–C26 67.24(19), S4–U–C26 65.79(19), N1–U–N2 83.5(2).

those of 2.323(3) and 2.47(2) Å (average) in the seven- and nine-coordinate complexes $[\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}(\text{BH}_4)_2(\text{THF})_2]$ and **1**, respectively.² The average U–S distance of 2.91(3) Å can be compared with those of 2.88(2) and 3.08(4) in the above compounds. The U–S–P–C–P–S cores are planar (rms deviations 0.081 and 0.062 Å). The planarity at the carbene carbon atoms, also demonstrated by the sums of the P–C–P and U–C–P angles being equal to 360°, shows the donation of both lone pairs from the dianionic fragment to the metal centre.

That these complexes are useful precursors was indicated by the synthesis of **5** by reaction of **3** or **4** with two mol equivalents of TiCp in THF. After 6 h at 20 °C and usual work-up, the orange powder of **5** was isolated in 79% yield and pale orange crystals of **5**·toluene were deposited from a toluene solution. A view of **5** is shown in Fig. 2 together with selected bond distances and angles. The bis(cyclopentadienyl) complex adopts the familiar bent-sandwich configuration with the planar U–S–P–C–P–S core (rms deviation 0.086 Å) lying in the equatorial girdle of the Cp_2U fragment. The short U–C1 and mean U–S distances of 2.336(4) and 2.868(2) Å are identical to those measured in $[\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}(\text{BH}_4)_2(\text{THF})_2]$.²

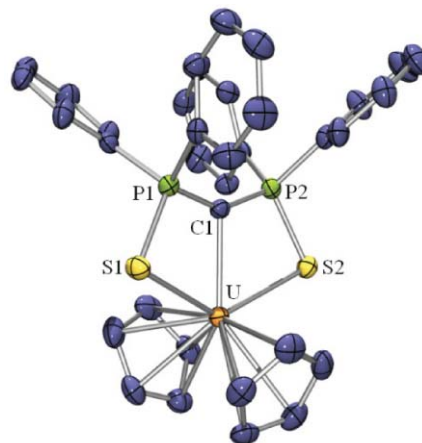


Fig. 2 View of $[\text{Cp}_2\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}]$ (**5**) with displacement ellipsoids drawn at the 50% probability level. The hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (°): U–S1 2.8656(11), U–S2 2.8694(12), U–C1 2.336(4), S1–U–C1 68.29(11), S2–U–C1 67.90(11).

In conclusion, we have demonstrated that either mono-, bis or even tris-carbene complexes of uranium can be conveniently prepared in good yields from UCl_4 either by substitution of the Cl groups with the methandiide compound $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$ or by comproportionation reactions between UCl_4 and the tris- or bis-carbene complexes. These syntheses are straightforward and the complexes, which are soluble in toluene, are easily separated from the LiCl by-product. These complexes are valuable precursors for the enlargement of the family of uranium nucleophilic carbene compounds, thus permitting further studies of their chemical properties and the nature of the U=C bond.

Notes and references

† Synthesis and characterization data. All manipulations were carried out under argon. The ^1H and ^{31}P NMR spectra were recorded at 23 °C in $\text{THF}-d_8$ on a Bruker DPX 200 spectrometer operating at 200.0 MHz for ^1H and 81.0 MHz for ^{31}P ; the ^1H NMR spectra are referenced internally

using the residual proton solvent resonances relative to tetramethylsilane (δ 0), the ^{31}P NMR chemical shifts are given relative to an 85% H_3PO_4 external reference.

$[\{\text{Li}(\text{OEt})_2\}_2\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}_3]$ (**1**): A flask was charged with UCl_4 (282.3 mg, 0.74 mmol) and a Et_2O solution (50 mL) of $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$ prepared *in situ* from $\text{H}_2\text{C}(\text{Ph}_2\text{PS})_2$ (1000 mg, 2.23 mmol) and MeLi (2.79 mL of a 1.6 M solution in Et_2O , 4.46 mmol). The reaction mixture was stirred for 2 d at 20 °C. After evaporation of the solvent, **1** was extracted with toluene (50 mL) and isolated as a yellow powder after drying under vacuum (1086 mg, 84%). Complex **1** was characterized by its ^1H and ^{31}P NMR spectra and its X-ray crystal structure.²

$[\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}_2(\text{THF})_2]$ (**2**): (a) A solution of $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$ (120 mg, 0.26 mmol) in toluene (20 mL) was poured with stirring into a solution of UCl_4 (50.0 mg, 0.13 mmol) in THF (4 mL). After 5 min at 20 °C, the solvents were evaporated off, **2** was extracted with toluene (20 mL) and isolated as a dark orange powder after evaporation under vacuum (159 mg, 95%). Found: C, 55.16; H, 4.53; S, 9.94. $\text{C}_{38}\text{H}_{36}\text{O}_2\text{P}_2\text{S}_4\text{U}$ ($M = 1275.25$) requires C, 54.63; H, 4.43; S, 10.06%. ^1H NMR: δ 25.72 (s, 16H, *o*-Ph), 12.77 (s, 16H, *m*-Ph), 11.41 (s, 8H, *p*-Ph). ^{31}P $\{^1\text{H}\}$ NMR: δ -324 ($w_{1/2} = 290$ Hz). (b) A flask was charged with **1** (500 mg, 0.29 mmol) and UCl_4 (54.6 mg, 0.14 mmol) in THF (30 mL). After 4 h at 20 °C, the solvent was evaporated off, **2** was extracted in toluene (3×20 mL) and isolated as a brown powder after evaporation to dryness (534 mg, 97%). (c) An NMR tube was charged with $\text{U}(\text{NEt}_3)_4$ (10.8 mg, 0.020 mmol) and $\text{H}_2\text{C}(\text{Ph}_2\text{PS})_2$ (18.4 mg, 0.041 mmol) in THF (0.35 mL). After 5 h at 60 °C, the ^1H NMR spectrum showed the presence of **2** and $[\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}(\text{NEt}_3)_2]$ (**6**) in the ratio 73 : 27. ^1H NMR of **6**: δ 49.00 (s, 12H, Me), 18.17 (s, 8H, *o*-Ph), 14.32 (s, 8H, *m*-Ph), 12.58 (s, 4H, *p*-Ph), -17.53 (s, 8H, CH_3).

$[\{\text{Li}(\text{THF})_2\}_2\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}_2\text{Cl}_4]$ (**3**): A solution of $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$ (60 mg, 0.13 mmol) in toluene (20 mL) was poured with stirring into a solution of UCl_4 (50 mg, 0.13 mmol) in THF (4 mL). After 5 min at 20 °C, the solvents were evaporated off, leaving the dark brown powder of **3** (143 mg, 98%). ^1H NMR: δ 21.3 (br s, $w_{1/2} = 215$ Hz, 8H, *o*-Ph), 11.68 (s, $w_{1/2} = 30$ Hz, 8H, *m*-Ph), 10.50 (s, $w_{1/2} = 30$ Hz, 4H, *p*-Ph). ^{31}P $\{^1\text{H}\}$ NMR: the signal was not detected.

$[\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}_2\text{Cl}_2(\text{THF})_2]$ (**4**): A flask was charged with **2** (100 mg, 0.078 mmol) and UCl_4 (29.78 mg, 0.078 mmol) in THF (15 mL). After 3 h at 20 °C, the solvent was evaporated off, leaving **4** as an orange powder (137 mg, 98%). Found: C, 43.94; H, 4.17; S, 6.95. $\text{C}_{33}\text{H}_{36}\text{Cl}_2\text{O}_2\text{P}_2\text{S}_2\text{U}$ ($M = 899.67$) requires C, 44.05; H, 4.03; S, 7.13%. ^1H NMR: δ 17.04 (s, 8H, *o*-Ph), 10.87 (t, $J = 7$ Hz, 8H, *m*-Ph), 9.88 (t, $J = 7$ Hz, 4H, *p*-Ph). ^{31}P $\{^1\text{H}\}$ NMR: δ -600.1.

$[\text{Cp}_2\text{U}\{\text{C}(\text{Ph}_2\text{PS})_2\}]$ (**5**): TiCp (283.8 mg, 1.06 mmol) was added to a solution of **3** prepared as described before from UCl_4 (200 mg, 0.53 mmol)

in THF (10 mL) and $\text{Li}_2\text{C}(\text{Ph}_2\text{PS})_2$ (30.9 mg, 0.53 mmol) in toluene (50 mL). After 6 h at 20 °C, the solvents were evaporated off and **5** was extracted with toluene (50 mL) and isolated as a pale orange powder after evaporation under vacuum (339 mg, 79%). Found: C, 51.17; H, 4.94; P, 7.25. $\text{C}_{35}\text{H}_{30}\text{P}_2\text{S}_2\text{U}$ ($M = 814.72$) requires C, 51.60; H, 3.71; P, 7.60%. ^1H NMR: δ 20.63 (t, $J = 7.2$ Hz, 8H, *o*-Ph), 11.14 (t, $J = 7.2$ Hz, 8H, *m*-Ph), 9.94 (t, $J = 7.2$ Hz, 4H, *p*-Ph), -13.60 (s, 10H, Cp). ^{31}P $\{^1\text{H}\}$ NMR: δ -361.4.

§ Crystal data for **2'**: $\text{C}_{69.5}\text{H}_{61.5}\text{N}_{3.5}\text{O}_{0.5}\text{P}_4\text{S}_4\text{U}$, $M = 1443.87$, monoclinic, space group $P2_1/c$, $a = 13.8488(4)$, $b = 28.6755(15)$, $c = 17.9735(10)$ Å, $\beta = 96.481(3)^\circ$, $V = 7092.1(6)$ Å³, $Z = 4$. Refinement of 847 parameters on 13 350 independent reflections out of 157 915 measured reflections ($R_{\text{int}} = 0.075$) led to $R_1 = 0.061$, $wR_2 = 0.162$, $S = 1.047$, $\Delta\rho_{\text{min}} = -1.49$, $\Delta\rho_{\text{max}} = 1.61$ e Å⁻³. Crystal data for **5**: $\text{C}_{42}\text{H}_{38}\text{P}_2\text{S}_2\text{U}$, $M = 906.81$, monoclinic, space group $P2_1/c$, $a = 13.0722(6)$, $b = 16.8709(9)$, $c = 16.7480(8)$ Å, $\beta = 90.816(3)^\circ$, $V = 3693.2(3)$ Å³, $Z = 4$. Refinement of 425 parameters on 6980 independent reflections out of 108 095 measured reflections ($R_{\text{int}} = 0.043$) led to $R_1 = 0.032$, $wR_2 = 0.074$, $S = 1.031$, $\Delta\rho_{\text{min}} = -1.21$, $\Delta\rho_{\text{max}} = 0.91$ e Å⁻³. Data were collected at 150(2) K on a Nonius Kappa-CCD area-detector diffractometer and processed with HKL2000.⁸ Absorption effects were corrected with SCALEPACK.⁸ The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXTL.⁹ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at calculated positions. The solvent molecules are badly resolved in **2'** and some of them were given 0.5 occupancy factors in order to retain acceptable displacement parameters.

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