[Cp$_2$V] Migration along an Octatetrayne Chain: From the Monometallic Complex [Cp$_2$V(3-4η-tBuC≡C−C$_2$−C≡CC≡CtBu)] to the Dimetallic Complex [(Cp$_2$V)$_2$(1-2η:7-8η-tBuC$_2$−C≡CC≡C−C$_2$$t$Bu)]

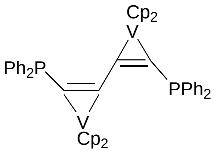
Robert Choukroun,*[a] **Bruno Donnadieu,**[a] **Christian Lorber,**[a] **Paul-Michael Pellny,**[b] **Wolfgang Baumann,**[b] **and Uwe Rosenthal**[b]

Abstract: The oxidative addition of one equivalent of [Cp$_2$V] (**4**) to the tetrayne ligand tBuC≡CC≡CC≡CC≡CtBu (**5**) gives the monometallic complex [Cp$_2$V(3-4η-tBuC≡C−C$_2$−C≡CC≡CtBu)] (**7**). Compound **7** reacts further with a second equivalent of [Cp$_2$V] to give the dimetallic complex [(Cp$_2$V)$_2$(1-2η:7-8η-tBuC$_2$−C≡CC≡C−C$_2$$t$Bu)] (**8**), which involves a shift of the first coordinated [Cp$_2$V] unit from the internal C3–C4 to the external C1–C2 positions on the alkynyl ligand. Compound **8** is also directly obtained by the addition of two equivalents of [Cp$_2$V] to **5**. Reversibly, reaction of **8** with **5** leads to **7**. This exchange reaction between **7** and **8** by adding successively **5** and **4** has been monitored by EPR spectroscopy. By contrast, the oxidative addition of one or two equivalents of [Cp$_2$V] to the tetrayne ligand PhC≡CC≡CC≡CC≡CPh (**6**) gives the homodimetallic complex [(Cp$_2$V)$_2$(1-2η:7-8η-PhC$_2$−C≡CC≡C−C$_2$-Ph)] (**9**). Both monometallic and dimetallic complexes **7**, **8**, and **9** have been characterized by X-ray diffraction. Magnetic moment measurements for **8** and **9** from 300 to 4 K indicated a weak antiferromagnetic J exchange coupling of -12.5 and -4.1 cm^{-1}, respectively.

Keywords: alkynes · metallocenes · structure elucidation · vanadium

Introduction

Fascinating chemistry from titanocene and zirconocene synthons with polyynes has been developed and investigated.[1] Depending on the metal (Ti or Zr) and the nature of the cyclopentadienyl ligand (Cp, Cp*), different types of Ti and Zr complexes have been been characterized.[2] We have extended this concept to vanadocene, a potentially stable d^2 paramagnetic species, which can be isolated in pure form, to develop the analogous chemistry. Conducting our studies on vanadocene chemistry and polyyne ligands, we have already shown that vanadocene leads to new types of structures by oxidative addition of the vanadocene to ethynyl -C≡C- bonds. Whereas the reaction of a diyne ligand with [Cp$_2$V] gave the expected vanadacyclopropenes **1a** or **1b**,[3] the triyne ligand led to an unusual homodimetallic V$^{\mathrm{III}}$–V$^{\mathrm{III}}$ complex **2**.[4] Additionally, [Cp$_2$V] and the bis(alkynyl)metallocene [(C$_5$H$_4$R)$_2$Zr(C≡CPh)$_2$] (R = H, Me, tBu, SiMe$_3$) gave the original heterodimetallic complex **3**, in which a butadiene framework arising from a CC coupling between both alkynyl ligands contains two planar tetracoordinate carbon atoms.[5]



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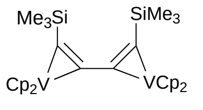

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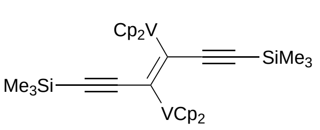

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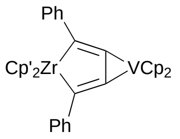

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Recently, Rosenthal et al. described the reaction of the octatetrayne ligand RC≡C−C≡C−C≡C−C≡CR (R = SiMe$_3$, tBu) with titanocene and zirconocene complexes.[6] The products obtained were dependent on the substituent R

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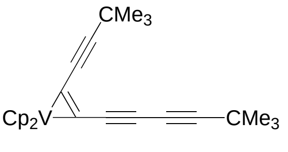
attached to the tetrayne and on the stoichiometry of the reaction. Here we report the oxidative addition of [Cp_2V] (**4**) to the alkyne bonds of an octatetrayne ligand $RC{\equiv}CC{\equiv}C\text{-}C{\equiv}CC{\equiv}CR$ (R = *t*Bu (**5**), Ph (**6**)), and the migration of the [Cp_2V] unit along the carbon chain as a consequence of the stoichiometry of the reaction.

Results and Discussion

The reaction of **4** with one equivalent of **5** in pentane gave the organometallic complex **7**, which was isolated as crystals. The



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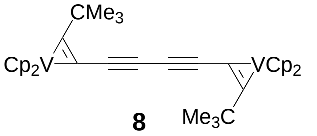

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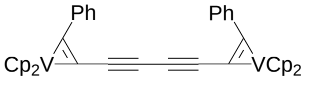

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molecular structure of **7** reveals four independent but very similar molecules in the unit cell; Figure 1 shows a ZORTEP perspective view of one single molecule. The Cp_2V unit is located at one of the internal positions of the C_8 carbon chain. The C3-V-C4 plane is nearly coplanar with the C_8 carbon skeleton plane of the ligand (175.5°). The reaction of two equivalents of **4** with one equivalent of **5** in pentane led to the homodimetallic complex **8**, which was isolated and structurally characterized by X-ray crystallography (Figure 2). The Cp_2V units are nearly *trans* oriented and are located at both extremities of the C_8 carbon chain. The carbon atoms of the C_8 ligand lie in the same plane and the dihedral angle between the plane of the C1-V-C2 and C1′-V′-C2′ unit is 174.8°; thus both vanadium units are almost coplanar with the C_8 carbon chain.

The reaction of three or four equivalents of **4** with one equivalent of **5** in pentane also led to **8**; the other two alkynyl bonds of the carbon chain remained intact. The complex **8** was also prepared as a crystalline product by adding one equivalent of **5** to a solution of **7** in THF (the cell parameters of the product were the same as those observed in the X-ray determination structure of **8**). Treatment of **8** with one equivalent of **5** gave a crystalline powder characterized as **7** (on the basis of its powder diffraction pattern, which was identical to that of the crystalline sample of complex **7**, isolated from a 1:1 mixture of **4** and **5**). On the other hand, the reaction of one or two equivalents of **4** with **6** in toluene gave exclusively the homodimetallic complex **9**, which was characterized by an X-ray structure determination (Figure 3). The dihedral angle between the VC_2 units (V1-C1-C2/V2-C7-C8) is 119° and only carbon atoms C1 to C6 lie in the same plane, C7 (0.207 Å) and C8 (−0.229 Å) are above and below this plane, respectively.

The different orientation of the Cp_2VC_2 units in **8** and **9** was also observed for complexes **1a**,**b** in which the R groups are $SiMe_3$ and PPh_2, respectively.[3] The structural features are nearly the same, but the alkynyl chain is longer in **8** and **9**. Variable-temperature magnetic susceptibility measurements were carried out for **7**, **8**, and **9**: the effective magnetic moment μ_{eff} was 1.88 μ_B for **7**, as expected for a V^{IV} complex, and 2.05 and 1.81 μ_B for **8** and **9**, respectively, at 300 K, calculated for one vanadium atom. The effective magnetic moment μ_{eff} for **8** and **9** decreases to 0.55 and 1.13 at 5 and 3.4 K, respectively. The antiferromagnetic interaction, which was calculated by fitting the data with an exchange interaction model, was determined to be $J = -12.5$ and $-4.1\ cm^{-1}$ for **8** and **9**, respectively.[7]

These results are consistent with a favorable "in-plane π-type" orientation of the Cp_2VC_2 unit through a linear combination of mainly p-orbital character of the carbon atoms of the tetrayne in the molecule **8**. This situation is disfavored in complex **9**, in which the Cp_2VC_2 unit and its magnetic contributions can be considered as orthogonal.[3]

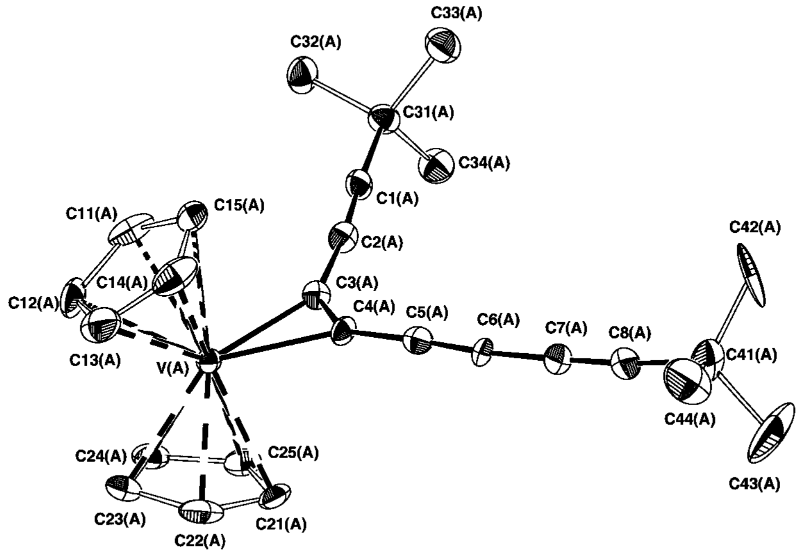

Figure 1. Molecular structure and atom-numbering scheme for **7**. Selected bond lengths [Å] and angles [°]: V–C(3) 2.076(6), V–C(4) 2.103(6), C(1)–C(2) 1.201(8), C(2)–C(3) 1.415(8), C(3)–C(4) 1.286(8), C(4)–C(5) 1.389(9), C(5)–C(6) 1.218(8), C(6)–C(7) 1356(11), C(7)–C(8) 1.213(10), V–Cp 1.960 (av); C(3)-V-C(4) 35.8(2), C(2)-C(3)-C(4) 142.3(6), C(3)-C(4)-C(5) 141.8(6), Cp-V-Cp 139.3(av). Cp denotes the centroids of the C_5H_5 rings C(11)–C(15) and C(21)–C(25).

The EPR spectra of **7**–**9** show no detectable differences and similar data are observed (nearly $g = 2.000$; $a(^{51}V) = 43.6$ G). Their high g values imply a significant electron delocalization across the alkynyl C_8 ligand. Nevertheless, the reactivity of **4** towards **5** can be monitored in solution by using EPR spectroscopy. The value of the integration I of the EPR spectra of monometallic **7** and homodimetallic **8** is related to the number of unpaired elec-

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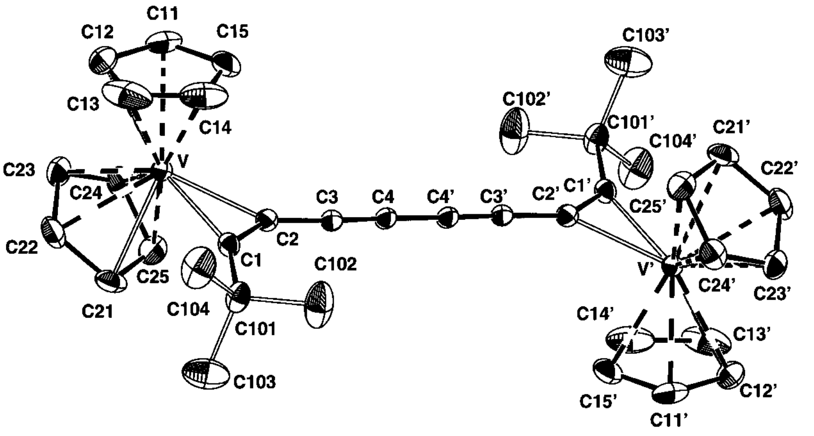


Figure 2. Molecular structure and atom-numbering scheme for **8**. Selected bond lengths [Å] and angles [°]: V–C(1) 2.078(3), V–C(2) 2.120(3), C(1)–C(2) 1.287(4), C(2)–C(3) 1.387(4), C(3)–C(4) 1.216(4), C(4)–C(4′) 1.364(6), V-Cp 1.968 (av); C(1)-V-C(2) 35.69(11) C(2)-C(1)-C(101) 138.5(3), C(1)-C(2)-C(3) 149.2(3), Cp-V-Cp 138.2 (av). Cp denotes the centroids of the C_5H_5 rings C(11) – C(15) and C(21) – C(25).

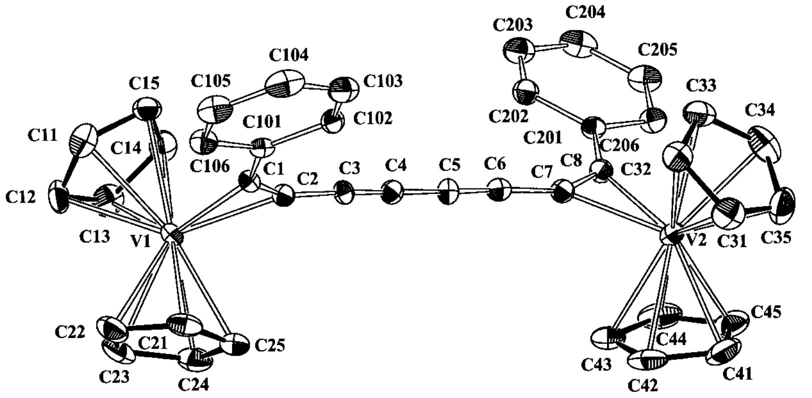


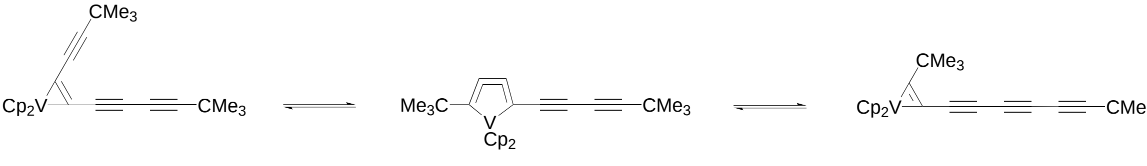
Figure 3. Molecular structure and atom-numbering scheme for **9**. Selected bond lengths [Å] and angles [°]: V(1)–C(1) 2.065(4), V(1)–C(2) 2.112(3), V(2)–C(7) 2.114(4), V(2)–C(8) 2.069(4), C(1)–C(2) 1.289(5), C(2)–C(3) 1.371(5), C(3)–C(4) 1.214(5), C(4)–C(5) 1.348(5), C(5)–C(6) 1.217(5), C(6)–C(7) 1.365(5), C(7)–C(8) 1.295(5), V–Cp 1.954 (av); C(1)-V(1)-C(2) 35.93(13), C(7)-V(2)-C(8) 36.05(13), C(2)-C(1)-C(101) 141.2(3), C(1)-C(2)-C(3) 153.2(4), C(7)-C(8)-C(201) 140.2(3), C(6)-C(7)-C(8) 152.4(4), Cp-V-Cp 140.0 (av). Cp denotes the centroids of the C_5H_5 rings C(11) – C(15), C(21) – C(25), C(31) – C(35), and C(41) – C(45).

trons *N*. Its theoretical ratio is for the system $I(\mathbf{8})/I(\mathbf{7}) = \sqrt{\Sigma N(N+2)}/\sqrt{N(N+2)} = \sqrt{2}$. Starting from a standardized THF solution of **4** (1 equiv) and **5** (1 equiv) or directly from **7** (1 equiv), the modification of the integration of the EPR spectrum was checked after addition of **4** (1 equiv) then **5** (1 equiv) and **4** (1 equiv) again to the mother solution. The successive formation of **8** then **7**, without having a preconceived idea about the position of Cp_2V unit in the C_8 chain, is in agreement with the ratio expected for two then one V^{IV} center. Parallel experiments on the HCl hydrolysis of these solutions show the formation of *cis* 3,4-*t*BuC≡CCH=CHC≡CC≡C*t*Bu from a 1:1 mixture of **4** and **5** (^1H NMR (250 MHz, $CDCl_3$): $\delta = 6.01, 5.40$ (d, =C*H*, $J = 12$ Hz), 1.25, 1.17 (s, *t*Bu); GC/MS; $M_w = 212$) and liberation of the free ligand **5** from a 1:1 mixture of [**4**+**5**]+**4** (GC/MS; $M_w = 210$). The reaction of **7** and **8** with HCl was examined and gave also the enetriyne and **5**, respectively (the release of the ligand has a precedent in vanadocene chemistry[8]), suggesting strongly that the same complexes are formed in solution and in the solid-state.

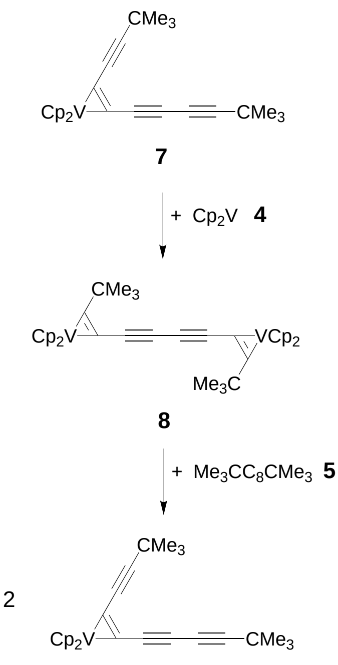
Although the reactivity of vanadium paramagnetic complexes could only be followed by X-ray structure determination, these results offer synthetically attractive compounds with puzzling features. $[Cp_2V]$ could migrate by sliding from an internal 3 – 4η position to an external 1 – 2η position on the carbon chain of the tetrayne ligand (Scheme 1). The sliding along a polyyne chain such as hexatriyne was recently observed by NMR spectroscopy for a permethylzirconocene complex. The η^2 complex $[Cp^*_2Zr(\eta^2\text{-}t\text{BuC}{\equiv}\text{C}{-}\text{C}_2{-}\text{C}{\equiv}\text{C}t\text{-Bu})]$ was considered as an intermediate for the observation of η^4 complexes $[Cp^*_2Zr(1\text{-}2\text{-}3\text{-}4\eta^4\text{-}t\text{BuC}_4{-}\text{C}{\equiv}\text{C}t\text{Bu})]$ versus $[Cp^*_2Zr(3\text{-}4\text{-}5\text{-}6\eta^4\text{-}t\text{BuC}{\equiv}\text{C}{-}\text{C}_4\text{-}t\text{Bu})]$.[9] The shift of the vanadocene unit from **7** (in the 3 – 4-position in the C_8 chain) to **8** (in the 1 – 2- and 7 – 8-position in the C_8 chain) by adding **4** and the re-formation of **7** by adding **5** (Scheme 2) could be dependent on the existence of a η^4 complex $[Cp_2V(\eta^4\text{-}t\text{BuC}_4{-}\text{C}{\equiv}\text{C}{-}\text{C}{\equiv}\text{C}t\text{Bu})]$. Therefore, further experimental and theoretical studies in this field are necessary in order to gain a better understanding of the processes taking place in the $[Cp_2V]$ migration along the octatetrayne chain. The formation of a V^{III} – V^{III} complex of type **2**[4] when complex **7** is approached by **4** as well as dissociation processes can not be excluded.

Experimental Section

All syntheses and subsequent manipulations were carried out under argon by conventional Schlenk-tube techniques or by using a dry box (Vacuum Atmosphere Dry-Lab) filled with argon. Liquids were transferred by



Scheme 1.



Scheme 2.

syringe or cannula. All solvents were dried by conventional methods, distilled under argon, and degassed before use. Compound **4** was prepared according to the method given in reference[10], **5** and **6** according to that in reference [11]. Elemental analyses were performed in the laboratory (C, H) and by the Service National de Microanalyses du CNRS (V). Magnetic susceptibilities were determined by using a SQUID susceptometer within the 4 to 300 K temperature regime. EPR spectra were obtained by using a BRUKER ESP300E spectrometer. NMR spectra were recorded at room temperature on a Fourier transform NMR spectrometer BRUKER AC250.

[Cp$_2$V(3–4η-*t*BuC≡C–C$_2$–C≡CC≡C*t*Bu)] (7): Compound **5** (42 mg, 0.2 mmol) in pentane (5 mL) was added to a solution of [Cp$_2$V] (34 mg, 0.187 mmol) in pentane (5 mL) at room temperature. After the mixture had been stirred for 10 min, the resulting brown solution was left for 48 h. Crystals of **7** were obtained from this solution that were suitable for an X-ray crystal structure determination (yield: 45 mg, 62 %). Elemental analysis for $C_{26}H_{28}V$ (%): (calcd): C 79.80, H 7.16, V 13.01; found: C 79.35, H 7.24, V 12.52; IR (Nujol): $\tilde{\nu} = 2223, 2095$ (ν(C≡C)), 1712 (ν(C=C)) cm^{-1}.

[(Cp$_2$V)$_2$(1–2η:7–8η-*t*BuC$_2$–C≡CC≡C–C$_2$*t*Bu)] (8): Compound **5** (131 mg, 0.624 mmol) in pentane (10 mL) was added to a solution of Cp$_2$V (226 mg, 1.25 mmol) in toluene (3 mL) at room temperature. After the mixture had been stirred for 5 min, the resulting brown-red solution was left for 48 h. Crystals of **8** were obtained from this solution that were suitable for an X-ray crystal structure determination (yield: 250 mg, 70 %). Elemental analysis for $C_{36}H_{38}V_2$ (%): calcd: C 75.52, H 6.64; found: C 75.0, H 6.12; IR (Nujol): $\tilde{\nu} = 2061$ (ν(C≡C)), 1717 (ν(C=C)) cm^{-1}.

[(Cp$_2$V)$_2$(1–2η:7–8η-PhC$_2$–C≡CC≡C–C$_2$Ph)] (9): Compound **6** (50 mg, 0.199 mmol) in toluene (5 mL) was added to a solution of [Cp$_2$V] (72 mg, 0.398 mmol) in toluene (5 mL) at room temperature. After the mixture had been stirred for 1 h, the dark red solution was layered with pentane for 48 h. Crystals of **9** were obtained that were suitable for an X-ray structure determination (yield: 80 mg, 65 %). Elemental analysis for $C_{40}H_{30}V_2$ (%): calcd: C 78.43, H 4.90, V 16.67; found: C 78.95, H 5.20, V 16.10; IR (Nujol): $\tilde{\nu} = 2059$ (ν(C≡C)), 1580 (ν(C=C)) cm^{-1}.

Magnetism: Using a Heisenberg Hamiltonian $H = -JS_AS_B$ with the local spin $S_A = S_B = 1/2$, the magnetic interaction was estimated with a model for dinuclear compounds.[7] The J, g parameters were determined by least-squares fitting. The agreement factor R is equal to 3.1×10^{-3} and 5.0×10^{-3} for **8** and **9**, respectively. The average value of the g factor was found as 2.13 and 1.93 for **8** and **9**, respectively.

EPR experiments: The sequence **4** (18 mg, 0.1 mmol) and **5** (21 mg, 0.1 mmol) was repeated twice; both products were introduced successively as solids to induce very small variation in the large volume of the THF solution (5 mL); an aliquot of the solution was introduced into a standardized capillary tube (50 μL) for EPR measurements, after each introduction of the reactant in the solution.

Crystallographic data collection and structure determination for the compounds 7, 8, and 9: For each air- and mositure-sensitive compound **7**–**9**, measurements were recorded on an oil-coated shock-cooled crystal[12] pasted on a glass fiber on a STOE imaging plate diffraction system (IPDS) diffractometer using a graphite-monochromated cooler device. Data were collected at 160(2) K, and the final unit cell parameters were obtained by least-squares refinement of a set of 5000 reflections. The crystal decay was determined by measuring 200 reflections; only insignificant fluctuations of diffracted intensities were observed. The structures were solved by using direct methods (SIR92[13]), and refined by least-squares procedures on F^2 with SHELX97[14] by minimizing the function: $\Sigma w(F_o^2 - F_c^2)^2$. The atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*.[15] All hydrogen atoms were located on difference Fourier maps, but were introduced in processes in the refinement in idealized positions. All non-hydrogen atoms were anisotropically refined, and a weighting scheme ($w = 1/[\sigma^2(F_o^2) + (XP)^2]$ where $P = (F_0^2 + 2F_c^2)/3$) was used in the last cycles of refinement. The absolute configuration of compound **7**, which crystallized in the space group $P1$, could be assigned unambiguously on the basis of the refinement of the Flack parameter[16] (–0.02(2)). This result clearly indicates the correctness of the enantiomer's choice in the crystal. Drawings of the molecules (using 50 % probability displacement ellipsoids for non-hydrogen atoms) were performed with the program ZORTEP.[17]

Crystal structure data of compounds **7** and [**8**; **9**]: Molecular weight 391.43 [572.54; 704.73], crystal system triclinic [monoclinic; monoclinic], space group $P1$ [$P2_1/c$; $P2_1/c$], $a = 11.8818(16)$ [8.534(2); 15.743(2)], $b = 13.2359(17)$ [14.994(3); 14.739(2)], $c = 14.732(2)$ [11.766(2); 15.729(2)] Å, $\alpha = 76.019(16)$, $\beta = 78.432(17)$ [108.53(3) ; 101.55(2)], $\gamma = 90.000(16)°$, cell volume = 2190.5 [1425.5; 3575.8] Å^3, $Z = 4$ [2;4], $\rho = 1.187$ [1.332; 1.309] g cm^{-3}, $\mu = 4.6$ [6.78; 5.06] cm^{-1}, $F(000)$ 828, [600; 1464], crystal size = 0.5 × 0.2 × 0.07 [0.4 × 0.1 × 0.07; 0.6 × 0.3 × 0.2] mm, crystal form plate [platelet; parallelepiped], crystal color dark red [red; deep red], radiation type Mo$_{K\alpha}$, wavelength = 0.71073 Å, temperature 160 [160; 160] K, number of measured reflections 16133 [9656; 22573], number of independent reflections 11740 [2225; 5631], $R_{av} = 0.0613$ [0.083; 0.0897], $R_{wb} = 0.0563$ [0.0392; 0.0431], goodness of fit 0.997 [0.924; 0.885], number of variables 997 [175; 443].

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-144051 (**7**), CCDC-144052 (**8**), CCDC-144053 (**9**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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