

Synthesis and structures of a 3-sila- β -diketiminatomagnesium bromide, ketenimide and triflate†

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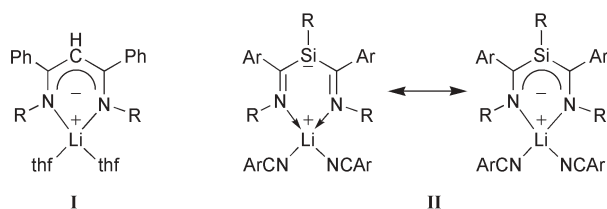
Received (in Cambridge, UK) 20th January 2005, Accepted 21st February 2005

First published as an Advance Article on the web 10th March 2005

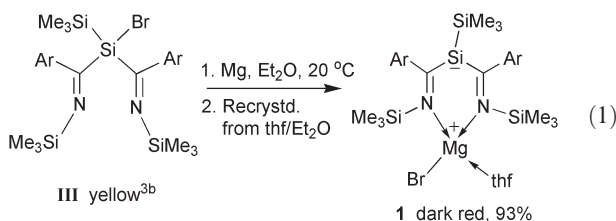
DOI: 10.1039/b500878f

The crystalline compounds $[\text{Mg}(\text{Br})(\text{L})(\text{thf})] \cdot 0.5\text{Et}_2\text{O}$ [$\text{L} = \{\text{N}(\text{R})\text{C}(\text{C}_6\text{H}_3\text{Me}_2-2,6)\}_2\text{SiR}$, $\text{R} = \text{SiMe}_3$] (**1**), $[\text{Mg}(\text{L})\{\text{N}=\text{C}=\text{C}(\text{Me})=\text{CH}_2\text{CH}_2\}(\text{D})_2]$ [$\text{D} = \text{NCC}_6\text{H}_3\text{Me}_2-2,6$] (**2**), **thf** (**3**)] and $[\{\text{Mg}(\text{L})\}_2\{\mu\text{-OSO}(\text{CF}_3)\text{O}-\mu\}]$ (**4**) were prepared from (a) $\text{Si}(\text{Br})(\text{R})\{\text{C}(\text{C}_6\text{H}_3\text{Me}_2-2,6)=\text{NR}\}_2$ and Mg for (**1**), (b) $[\text{Mg}(\text{SiR}_3)_2(\text{thf})_2]$ and 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{CN}$ (5 mol for (**2**), 3 mol for (**3**)), and (c) (**2**) + $\text{Me}_3\text{SiOS}(\text{O})_2\text{CF}_3$ for (**4**); a coproduct from (c) is believed to have been the trimethylsilyl ketenimide $\text{Me}_3\text{SiN}=\text{C}=\text{C}\{\text{C}(\text{Me})=\text{CH}_2\}_2$ (**5**).

β -Diketiminates are currently among the most widely used spectator ligands;¹ they are generally π -delocalised and N,N' -chelating, as in **I** ($\text{R} = \text{SiMe}_3$).² By contrast, in a 3-sila-analogue, much of the negative charge is localised at the 3-silicon atom, as in **II**, prepared from $[\text{Li}(\text{SiR}_3)(\text{thf})_3]$ and 2 ArCN ($\text{Ar} = \text{C}_6\text{H}_3\text{Me}_2-2,6$).³ The only other 3-sila- β -diketiminatometal complexes to have been described are $[\text{M}\{\text{N}(\text{R})=\text{C}(\text{Ar})_2\text{SiR}\}_2]$ ($\text{M} = \text{Na},^4 \text{K},^4 \text{Rb}^{3b}$), $[\text{Hg}\{\text{Si}(\text{R})\text{C}(\text{Ar})=\text{NR}\}_2]$,^{3b} $[\text{R}_2\text{Si}\{\text{C}(\text{Ar})=\text{NR}\}_2]$,^{3b} and $[\text{RSi}(\text{SnMe}_3)\{\text{C}(\text{Ar})=\text{NR}\}_2]$.^{3b}

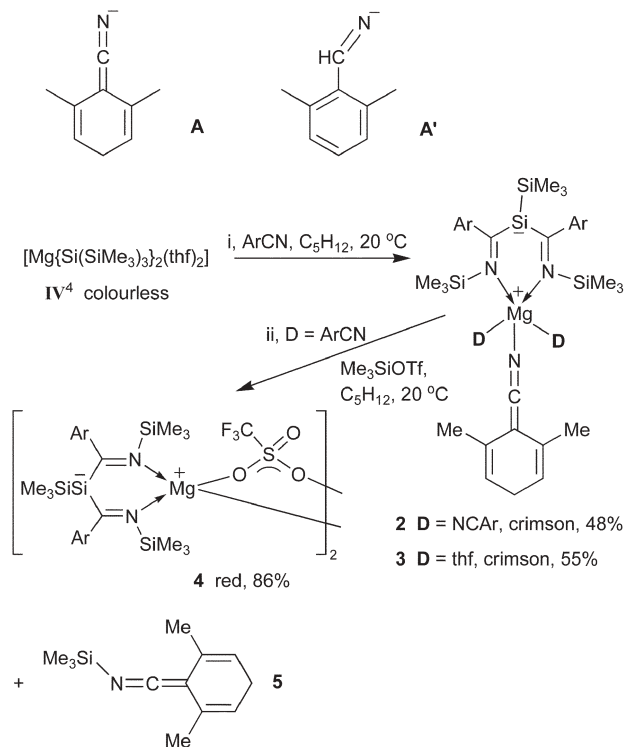


We now present data on four crystalline heteroleptic 3-sila- β -diketiminatomagnesium complexes. The bromide **1** was obtained by a quasi-Grignard procedure from the bis(imido)trimethylsilyl-(bromo)silane **III**,^{3b} eqn. (1).[‡] Silyl Grignard reagents⁵ are usually prepared *via* transmetalation with an alkali metal silyl;^{5a,b} the direct synthesis from halosilanes required the use of pyrophoric magnesium and an additional chelating donor ligand.^{5c} Two imido substituents in the bromosilane **III** activate its Si-Br bond and serve as N -donor ligands thus facilitating the reaction with Mg metal.



The remarkable compounds **2** and **3**, containing rare examples of a terminally coordinated ketenimido ligand $>\text{C}=\text{C}=\text{N}^-$ (specifically **A**), were prepared (i in Scheme 1) from the magnesium silyl **IV**^{5a} with 2,6-dimethylbenzonitrile (>4 mol for **2**,[‡] or 3 mol for **3**[†]). The 2,6-dimethylbenzaldiminato ligand **A'** is the tautomer of **A**.

The “extra” hydrogen atom attached to the six-membered ring of **A** in **2** or **3** did not arise from solvent, because when the reaction i of Scheme 1 was performed in toluene- d_8 or thf- d_8 no ^2H incorporation into the product was observed. Hence, we conclude that the H-source is the eliminated SiR_3 . The compound $[\text{Mg}\{\{\text{N}(\text{R})\text{C}(\text{Ar})\}_2\text{SiR}\}(\text{NCAr})(\text{D})_2][\text{SiR}_3]$, as a tight ion or radical pair, either affords **2/3** *via* a $\text{C}\dots\text{SiR}_3$ intermediate (**C32** in Figs. 2 or 3) or does so *via* $[\text{Mg}(\text{H})\{\{\text{N}(\text{R})\text{C}(\text{Ar})\}_2\text{SiR}\}(\text{NCAr})(\text{D})_2]$. The possible coproduct, $\text{R}_2\text{SiCH}_2\text{SiMe}_2$, its dimer, or HSiR_3 , have not been identified by GC/MS. That the compounds **2** and **3** contain **A**, rather than **A'**, is attributed to steric constraints. In support, we note that from $[\text{Mg}(\text{SiR}_3)_2(\text{thf})_2]$ (**IV**) and 2- or 4- $\text{MeC}_6\text{H}_4\text{CN}$ or



Scheme 1

† Electronic Supplementary Information (ESI) available: (i) synthesis of **3** and **4**; (ii) X-ray data for **1**, **2**, **3** and **4**. See <http://www.rsc.org/suppdata/cc/b5/b500878f/>

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PhCN in place of ArCN, a dearomatised product was not observed (as shown by the absence of vinyl and allylic proton signals in the ^1H NMR spectra of the reaction mixtures).

Treatment of **2** with trimethylsilyl triflate yielded (ii in Scheme 1) the binuclear bis(triflate)-bridged magnesium 3-sila- β -diketiminate **4**,[†] demonstrating the greater ease of nucleophilic displacement from **2** of the ketenimido ligand than of the 3-sila- β -diketiminate. Although the presumed major coproduct trimethylsilyl ketenimide **5** was not isolated in the crystalline state and complete separation from ArCN was not achieved, the ^1H NMR spectrum (see ESI)[†] supports its formulation to be as shown in Scheme 1 and not of the tautomer

N-trimethylsilyl-2,6-dimethylbenzaldimine $\text{ArCH}=\text{NSiMe}_3$. Thus, the four ring protons of the A ligand of **5** gave rise to multiplets, in the ^1H NMR spectrum in C_6D_6 , centred at δ 3.10 (CH_2 : 3J 6.4, 5J 2.0 Hz) and δ 5.10 [CH]: 3J 6.4, 4J 2.0 Hz), with the CCH_3 protons centred at δ 1.80. The singlet at δ -0.32 is assigned to the SiMe_3 protons. The complexity of the ring proton signals is attributed to the inequivalence of the two protons of the CH_2 group and the two sets of CH ring protons, due to the SiMe_3 group being neither coplanar with nor orthogonal to the ring plane; this was confirmed by selective irradiation of the CCH_3 protons, when the multiplets at δ 3.10 and δ 5.10 collapsed into triplets. Similar features were observed, attributed to the A ligand, in the ^1H NMR spectra of **2** or **3** in C_6D_6 .

The molecule of the monomeric crystalline **1**, illustrated in Fig. 1, lies on a mirror plane, with the ligated thf disordered across the mirror.[§] The ether solvate is disordered over a site of $2/m$ symmetry. The 3-sila- β -diketiminato ligand parameters of **1** differ from those in **II** in that the N–C bonds are longer ($1.306 \pm 0.003 \text{ \AA}$ in **II**)³ and the endocyclic C–Si bonds are shorter (1.881 \AA in **II**).³ The six-membered ring in both **1** and **II**³ has a pronounced boat conformation, the Si1 and Mg atoms in **1** being *ca.* 0.41 and *ca.* 0.65 \AA , respectively, out of the C1N1C1'N1' plane. The sum of the three angles at Si1 is $346.7(4)^\circ$, that at N1 is 360° .

In the structure of the crystalline **3**, shown in Fig. 2, the magnesium atom has a distorted trigonal-bipyramidal environment and is coplanar with the three equatorial nitrogen atoms, the two oxygen atoms occupying the axial positions.[§] The bite angle

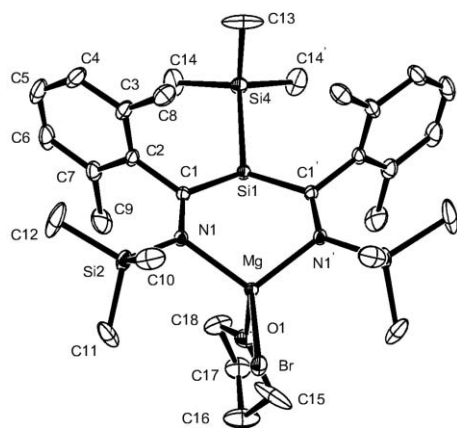


Fig. 1 Molecular structure of crystalline **1**. Selected bond lengths (\AA) and angles ($^\circ$): Mg–Br 2.4692(15), N1–C1 1.323(4), C1–Si1 1.858(3), Mg–N1 2.074(3), Mg–O1 2.021(4) \AA ; N1–Mg–N1' 106.33(16), Mg–N1–C1 115.6(2), N1–C1–Si1 126.5(2), C1–Si1–Si4 117.78(10) $^\circ$.

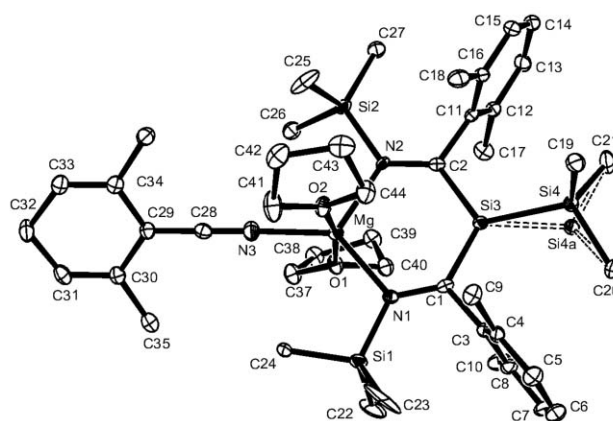


Fig. 2 Molecular structure of crystalline **3**. Selected bond lengths (\AA) and angles ($^\circ$) (see also Fig. 3): Mg–N1 2.124(4), Mg–N2 2.133(4), Mg–N3 2.061(5), Mg–O1 2.152(3), Mg–O2 2.158(3), N1–C1 1.345(6), N2–C2 1.328(6), C1–Si3 1.839(5), C2–Si3 1.855(5) \AA ; Mg–N3–C28 178.3(4), N1–Mg–N2 108.71(16), N1–C1–Si3 127.0(3), C1–Si3–C2 117.4(2), N2–C2–Si3 128.1(3), Mg–N1–C1 119.3(3), Mg–N2–C2 118.6(3), O1–Mg–O2 170.73(15), O1–Mg–N1 89.84(14), O1–Mg–N2 92.64(14) $^\circ$.

N1–Mg–N2 of the 3-sila- β -diketiminato ligand is the narrowest of the equatorial angles subtended at the Mg atom. Of the three Mg–N bonds, that to A (Mg–N3) is shorter than the other two. The angles subtended at N3 and the adjacent C28 are close to 180° , and the geometric parameters of the A ligand (Fig. 3) confirm that it is correctly formulated. The 3-sila- β -diketiminato ligand parameters of **3** differ from those in **II** in that (i) the N–C bonds are longer but similar to those in **1**; (ii) the endocyclic C–Si bonds are shorter and close to those in **1**; (iii) the conformation of the 6-membered ring is a shallow chair, the Mg and Si atoms being *ca.* -0.12 and *ca.* 0.10 \AA out of the C1N1C2N2 plane; and (iv) the endocyclic angle at Si3, similar to that in **1**, is much wider than in **II** [$108.8(1)^\circ$].³ The structure of crystalline **2** (see ESI)[†] is closely similar to that of **3**, except that in **3** the axial positions are occupied by thf rather than the ArCN ligands of **2**.

There are rare examples of complexes with bridging ketenimido ligands: $[\text{Li}(\text{tmen})\{\mu\text{-N}=\text{C}=\text{C}(\text{H})\text{Ph}\}]_2$,^{6a} $[\{\text{Li}(\text{tmen})\}_2\{\mu\text{-N}=\text{C}=\text{C}(\text{H})\text{Ph}\}(\mu\text{-NPr}_2)]$ ^{6b} (an example of a quasi-dianion complex, QUADAC⁷), $[\text{Na}\{\mu\text{-N}=\text{C}=\text{CMe}_2\}(\text{tmen})]_4$ ^{6c} and $[\text{MMe}_2\{\mu\text{-N}=\text{C}=\text{CPh}_2\}(\text{thf})]_2$ ($\text{M} = \text{Ga}$ or In).^{6d} These have C=N and C=C bond lengths very similar to those in A of **2** or **3** [C=N: 1.15(3),^{6a} 1.173(7),^{6b} av. 1.187^{6c} and 1.188(5) \AA (In);^{6d} and

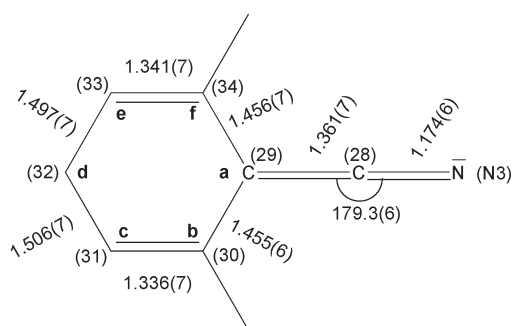


Fig. 3 Bond lengths (\AA) and angles ($^\circ$) of the A ligand of crystalline **3**: a 117.1(5), b 121.4(5), c 124.3(5), d 111.4(5), e 124.3(5), f 121.4(5) $^\circ$.

C=C: 1.38(2),^{6a} 1.383(8),^{6b} av. 1.360^{6c} and 1.359(5) Å (In)^{6d}. Examples of terminally coordinated ketenimido complexes include [Ir(η⁵-C₅Me₅)(N=C=CPh₂)(Ph)(PMe₃)] with N=C and C=C bond lengths of 1.168(6) and 1.377(7) Å, respectively,^{8a} and [Ir{N=C=C(CN)CH(CN)}₂](TCNE)(PPh₃)₂.^{8b} The closest equivalent to compounds **2** and **3** is the head-to-tail dimer of the coordinated nitrile, obtained from [Mo(H)(η⁵-Me₂CNAr)(NPr¹Ar)₂] and 9-cyanoanthracene (Ar = C₆H₃Me₂-3,5), in which the Mo–N=C=C(9)< fragment has N=C and C=C bond lengths of 1.213(7) and 1.347(7) Å, respectively, the C(10) of these compounds were obtained by deprotonation of an acidic α-CH group of the parent nitrile;^{6,8a} the only example of an aromatic nitrile being dearomatised is the Mo complex, where such an unusual reactivity was accounted for by the increased steric demands of the bulky 9-anthracenyl moiety.⁹

In conclusion, four crystalline heteroleptic 3-sila-β-diketiminatomagnesium compounds Mg(L)X [L = {N(R)C(Ar)}₂SiR] (Ar = C₆H₃Me₂-2,6, R = SiMe₃) **1–4** have been prepared and structurally characterised. The following features are noteworthy. (i) The bromide [Mg(Br)(L)(thf)]·0.5Et₂O (**1**) was made by a quasi-Grignard procedure, involving direct interaction of Mg metal with a corresponding bromosilane. (ii) The ketenimides [Mg(L)(A)(D)₂] [D = NCAr (**2**), thf (**3**)], obtained from [Mg(SiR₃)₂(thf)₂] and ArCN, are rare examples of compounds containing a terminal ketenimido ligand $\bar{N}=\text{C}=\text{C}\{\text{C}(\text{Me})=\text{CH}\}_2\text{CH}_2$ (=A), rather than its tautomer $\bar{N}=\text{C}(\text{H})\text{Ar}$ (=A'). (iii) The triflate {[Mg(L)]₂{μ-O-SO(CF₃)O-μ}₂} (**4**) was derived from **2** and Me₃SiOS(O)₂CF₃; evidence for the trimethylsilyl ketenimide Me₃SiN=C=C{C(Me)=CH}₂CH₂ (**5**) as a coproduct came from analysis of ¹H NMR spectra.

We thank BASF (Ludwigshafen) for providing a studentship for J. D. F., EPSRC for a fellowship for A. V. P., and Dr. A. G. Avent for useful discussions.

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Notes and references

† *Synthesis*: Magnesium powder (0.5 g, 20.8 mmol) was added to a stirred solution of the yellow Si(Br)(R){C(C₆H₃Me₂-2,6)=NR}₂ (**III**) (1.12 g, 1.90 mmol) in Et₂O (20 ml) at ca. 20 °C. After ca. 24 h the dark red mixture was filtered and thf (1 ml) was added. The filtrate was concentrated and stored at –30 °C, yielding dark red crystals of compound **1** (1.28 g, 93%) (Found: C, 52.0; H, 7.91; N, 3.91. C₃₃H₃₈BrMgN₂O_{1.5}Si₄ requires C, 54.8; H, 8.08; N, 3.87%), mp 230 °C, decomp. ca. 240 °C. ¹H NMR: δ –0.38 (9H, s, SiSiMe₃), 0.23 (18H, s, NSiMe₃), 1.31 (4H, m, thf), 2.3 (3H, t, J = 6.9, Et₂O), 2.41 (12H, s, C₆H₃Me₂), 3.26 (2H, q, J = 6.9, Et₂O), 4.01 (4H, m, thf), 6.78 (4H, d, J = 7.6, m-H of Ar), 6.91 (2H, t, J = 7.6, p-H of Ar); ¹³C: δ 1.45 (SiSiMe₃), 3.12 (NSiMe₃), 15.72 (Et₂O), 20.75 (C₆H₃Me₂), 25.38 (thf), 66.01 (Et₂O), 70.80 (thf), 128.08 (p-C of Ar), 128.31 (m-C of

Ar), 134.45 (o-C of Ar), 146.86 (ipso-C of Ar), 220.42 (N=C–Si); ²⁹Si: δ –13.59 (SiSiMe₃), –2.21 (SiSiMe₃), 5.47 (NSiMe₃). 2,6-Dimethylbenzotrile (1.70 g, 13.0 mmol) was added to a stirred solution of [Mg{Si(SiMe₃)₃}₂(thf)₂] (**IV**) (2.15 g, 3.24 mmol) in pentane (100 ml) at –78 °C. The mixture slowly became an intense crimson upon warming to ca. 20 °C. After 1 d, volatiles were removed *in vacuo*. The residue was extracted into pentane (60 ml), concentrated and stored at –30 °C for 1 d, yielding crimson crystals of compound **2** (1.44 g, 48%), (Found: C, 68.4; H, 7.85; N, 7.38. C₅₄H₇₃MgN₅Si₄ requires C, 69.8; H, 7.92; N, 7.54%), decomp. at ca. 85 °C. ¹H NMR: δ –0.34 (9H, s, SiSiMe₃), 0.14 (18H, s, NSiMe₃), 2.17 (12H, s, C₆H₃Me₂), 2.24 (6H, s, Me₂ of A), 2.40 (12H, s, NCC₆H₃Me₂), 3.77 (2H, m, CH₂ of A), 5.02 (2H, m, CH of A), 6.42 to 6.51 (m, 4H), 6.73 to 6.82 (m, 6H), 6.89 to 6.96 (m, 2H); ¹³C NMR: δ 1.06 (SiSiMe₃), 1.86 (NSiMe₃), 20.3 (C₆H₃Me₂), 20.48 (NCC₆H₃Me₂), 22.56 (Me₂ of A), 34.39 (CH₂ of A), 105.95 (C=C=N of A), 132.2 (CH of A), 134.2 (CMe of A), 146.50 (C=C=N of A), 218.44 (endocyclic C of L). § *Crystal data*: **1**: C₃₁H₅₃BrMgN₂O₅Si₄·0.5(C₄H₁₀O), *M* = 723.38, orthorhombic, space group *Pnmm* (No. 58), *a* = 13.7171(3), *b* = 18.2354(5), *c* = 16.7049(5) Å, *V* = 4178.5(2) Å³, *Z* = 4, μ(Mo–K_α, 0.71073 Å) = 1.14 mm^{–1}, *T* = 173(2) K, *R*₁ = 0.065 [for 3695 reflections with *I* > 2σ(*I*)], *wR*₂ = 0.173 (all data). **2**: C₅₄H₇₃MgN₅Si₄, *M* = 928.84, monoclinic, space group *P2₁/n* (No. 14), *a* = 12.5706(3), *b* = 34.3614(8), *c* = 12.8282(4) Å, β = 94.777(1)°, *V* = 5521.8(3) Å³, *Z* = 4, μ(Mo–K_α, 0.71073 Å) = 0.16 mm^{–1}, *T* = 173(2) K, *R*₁ = 0.062 [for 6636 reflections with *I* > 2σ(*I*)], *wR*₂ = 0.147 (all data). **3**: C₄₄H₇₁MgN₅O₂Si₄, *M* = 810.71, triclinic, space group *P1̄* (No. 2), *a* = 10.6444(11), *b* = 13.2595(17), *c* = 17.768(2) Å, α = 90.285(5)°, β = 98.141(8)°, γ = 110.075(8)°, *V* = 2327.8(5) Å³, *Z* = 2, μ(Mo–K_α, 0.71073 Å) = 0.18 mm^{–1}, *T* = 173(2) K, *R*₁ = 0.062 [for 3826 reflections with *I* > 2σ(*I*)], *wR*₂ = 0.140 (all data). **4**: C₅₆H₉₀F₆Mg₂N₄O₆Si₈, *M* = 1366.78, monoclinic, space group *P2₁/c* (No. 14), *a* = 16.8609(2), *b* = 23.2225(4), *c* = 19.0143(3) Å, β = 92.4670(10)°, *V* = 7438.19(19) Å³, *Z* = 4, μ(Mo–K_α, 0.71073 Å) = 0.28 mm^{–1}, *T* = 173(2) K, *R*₁ = 0.053 [for 14520 reflections with *I* > 2σ(*I*)], *wR*₂ = 0.151 (all data). CCDC numbers: **1**: 260822; **2**: 260823; **3**: 260824; **4**: 260825. See <http://www.rsc.org/suppdata/cc/b5/b500878f/> for crystallographic data in .cif format

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