Vanadium–Alkylidene Complexes

Cationic and Neutral Four-Coordinate Alkylidene Complexes of Vanadium(IV) Containing Short V=C Bonds**

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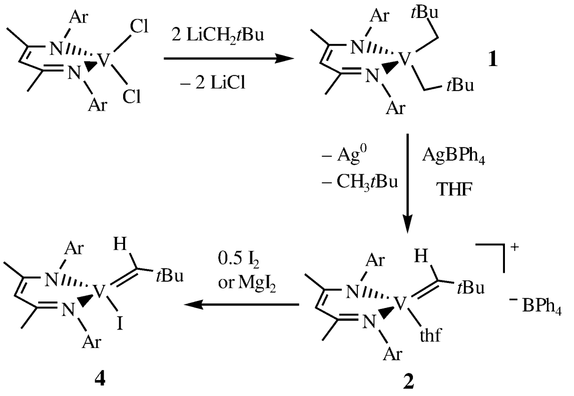
High-oxidation state transition-metal alkylidenes have received considerable attention in the past few years since these systems are capable of catalyzing important processes such as olefin metathesis, alkyne polymerization, and Wittig-type reactions.[1,2] Although transition-metal alkylidene complexes of the nucleophilic "Schrock-type" have been extensively studied for the 4d and 5d metals of Group 5, the chemistry for 3d vanadium systems has been far less explored. The first example of a vanadium(III)–alkylidene complex, [CpV(CH*t*Bu)(dmpe)] (dmpe = bis(dimethylphosphanyl)-ethane), was reported by Hessen, Teuben, and co-workers and involved α-hydrogen abstraction of the bis(alkyl) precursor.[3] In contrast to the heavier d^0 alkylidene congeners, which are prepared by α-hydrogen abstraction, the synthesis of the first vanadium(V)–alkylidene complex [CpV(NAr)(CHPh)(PMe_3)] (Ar = 2,6-($CHMe_2)_2C_6H_3$) involved a two-electron oxidation of the precursor [CpV(NAr)($PMe_3)_2$] with the Wittig reagent Ph_3P=CHPh by alkylidene transfer.[4] Since there are only a handful of vanadium–alkylidene complexes known,[3–6] we report the synthesis of the first cationic and neutral four-coordinate vanadium(IV)–neopentylidene complexes [(Nacnac)V=CH*t*Bu(thf)](BPh_4) and [(Nacnac)V=CH*t*Bu(I)] ($Nacnac^-$ = [Ar]NC(Me)CHC(Me)N[Ar], Ar = 2,6-($CHMe_2)_2C_6H_3$), and subsequent thermolysis of each system. These d^1 paramagnetic species reported herein are kinetically stable, and contain the shortest V=C bonds reported so far.

Our recent strategy to prepare the first four-coordinate titanium–neopentylidene complex by an oxidatively induced α-hydrogen abstraction reaction[7] motivated us to pursue other 3d transition metals containing this reactive motif. Unlike titanium, vanadium displays more diverse redox chemistry, hence oxidation states ranging from +2 to +5 can occur. Using the precursor [(Nacnac)VCl_2][8] developed by Budzelaar and co-workers and two equivalents of $LiCH_2$-*t*Bu,[1g] we prepared the corresponding bis(neopentyl) complex [(Nacnac)V(CH_2*t*Bu$)_2$] (**1**) in 80% yield as dark brown needles (Scheme 1). Attempts to obtain crystals suitable for a single-crystal X-ray structure determination were unsuccessful, but elemental analysis, magnetic susceptibility measurements (μ_{eff} = 2.96 μ_B), and reactivity (vide infra) are in agreement with the formation of **1**.[9] Complex **1** is a close analogue of the *n*Bu derivative prepared by Budzelaar and co-workers, differing only by the lack of β-hydrogen atoms.[8] Cyclic voltammograms of **1** (TBAH, THF; TBAH = tetra-*n*-butylammonium hexafluorophosphate) revealed reversible oxidation and reduction waves at −0.35 and −2.68 V, respectively, which correspond to the V^{III}/V^{IV} and V^{III}/V^{II} redox couple (referenced versus [$FeCp_2$]/[$FeCp_2$]$^+$]).[9] Chemical oxidation of **1** with $AgBPh_4$ leads to formation of a Ag^0 mirror concurrent with the vanadium(IV)–alkylidene complex [(Nacnac)V=CH*t*Bu(thf)](BPh_4) (**2**) in 74% yield (Scheme 1). Complex **2** is stable in the solid state, but its solutions (Et_2O, C_6H_6, THF) gradually decompose over several hours at room temperature.



Scheme 1. Synthesis of the vanadium(IV)–alkylidene complexes **2** and **4**.

Dark brown single crystals of **2** were grown from THF solutions of the complex layered with Et_2O at −35 °C. The structure of **2** (Figure 1) reveals a cationic and four-coordinate vanadium center with pseudotetrahedral geometry, a very short V=C bond length (V(1)−C(33) 1.795(3) Å), and an obtuse V(1)-C(33)-C(34) angle of 159.8(4)°.[9,10] The highly distorted neopentylidene ligand suggests that there is a significant α-agostic CH interaction with the metal center. Since **2** is a d^1 complex, α-elimination is inhibited, and the complex distorts to form an unusually short V=C bond. The vanadium center deviates from the N(2)-N(6)-C(33) mean plane by 0.592(6) Å, and as consequence of the cationic nature of the metal center, a coordinated molecule of THF occupies the fourth site. EPR (g_{iso} = 1.982, A_{iso} = 88 × 10^{-4} cm^{-1}, ^{51}V, I = 7/2, 99.6%, Figure 2) and magnetic susceptibility measurements (SQUID, μ_{eff} = 1.85 μ_B; Evans',

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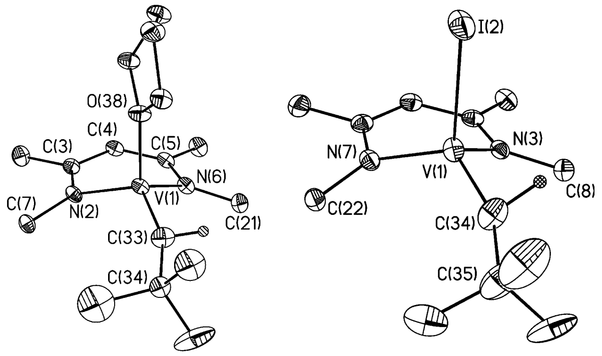


2 **4**

Figure 1. Molecular structure of complexes [(Nacnac)V=CH*t*Bu(thf)]-(BPh$_4$) (**2**) and [(Nacnac)V=CH*t*Bu(I)] (**4**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms with the exception of the alkylidene carbon atoms (C(33), **2**; C(34), **4**), and aryl groups on the nitrogen atoms with the exception of the *ipso*-carbon atoms (C(7), C(21), C(8), C(22)) are omitted for clarity. The [BPh$_4$]$^-$ ion and two disordered THF solvent molecules are omitted for clarity in the structure of **2**. Selected bond lengths [Å] and angles [°]: for **2**: V(1)-C(33) 1.795(3), V(1)-N(2) 1.942(3), V(1)-N(6) 1.964(3), V(1)-O(38) 2.000(2); V(1)-C(33)-C(34) 159.8(4), O(38)-V(1)-C(33) 101.87(13), C(33)-V(1)-N(6) 112.82(15), C(33)-V(1)-N(2) 122.03(15), N(6)-V(1)-N(2) 96.12(11). For **4**: V(1)-C(34) 1.787(3), V(1)-N(3) 1.989(2), V(1)-N(7) 1.935(2), V(1)-I(2) 2.6478(6); V(1)-C(34)-C(35) 158.7(3), I(2)-V(1)-C(34) 110.65(12), C(34)-V(1)-N(3) 107.08(12), C(34)-V(1)-N(7) 123.41(15), N(7)-V(1)-N(3) 94.93(9).

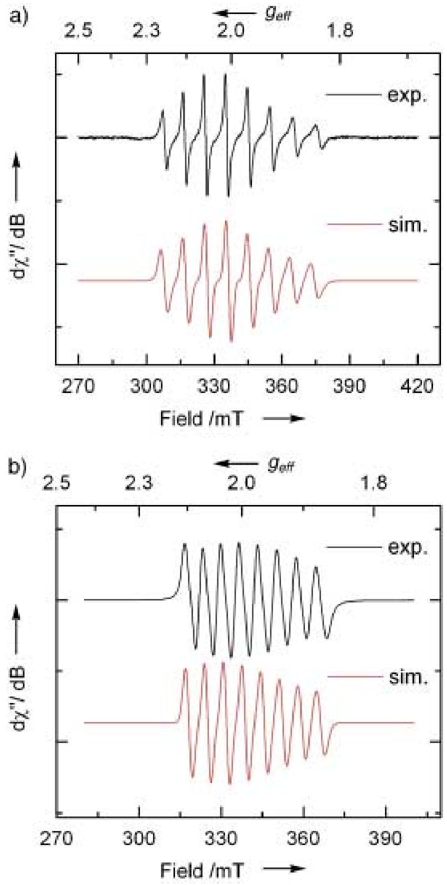
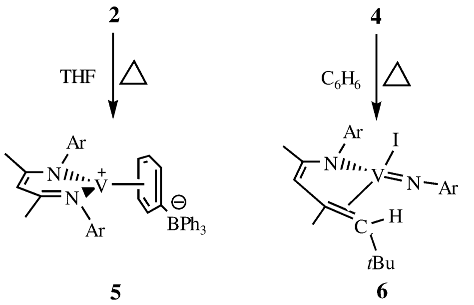


Figure 2. X-band EPR spectrum of **2** (a) and **4** (b) recorded at room temperature in toluene. Experimental spectra (exp.) are above the simulated spectra (sim.).

$\mu_{eff} = 1.87\ \mu_B$) are in accordance with a d^1 paramagnetic species and unambiguously rule out the possibility that oxidation of a V−C bond in **1** occurred instead to give the V^{III} cation [(Nacnac)V(CH$_2$*t*Bu)(thf)]$^+$. Similar species have been prepared by protonation reactions of the corresponding bis(alkyl) systems.[11] The role of the anion in the oxidation of **1** to form **2** is key in the oxidatively induced α-hydrogen abstraction process inasmuch as oxidation of **1** with AgOTf oxidizes the vanadium–carbon bond instead of the vanadium center. Hence, the V^{III} complex [(Nacnac)V(CH$_2$*t*Bu)(OTf)] (**3**) is formed in good yields (78%) when **1** is treated with AgOTf. Elemental analysis, solution magnetic susceptibility data, and single-crystal X-ray diffraction studies are consistent with the connectivity proposed for complex **3**.[9] Complex **2** can undergo smooth anion exchange with 0.5 equivalents of I$_2$ (47% yield) or excess MgI$_2$ (69% yield) to produce the neutral, four-coordinate vanadium–alkylidene complex [(Nacnac)V=CH*t*Bu(I)] (**4**) (Scheme 1). In the reaction of **2** with I$_2$, we also detect, by ^{11}B NMR spectroscopy, the formation of BPh$_3$ as a side product. This observation suggests that I$_2$ might be also oxidizing the B−C(phenyl) bond of the BPh$_4^-$ counter anion to afford **4**. Magnetic susceptibility measurements (Evans', $\mu_{eff} = 1.94\ \mu_B$), single-crystal X-ray diffraction study, and solution EPR ($g_{iso} = 1.976$, $A_{iso} = 64 \times 10^{-4}$ cm^{-1}, ^{51}V, $I = 7/2$, 99.6%, Figure 2) spectra are consistent with the d^1 vanadium(IV) complex **4** containing a terminal alkylidene functionality. Cyclic voltammograms of **4** (TBAH, THF) revealed irreversible oxidation and reduction waves at −0.18 and −2.28 V, respectively (referenced versus [FeCp$_2$]/[FeCp$_2$]$^+$).[9] This suggests that on the cyclic voltammetry time scale the putative vanadium(III) and vanadium(V) systems of **4**, generated by one-electron reduction and one-electron oxidation, respectively, appear to be unstable. In addition, chemical reduction and oxidation of complex **4** resulted in decomposition products. The molecular structure of **4** is depicted in Figure 1 and reveals the shortest V=C$_\alpha${alkylidene} bond reported so far (V(1)−C(34) 1.787(3) Å) as well as an obtuse V-C$_\alpha$-C$_\beta$ angle (V(1)-C(34)-C(35), 158.7(3)°).[12] Complexes **2** and **4** are isostructural, where the bound THF molecule and cationic charge in **2** are replaced with I$^-$ to generate the neutral complex **4**.

Owing to the instability of the previously reported four-coordinate alkylidene complex [(Nacnac)Ti=CH*t*Bu(OTf)],[7] it was presaged that complexes **2** and **4** would also be prone to "Wittig-like" reactivity involving the metal–alkylidene functionality. Accordingly, when complex **2** is heated at 60°C for 6 h in THF, extrusion of neopentane is observed (by ^{1}H NMR spectroscopy and GC MS analysis) concomitant with the formation of the zwitterion vanadium(II) product [(Nacnac)V(η^6-C$_6$H$_5$BPh$_3$)] (**5**) (77% yield, Scheme 2). THF is dehydrogenated during the thermolysis inasmuch as [D$_2$]neopentane is observed when the reaction is carried out in [D$_8$]THF. Complex **5** is an orange, paramagnetic species, and the X-band EPR solution spectra in toluene, as well as solution and solid-state magnetic susceptibility measurements are in accordance with the molecule having a quartet ground



Scheme 2. Thermolysis of complexes **2** and **4** to prepare **5** and **6**, respectively.

state spin configuration (SQUID, $\mu_{\text{eff}} = 3.93\ \mu_B$; Evans', $\mu_{\text{eff}} = 3.68\ \mu_B$).[9] The structure determined for **5** by using suitable single crystals also substantiates the proposed connectivity and illustrates clearly a low-valent, two-coordinate (Nacnac)-V^{II} scaffold coordinating to one of the phenyl groups attached to the borate (Figure 3).[13] In contrast to the transformation of **2** to **5**, when a solution of **4** in benzene is thermolyzed for 6 h at 60 °C, "Wittig-like" reactivity is observed, which is evidenced by the formation of the vanadium(IV)–imide complex [([Ar]NC(Me)CHC(Me)CH*t*Bu)V=NAr(I)] (**6**) (57 % yield; Scheme 2). Solution EPR and magnetic susceptibility measurements are consistent with a d^1 system.[9] In addition, the molecular structure of **6** was obtained from single-crystal X-ray diffraction studies and disclosed a low-coordinate vanadium(IV) center supported by an imide, and an anilide with a η^2-coordinated diene pendant arm.[14] The low-coordination environment at the metal center promotes η^2 coordination of the ene motif, which is now part of the former Nacnac$^-$ ligand (Figure 3). Similar transformations have been reported by our group for four-coordinate [(Nacnac)Ti^{IV}] complexes with reactive alkylidene or phosphinidene functionalities.[7,15] Concentration-dependent experiments on the titanium–alkylidene system (by ^{1}H NMR spectroscopy) determined the cross-metathesis reaction to be first-order in titanium, hence we suspect the same to be valid for the thermolytic transformation of **4** to **6**.

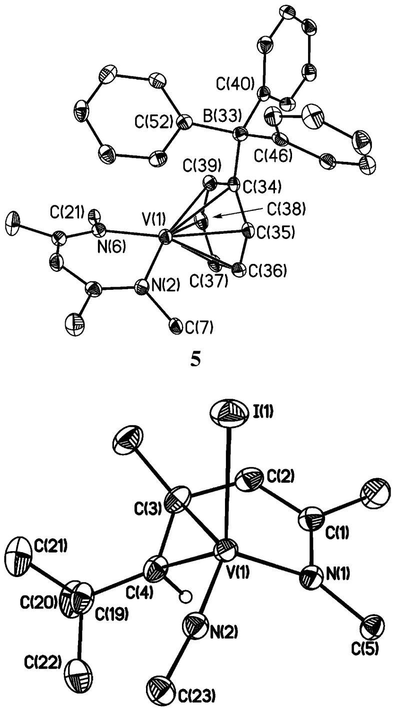


Figure 3. Molecular structure of complexes [(Nacnac)V(η^6-$C_6H_6BPh_4$)] (**5**) and [([Ar]NC(Me)CHC(Me)CH*t*Bu)V=NAr(I)] (**6**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms with the exception of the olefinic carbon atom (C(4), **6**), and aryl groups on the nitrogen atoms with the exception of the *ipso*-carbon atoms (C(7), C(21), C(5), C(5)) are omitted for clarity. Selected bond lengths [Å] and angles [°]: For **5**: V(1)-C(34) 2.445(2), V(1)-C(35) 2.363(2), V(1)-C(36) 2.340(2), V(1)-C(37) 2.322(2), V(1)-C(38) 2.353(2), V(1)-C(39) 2.383(2), V(1)-N(6) 2.066(8), V(1)-N(2) 2.082(8); N(6)-V(1)-N(2) 90.89(7). For **6**: V(1)-N(1) 1.985(7), V(1)-N(2) 1.687(8), V(1)-I(1) 2.6589(4), V(1)-C(4) 2.219(2), V(1)-C(3) 2.387(2), C(4)-C(3) 1.404(3); C(3)-C(4)-C(19) 127.2(9), I(1)-V(1)-C(4) 125.89(6), N(2)-V(1)-N(1) 112.69(8), C(4)-V(1)-N(2) 100.42(8), C(4)-V(1)-N(1) 89.76(8).

In summary, the cationic and neutral four-coordinate complexes (**2** and **4**, respectively) derived from the one-electron oxidation of the bis(alkyl)vanadium(III) precursor **1** represent a new class of alkylidene systems in the context of the organometallic chemistry of vanadium. Further applications of these unique d^1 metal radicals of vanadium containing metal–ligand multiple bonds to reactions such as group- or atom-transfer radical polymerization (ATRP),[16] and olefin metathesis will be described in due course.

Experimental Section

Synthetic and characterization details for compounds **1**–**6** (including single-crystal X-ray data for **2**–**6**)[17] are described in the Supporting Information.

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[9] See Supporting Information for complete experimental, spectral, and crystallographic details.

[10] Crystallographic details for **2**·2THF**:** A dark crystal of approximate dimensions $0.30 \times 0.30 \times 0.06$ mm^3 was selected and mounted on a glass fiber. A total of 88763 reflections ($-54 \leq h \leq 52$, $-20 \leq k \leq 20$, $-24 \leq l \leq 24$) was collected at $T = 136(2)$ K in the range of 2.27 to 27.46°, of which 8308 were observed ($R_{\text{int}} = 0.0957$); Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters. The residual peak and hole electron densities were 1.692 and $-0.604\,e\,A^{-3}$, respectively. The absorption coefficient was 0.213 mm^{-1}. The least-squares refinement converged normally with residuals of $R(F) = 0.0733$, $wR(F^2) = 0.2286$, and a GOF = 0.934 ($I > 2\sigma(I)$). $C_{70}H_{95}BN_2O_3V$, space group $C2/c$, monoclinic, $a = 42.3319(19)$, $b = 15.8991(7)$, $c = 19.1013(9)$ Å, $\beta = 110.2890(10)°$, $V = 12058.3(9)$ A^3, $Z = 8$, $\rho_{\text{calcd}} = 1.183$ mg m^{-3}, $F(000) = 4648$.[17]

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[12] Crystallographic details for **4:** A crystal of approximate dimensions $0.20 \times 0.20 \times 0.15$ mm^3 was selected and mounted on a glass fiber. A total of 29941 reflections ($-13 \leq h \leq 13$, $-36 \leq k \leq 36$, $-13 \leq l \leq 15$) was collected at $T = 112(2)$ K in the range of 2.92 to 25.35°, of which 5437 were observed ($R_{\text{int}} = 0.0804$); Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. The residual peak and hole electron densities were 1.104 and $-0.608\,e\,A^{-3}$, respectively. The absorption coefficient was 1.215 mm^{-1}. The least-squares refinement converged normally with residuals of $R(F) = 0.0387$, $wR(F^2) = 0.0810$ and a GOF = 0.894 ($I > 2\sigma(I)$). $C_{34}H_{51}IN_2V$, space group $P2(1)/n$, monoclinic, $a = 10.4492(9)$, $b = 27.924(2)$, $c = 12.3261(10)$ Å, $\beta = 107.904(2)°$, $V = 3422.4(5)$ A^3, $Z = 4$, $\rho_{\text{calcd}} = 1.292$ mg m^{-3}.[17]

[13] Crystallographic details for **5**·2Et$_2$O**:** A crystal of approximate dimensions $0.25 \times 0.25 \times 0.08$ mm^3 was selected and mounted on a glass fiber. A total of 43991 reflections ($-15 \leq h \leq 15$, $-19 \leq k \leq 19$, $-27 \leq l \leq 34$) was collected at $T = 111(2)$ K in the range of 2.07 to 27.53°, of which 5447 were observed ($R_{\text{int}} = 0.1258$); Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. A disordered diethyl ether solvent molecule was located in the cell at an inversion center. All non-hydrogen atoms were refined with anisotropic displacement parameters. The residual peak and hole electron densities were 0.267 and $-0.374\,e\,A^{-3}$, respectively. The absorption coefficient was 0.260 mm^{-1}. The least-squares refinement converged normally with residuals of $R(F) = 0.0461$, $wR(F^2) = 0.0839$ and a GOF = 0.835 ($I > 2\sigma(I)$). $C_{55}H_{66}N_2O_{0.5}V$, space group $P2(1)/n$, monoclinic, $a = 11.5823(11)$, $b = 15.0376(15)$, $c = 26.496(2)$ Å, $\beta = 101.522(3)°$, $V = 4521.8(7)$ A^3, $Z = 4$, $\rho_{\text{calcd}} = 1.212$ mg m^{-3}.[17]

[14] Crystallographic details for **6:** A crystal of approximate dimensions $0.30 \times 0.30 \times 0.24$ mm^3 was selected and mounted on a glass fiber. A total of 21477 reflections ($-12 \leq h \leq 12$, $-13 \leq k \leq 15$, $-23 \leq l \leq 23$) was collected at $T = 130(2)$ K in the range of 2.03 to 30.02°, of which 7739 were observed ($R_{\text{int}} = 0.0320$); Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The residual peak and hole electron densities were 1.105 and $-0.614\,e\,A^{-3}$, respectively. The absorption coefficient was 1.295 mm^{-1}. The least-squares refinement converged normally with residuals of $R(F) = 0.0341$, $wR(F^2) = 0.0869$ and a GOF = 1.020 ($I > 2\sigma(I)$). $C_{34}H_{51}IN_2V$, space group $P\bar{1}$, triclinic, $a = 9.0935(4)$, $b = 11.0457(5)$, $c = 17.0793(8)$ Å, $\alpha = 102.4790(10)°$, $\beta = 92.1090(10)°$, $\gamma = 98.7240(10)°$, $V = 1651.30(13)$ A^3, $Z = 2$, $\rho_{\text{calcd}} = 1.339$ mg m^{-3}.[17]

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[17] CCDC-222957 (**2**), CCDC-222958 (**3**), CCDC-222959 (**4**), CCDC-222960 (**5**), and CCDC-222961 (**6**) contain the supplementary crystallographic data for this paper. 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 CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).