Metallaheteroborane clusters of group 5 transition metals derived from dichalcogenide ligands

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Abstract

Treatments of group 5 metal polychlorides such as, \([\text{Cp}_n\text{MCln}_x]\) \((M = V; n, x = 2; M = Nb; n = 1, x = 0), or \([\text{Cp}^*\text{TaCl}_4]\) \((\text{Cp} = \eta^1\text{C}_5\text{H}_5\text{C}_5\text{H}_4\text{Me}_2; \text{Cp}^* = \eta^1\text{C}_5\text{H}_4\text{Me}_3)\), with \([\text{LiBH}_4\text{-THF}]\) followed by thermolysis in the presence of diphenyl diselenide yielded metallaheteroborane clusters \([\text{Cp}(\mu\text{-SePh})]_2(\mu\text{-Se})\), \(1\). \([\text{CpNb}_2\text{B}_9\text{H}_{11}(\mu\text{-SePh})], 2\) and \([\text{Cp}^*\text{Ta}^2\text{B}_9\text{H}_{11}(\text{SePh})], 3\) in moderate yields. Compound 1 is an organovanadium selenolato cluster, in which two \((\text{CpV})\) moieties bridged by \((\mu\text{-Se})\) and two \((\mu\text{-SePh})\) ligands. Compound 2 exhibits a bicapped tetrahedral core with one \((\mu\text{-SePh})\) ligand. 3 is a tantalahexaborane cluster in which one of the terminal BH protons is substituted by SePh. Compounds 1–3 have been characterized by mass spectrometry, \(^1\)H, \(^13\)C NMR spectroscopy, and the geometric structures were unequivocally established by crystallographic analysis of 1–3.

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1. Introduction

The metallaborane chemistry \([1–4]\), a part of inorganometallic chemistry \([5]\), is concerned with compounds containing direct \(\text{M}\text{–B}\) bonding. There are now a large number of metallaboranes known \([6,7]\), and both the electron-counting rules and the isovalent principle revealed interconnections between ostensibly unrelated molecules and defined the scope of the area \([8,9]\). On the other hand, the metallaborane chemistry is extensive and has developed largely by the incorporation of one, two, or three atoms other than boron into the borane cluster. The conventional route to metallaboranes proceeds in a sequence of steps leading from other than boron into the borane cluster. The conventional route to metallaboranes is extensive and has developed largely by the incorporation of one, two, or three atoms other than boron into the borane cluster. The conventional route to metallaboranes proceeds in a sequence of steps leading from other than boron into the borane cluster.

Part of our studies has focused on the syntheses and characterizations of novel metallaboranes of group 5–8 and their derivatives \([12–15]\). We have recently reported the reaction of \([\text{Cp}^*\text{MoCl}_4]\) with \([\text{LiBH}_4\text{-THF}]\) in presence of dichalcogenide ligands which yielded a new class of open cage dimolydbenlaheteroborane clusters \([13]\). This reactivity prompted us to investigate the chemistry of group 5 metal chlorides sources \([\text{Cp}^*\text{MCln}_x]\) \((M = V; n, x = 2; M = Nb; n = 1, x = 0), or \([\text{Cp}^*\text{TaCl}_4]\) \((\text{Cp} = \eta^1\text{C}_5\text{H}_5\text{C}_5\text{H}_4\text{Me}_2; \text{Cp}^* = \eta^1\text{C}_5\text{H}_4\text{Me}_3)\), with \([\text{LiBH}_4\text{-THF}]\) followed by thermolysis in the presence of diphenyl diselenide yielded metallaheteroborane clusters \([\text{Cp}(\mu\text{-SePh})]_2(\mu\text{-Se})\), \(1\). \([\text{CpNb}_2\text{B}_9\text{H}_{11}(\mu\text{-SePh})], 2\) and \([\text{Cp}^*\text{Ta}^2\text{B}_9\text{H}_{11}(\text{SePh})], 3\) in moderate yields. Compound 1 is an organovanadium selenolato cluster, in which two \((\text{CpV})\) moieties bridged by \((\mu\text{-Se})\) and two \((\mu\text{-SePh})\) ligands. Compound 2 exhibits a bicapped tetrahedral core with one \((\mu\text{-SePh})\) ligand. 3 is a tantalahexaborane cluster in which one of the terminal BH protons is substituted by SePh. Compounds 1–3 have been characterized by mass spectrometry, \(^1\)H, \(^13\)C NMR spectroscopy, and the geometric structures were unequivocally established by crystallographic analysis of 1–3.

2. Result and discussion

As shown in Scheme 1, reaction of \([\text{Cp}_n\text{MCln}_x]\) \((M = V; n, x = 2; M = Nb; n = 1, x = 0), or \([\text{Cp}^*\text{TaCl}_4]\) with excess of \([\text{LiBH}_4\text{-THF}]\), followed by thermolysis in the presence of diphenyl diselenide \((\text{Ph}_2\text{Se})_2\) at 85 °C resulted 1, 2 and 3. In parallel with the formation of 1 and 2, reaction of \([\text{Cp}_2\text{VCl}_2]\) and \([\text{CpNbCl}_4]\) yielded \([\text{Cp}(\mu\text{-SePh})]_2(\mu\text{-Se})\) and \([\text{Cp}-\text{V}^2\text{B}_9\text{H}_{11}]_2\) respectively \([14b]\). On the other hand, compound \([\text{Cp}^*\text{TaCl}_4]\) under the same reaction conditions, resulted in 3 and \([\text{Cp}^*\text{Ta}^2\text{B}_9\text{H}_{11}(\text{SePh})], 14a\). Details of spectroscopic and structural characterization of 1–3 are follows.

2.1. \([\text{Cp}(\mu\text{-SePh})]_2(\mu\text{-Se})\), \(1\)

Group 5 metal carbonyl compounds, such as \([\text{CpV}(\text{CO})_4]\), \([\text{CpV}^2(\text{CO})_4]\) or \([\text{CpTa}(\text{CO})_4]\) are known to react with dichalcogenide...
ligands, of the type \(E_2R_2\) or \(REH\), \((E = S, Se, Te; R = Me, Ph)\), to generate binuclear bis(organochalcogenolato)-bridged complexes \([\text{CpM(CO)}_2(\muER)]_2\) and the non-carbonyl complexes \([\text{CpM(\muER)}_2]_2\) \((M = V, Ta; E = S, Se, Te)\) under vigorous conditions [17]. In contrast, \([\text{Cp}_2VCl}_2\) on reaction with \(\text{Ph}_2\text{Se}_2\) yielded 1, in parallel with the formation of \([(\text{Cp}V)_2(B_2H_6)_2]\). The definitive assignment of the structure of 1 was obtained by X-ray crystallography. As shown in Fig. 1, two \(\text{SePh}\) moieties and one selenium \((\text{Se}3)\) are bridged to two vanadium atoms of the \(\text{VCp}\) units. The \(\mu-\text{Se}3\) atom is disordered over two positions, each with an occupancy ratio of 2:3. Compound 1 is isosstructural with the \(S\) analogue, \([(\text{CpCr(\mu-SPh)})_2(\mu-S)]\) [18]. Each vanadium atom in 1 is in an elongated tetrahedral coordination environment with the \(\text{Cp}\) ligand occupying the apical position and the two coordination polyhedra sharing a common basal plane comprising three bridging \(\text{Se}\) atoms.

The vanadium atoms \(V1\) and \(V2\) are joined by a \(V–V\) single bond (2.7435(6) Å). The dihedral angle between the planes of \(V1–\text{Se}1–V2\) and \(V1–\text{Se}2–V2\) is 97.7°. The mean \(V–\text{Se}(\text{selenolato})\) bond distance is 2.542 Å, which is longer than the \(V–\text{Se}(\text{selenido})\) bond distance of 2.404 Å in \([(\text{CpV})_2(\mu_\text{h}1\text{-Se}2)(\mu-S)_2]\) [19]. Selenium-carbon(phenyl) distances of 1.938(3) and 1.939(3) Å, compare favorably with other \(\text{Se}–\text{C}\) distances, e.g., 1.935 Å in \([(\text{CO})_2\text{Mn(\mu-SePh)}_2\text{Fe(CO)}_3]\) [20]. The two cyclopentadienyl ligands are approximately in an eclipsed configuration about the \(V1–V2\) bond, and the dihedral angle between their least-squares planes is 6.70°.

Scheme 1. Synthesis of 1–3 (\(\text{Cp}\) and \(\text{Cp}^\star\) ligands are not shown for clarity).

Fig. 1. Molecular structure and labeling diagram for 1. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): \(V1–V2\) 2.7435(6), \(V1–\text{Se}1\) 2.5446(5), \(V2–\text{Se}1\) 2.5294(5), \(V1–\text{Se}2\) 2.4937(5), \(V2–\text{Se}2\) 2.4948(5); \(V1–\text{Se}1–V2\) 65.461(14), \(V1–\text{Se}2–V2\) 65.151(15), \(V1–\text{Se}2–\text{Se}3\) 65.726(16).
Consistent with the X-ray results, the $^1$H NMR spectrum of 1 suggests the structure, if static, of higher symmetry. The NMR spectra of 1 did not give any indications of the existence of isomers in solution; only one signal was found for two Cp ligands. The $^{77}$Se NMR of 1 shows two resonances, one at $\delta$ 557 ppm for the bridged $\mu$-SePh and another downfield resonance at $\delta$ 671 ppm for the $\mu$-Se atom. The $^{51}$V chemical shift of the binuclear complex 1 is observed at $\delta$ – 644 ppm, which is comparable with those of other binuclear vanadium complexes, [Cp(V)CO$_2$(μ-Se)$_2$] and [Cp V(CO)$_2$(μ-Se)$_2$] (E = S, Se; R = Me, Ph) (Table 1) [21].

In order to confirm the spectroscopic assignments and determine the full molecular and crystal structure of 2 an X-ray analysis was undertaken. Suitable crystals were obtained from a solution in hexane/dichloromethane (9:1) at – 10 °C. The molecular structure of 2, shown in Fig. 2, contains a bicapped tetrahedral geometry of [(CpNb)$_2$B$_4$H$_9$(μ-SePh)]. The IR spectrum of 2 features strong bands at 2466 and 2418 cm$^{-1}$ owing to the terminal B–H stretches. The $^{11}$B NMR spectrum of 2 rationalizes the presence of four $^{11}$B resonances with an equal intensity. Besides the BH terminal resonance at $\delta$ 8.55 ppm, which bridge the open face of boron atoms. The resonance at $\delta$ – 6.75 ppm has been assigned to the proton which is bonded to the tetrahedral core (Nb–H–B or Nb–H–B$^\text{3}$). Similarly, at low temperature the Cp protons at $\delta$ 6.05 ppm splits into two peaks $\delta$ 6.11 and 6.04 ppm with a relative intensity of 5:5. The above results demonstrate that at the lowest experimental temperatures, both Nb1 and Nb2 become inequivalent owing to the asymmetric arrangements of the bridging H atoms.

Comparison of the structural parameters and chemical shift of 2 with those of Cr [26], Re [27], Ta [14a] and Mo analogues [13], reveals several contrasting features (Table 2). Although, the M–M distance in 2 is comparable, the average M–B distances are markedly longer. The distance between the two capping boron atoms differ to some extent with respect to the size of the open face of the

Table 1
Characteristic structural and spectroscopic data of 1 and the other binuclear complexes.

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<tr>
<td>[Cp[V(CO)$_2$(μ-Se)$_2$]]$_2$</td>
<td>3.07</td>
<td>2.78</td>
<td>77.7, 77.7</td>
<td>80.7, 93.6</td>
<td>686</td>
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<tr>
<td>[(Cp[V(μ-SePh)$_2$])](μ-Se]$_2$</td>
<td>2.74</td>
<td>3.22</td>
<td>65.4, 65.1, 66.7</td>
<td>97.7, 91.5</td>
<td>644</td>
</tr>
<tr>
<td>[Cp[V(CO)$_2$(μ-TePh)$_2$]]$_2$</td>
<td>3.29</td>
<td>3.19</td>
<td>74.5, 73.5</td>
<td>84.3, 86.1</td>
<td>804</td>
</tr>
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* E = S, Se, Te.

$^a$ Dihedral angles at Se(Ph) – Se(Ph).

have indubitably been located by low temperature $^1$H$^{11}$B NMR spectra (Fig. 3). At room temperature the $^1$H$^{11}$B NMR of compound 2 shows single resonance at $\delta$ – 8.55 ppm corresponds to five Nb–H–B protons. Upon lowering the temperature to – 60 °C, the resonance at $\delta$ – 8.55 ppm splits into three distinct peaks (Δ $\delta$ – 8.58, – 8.60 and – 16.75 ppm) in a 2:2:1 ratio. This evidently implies that three resonances merged into a single broad peak at $\delta$ – 8.55 ppm at room temperature. Based upon the pattern of assembly of peaks for the bridging protons in $^1$H NMR spectra, the resonances at $\delta$ – 8.58 and – 8.60 ppm have been assigned to those which bridge the open face of boron atoms. The resonance at $\delta$ – 16.75 ppm has been assigned to the proton which is bonded to the tetrahedral core (Nb–H–B or Nb–H–B$^3$).

Fig. 2. Molecular structure and labeling diagram for 2. Phenyl group is not shown for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (°): Nb(1)–Nb(2) 2.8618(5), Nb(1)–B(1) 2.406(6), Nb(1)–Se(1) 2.7022(6), Nb(2)–Se(1) 2.6962(6), Nb(2)–B(1) 2.403(6), B(1)–B(2) 1.779(9), B(2)–B(3) 1.727(8); B(1)–B(2)–B(3) 126.0(4), B(2)–Nb(1)–B(1) 43.9(2), Nb(2)–B(1)–Nb(1) 67.8(3), Nb(1)–Se(1)–Nb(2) 64.02(15).
cluster, which is more open in 2. The $^{11}$B resonances, on going from the lighter to the heavier metal atom, appeared at high field. As the qualitative cluster shapes of 2 and [(Cp$^{3}$Mo)$_{2}$B$_{2}$H$_{2}$SePh$_{2}$] are similar to that observed for [(Cp$^{3}$Ta)$_{2}$B$_{2}$H$_{11}$] [14a]. The composition of 3 is recognized from the elemental analysis together with multinuclear NMR spectroscopy. The $^{11}$B NMR spectrum of 3 exhibits three signals at $\delta$ 0.1, -3.3 and -8.0 ppm with 1:2:1 intensity ratio. The chemical shift at $\delta$ -8.0 ppm is assigned to the B-SePh as it remained a singlet in coupled $^{11}$B spectrum, whereas the other peaks became doublet. The $^1$H($^{11}$B) spectrum suggests the presence of two kind of terminal H atoms and three kind of bridging H atoms, at $\delta$ -9.4, -10.5 and -10.9 ppm with 1:2:1 intensity ratio. The $^{77}$Se NMR of 3 shows single resonance at $\delta$ 573 ppm for the cage B-SePh group.

The molecular structure of 3, shown in Fig. 4, is consistent with the analysis of the observed spectroscopic data and reveals core geometry that is the same as that observed for [(Cp$^{3}$Ta)$_{2}$B$_{2}$H$_{6}$] [14b]. The Ta–B bond lengths of 3 ranges from 2.36 Å to 2.41 Å and are similar to that observed for [(Cp$^{3}$Ta)$_{2}$B$_{2}$H$_{11}$]. The B–B distances in 3 range from 1.75 Å to 1.80 Å in the range expected for the directly bonded ethane-like (BH$_{2}$–BH$_{3}$)$_{2}^{2-}$ ligand, however, markedly shorter than that observed for the hydrogen-bridged (H$_{2}$BHBBH)$_{2}^{2-}$ ligand in [(Cp$^{3}$Ta)$_{2}$B$_{2}$H$_{6}$] [18a]. The B–Se distance (2.046(9) Å) is longer comparable to that observed in [(Cp$^{3}$Mo)$_{2}$B$_{4}$H$_{5}$Se$_{2}$] [12b]. However, they are significantly shorter when compared to those observed in other selenaborane clusters [29]. This may be due to the tendency of the boron and selenium atoms to form polarized bonds that have a localized two-center character resulting in the observed distances [30]. The bond angle of the B–Se–C moiety (104.7(4)$^\circ$) in 3 suggests that the selenium atom is in sp$^3$ hybridization.

3. Conclusions

We have established the synthesis of group 5 organoselenolato-bridged complex, and two metallaheteroborane compounds 2 and 3, from the reaction of metal polychlorides with [LiBH$_{4}$:THF] and Ph$_{2}$Se$_{2}$. The difference in reactivity pattern of the group 5 metal chlorides with dichalcogenide ligand is also reflected in the observed product distribution. Apparently, these results highlight the possibility of the synthesis of a new class of metallaheteroborane clusters.

4. Experimental

4.1. General procedures and instrumentation

All the operations were conducted under an Ar/N$_{2}$ atmosphere using standard Schlenk techniques or glove box. Solvents were
distilled prior to use under Argon. [(Cp)2VCl2], [CpNbCl4], [CpTaCl4] and [LiBH4·THF] were used as received (Aldrich), [Ph2Se2] [31] was prepared as described in literature. The external reference [Bu4N[B3H8]] for the 11B NMR, [32] 13C NMR spectrum was recorded on 400 MHz Bruker FT-NMR spectrometer operating at 105 MHz (31P) and chemical shifts are in parts per million relative to a VOCI3 external reference. Thin layer chromatography was carried on 250 mm dia aluminum supported silica gel TLC plates (MERCK TLC Plates). NMR spectra were recorded on a 400 and 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (δ, ppm, CDCl3, 7.26), while a sealed tube containing [Bu4N[B3H8]] in [D6] benzene (δ9, ppm, –30.07) was used as an external reference for the 11B NMR. Microanalyses for C and H were performed on Perkin Elmer Instruments series II Model 2400. Infrared spectra were recorded on a Nicolet 6700 FT spectrometer. Mass spectra were obtained on ESI Q-ToF Micro mass Spectrometer and Jeol SX 102/Da-600 mass spectrometer/data system using Argon/Xenon (6 kv, 10 mA) as the FAB gas.

4.2. General synthesis of 1–3

In a typical reaction, [(Cp)2VCl2] (0.08 g, 0.32 mmol) was loaded in toluene (12 mL) and cooled to –70 °C, [LiBH4·THF] (1.0 mL, 1.92 mmol) was added via syringe and the reaction mixture was allowed to warm slowly to room temperature and left stirring for an additional hour. The solvent was evaporated under vacuum, the residue was extracted into hexane and filtration afforded an extremely air and moisture-sensitive red-blue intermediate. The filtrate was concentrated and a toluene solution (15 mL) of the residue was subjected to chromatographic work up using silica gel TLC plates. Elution with a hexane/CH2Cl2 (90:10 v/v) mixture yielded air-stable red orange 1 (0.03 g, 15%). Under same reaction conditions green 2 (0.03 g, 21%) and purple 3 (0.04 g, 27%) were isolated from the reaction of Ph2Se with [CpNbCl4] and [CpTaCl4] respectively.

Note that compounds 1–3 have been isolated along with the metallaborane [(Cp2)2B2H3] [(M = V, Nb)] and [(Cp2)TaB2H4] respectively reported earlier [14a,b].

1: 31P NMR (105 MHz, CDCl3, 22 °C): δ -644.0 (s, br, 2 V); 1H NMR (400 MHz, CDCl3, 22 °C): δ 7.78–6.68 (m, 10H, 2C6H5), 5.96 (s, 2Cp); 13C NMR (100 MHz, CDCl3, 22 °C): δ 134.0, 126.4, 125.3 (s, C6H5), 98.6 (s; C5H5), 77Se NMR (95.38 MHz, CDCl3, 22 °C): δ 671 (s; Se), 557 (s, 2SePh); MS (ESI+): m/z (%) = 623 [M+]; elemental analysis calc (%) for C22H20SeVCl2: C 42.40, H 3.23; found: C 41.68, H 3.05.

2: 11B NMR (128 MHz, CDCl3, 22 °C): δ 18.2 (br, 1B), 15.1 (br, 1B), 3.0 (br, 1B), –0.2 (br, 1B); 1H NMR (400 MHz, CDCl3, 22 °C): δ 7.48–6.78 (m, 5H; C5H5), 6.04 (s, 2Cp), 4.58 (partially collapsed quartet (pq) 1B8H4), 4.34 (pq, 1B8H4), 2.01 (pq, 1B8H4), 1.28 (pq, 1B8H4), –8.55 (br, 5N–H = B); 13C NMR (100 MHz, CDCl3, 22 °C): δ 134.1, 127.8, 126.4, 124.6 (C6H5), 975 (s; C5H5), 77Se NMR (95.38 MHz, CDCl3, 22 °C): δ 533 (s, Se), IR (hexane): vbr = 2466 and 2418 cm–1 (BH); MS (FAB) P+ (max): m/z(%): 524 (isotopic pattern for 2Nb; 4B and 15e atoms); elemental analysis calc (%) for C26H46B4SeNbV2: C 37.05, H 5.50; found: C 37.04, H 5.56.

4.3. X-ray structure determination

Crystal data for 1 and 3 were collected and integrated using OXFORD DIFFRACTION XALIBUR-S CCD system equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) radiation at 150 K. Crystal data for 2 were collected and integrated using a Bruker Axs kappa apex 2CCD diffractometer, with graphite-monochromated Mo-Kα (λ = 0.71073 Å) at 173 K. The structures were solved by heavy atom methods using SHELXS-97 or SIR92 [33] and refined using SHELXL-97 (Sheldrick, G.M., University of Göttingen) [34,35].

Crystal data for 1: CCDC 819252, Formula, C22H20Se3V2; Formula weight, 662.14 g/mol; Crystal system, space group: monoclinc, P21/c. Unit cell dimensions, a = 15.2867(3), b = 8.29110(10), c = 18.4289(4) Å, β = 110.210(2)°; Z = 4. Final R indices [I > 2σ(I)] R1 = 0.0268, wR2 = 0.0703. Index ranges –21 ≤ h ≤ 20, –11 ≤ k ≤ 11, –21 ≤ l ≤ 25. 29% range for data collection 3.26–30.00°. Crystal size 0.33 × 0.28 × 0.21 mm3. Density (calculated) 1.888 Mg/m3. Reflections collected 22896, independent reflections 6394 [R(int) = 0.0295], Goodness-of-fit on F2 0.956.

Crystal data for 2: CCDC 819250, Formula, C26H46B4SeTa2; Formula weight, 842.73 g/mol; Crystal system, space group: triclinic, P-1. Unit cell dimensions, a = 9.9310(4), b = 10.5787(5), c = 11.0913(5) Å, α = 79.902(2), β = 72.534(2), γ = 88.369(2); Z = 2. Final R indices [I > 2σ(I)] R1 = 0.0381, wR2 = 0.0818. Index ranges –13 ≤ h ≤ 12, –10 ≤ k ≤ 14, –11 ≤ l ≤ 14, 0 range for data collection 1.95–28.40°. Crystal size 0.23 × 0.20 × 0.10 mm3. Density (calculated) 1.847 Mg/m3. Reflections collected 14533, independent reflections 5141 [R(int) = 0.0274], Goodness-of-fit on F2 1.040.

Crystal data for 3: CCDC 819249, Formula, C26H46B4SeTa2; Formula weight, 842.73 g/mol; Crystal system, space group: monoclinic, P21/c. Unit cell dimensions, a = 11.739(3), b = 10.050(3), c = 25.4381(10) Å, α = 98.074(3); Z = 4. Final R indices [I > 2σ(I)] R1 = 0.0463, wR2 = 0.1128. Index ranges –15 ≤ h ≤ 15, –13 ≤ k ≤ 12, –33 ≤ l ≤ 33. 0 range for data collection 3.26–27.50°. Crystal size 0.28 × 0.23 × 0.22 mm3. Density (calculated) 1.891 Mg/m3. Reflections collected 23773, independent reflections 6747 [R(int) = 0.0821], Goodness-of-fit on F2 0.963.

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Appendix A. Supplementary material

CCDC 819249, 819250 and 819252 contains 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.

Appendix B. Supplementary material

Supplementary data associated with this article can be found in the on-line version at doi:10.1016/j.jorganchem.2011.06.040.
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