Synthesis and characterization of a dimeric acetone coupling product with a titanium–pentadienyl complex☆

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Abstract

The reactions of $Ti(C_5H_4R)(C_5H_7)(PMe_3)$ complexes (R = H, CH_3; C_5H_7 = pentadienyl) with acetone lead to the coupling of each dienyl terminus to a molecule of acetone, as had earlier been observed for the 2,4-dimethylpentadienyl ligand. However, in this case, dimeric rather than monomeric species were isolated. Confirmation of their formulations has been accomplished through a single crystal diffraction study. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Pentadienyl; Coupling reaction; Pi donation

1. Introduction

As has been observed for diene complexes of early transition metals [1], pentadienyl complexes of titanium [2] and zirconium [3] have been observed to undergo facile coupling reactions with ketones, imines, nitriles, isonitriles, and alkynes. Most of the effort in this area to date has focussed on complexes employing the 2,4-C_7H_{11} (C_7H_{11} = dimethylpentadienyl) ligand, whose enhanced favorability for the U conformation may be a key to its generally greater utilization [4]. Naturally, for any real synthetic application, other substitution patterns would be desirable; however, it is quite possible that their reactions could also lead to entirely different chemical outcomes. We have therefore begun to examine coupling reactions for the C_5H_7 and 3-C_6H_9 (C_6H_9 = methylpentadienyl) ligands, which do not possess an inherent preference for the U conformation. Herein we report some of our observations for the

C_5H_7 complexes, which do indeed exhibit significant differences relative to the 2,4-C_7H_{11} species.

2. Experimental

All operations were conducted under a nitrogen atmosphere in either Schlenk apparatus or in a glovebox. All solvents were dried and deoxygenated by distillation from sodium benzophenone ketyl under a nitrogen atmosphere. Spectroscopic data were obtained as previously described [5]. The ^{13}C-NMR spectra were not precisely integrated, but numbers of carbon atoms are given in accord with their assignments. $Ti(C_5H_4R)Cl_3$ (R = H, CH_3) and KC_5H_7 were prepared according to published procedures [6,7]. Elemental analyses were obtained from E + R Microanalytical Laboratories.

2.1. Ti(CH₃C₅H₄)(C₅H₇)[P(CH₃)₃]

To a red solution of $Ti(CH_3C_5H_4)Cl_3$ (3.00 g, 12.9 mmol) in 50 ml THF under a nitrogen atmosphere was added activated zinc dust (2.00 g, 30.6 mmol), leading to the formation of a green–blue solution, which was

stirred overnight. To the aquamarine solution was then added $P(CH_3)_3$ (1.40 ml, 13.5 mmol) and the mixture was stirred for 3 h. The solution was then cooled to $-78°C$ and $K(C_5H_7)$ (4.10 g, 38.6 mmol) in 50 ml of THF was added dropwise via a pressure equalizing addition funnel. The reaction mixture turned violet immediately and was allowed to warm to room temperature. Upon warming to room temperature, the mixture turned red-brown. Next, the solvent was removed in vacuo to give a brown-red solid. Extraction of the solid with three 100 ml portions of ether and filtration through a Celite pad on a coarse frit gave a red-brown filtrate. Concentration in vacuo of the filtrate to ca. 100 ml and cooling to $-90°C$ for 1 week gave 0.85 g (25%) of the product as an air-sensitive brown solid (m.p. 48–50°C).

Anal. Calc. for $C_{14}H_{23}PTi$: C, 62.20; H, 8.58. Found: C, 62.10; H, 8.77.

^{1}H-NMR (benzene-d_6, ambient): δ 6.09 (t, 1H, $J = 9.8$ Hz, H-3), 5.22 (q, 2H, $J = 2.9$ Hz, Cp), 4.86 (q, 2H, $J = 2.9$ Hz, Cp), 4.42 (q, 2H, $J = 10.9$ Hz, H-2,4), 1.81 (m, 2H, H-1,5$_{exo}$), 1.21 (s, 3H, CH_3Cp), 0.93 (d, 9H, $J = 5.5$ Hz, $P(CH_3)_3$), -1.04 (m, 2H, H-1,5$_{endo}$).

^{13}C-NMR (benzene-d_6, ambient): δ 114.8 (d of septets, 1C, $J = 158, 5$ Hz, C-3), 112.4 (s, 1C, Cp), 100.3 (d of m, 2C, $J = 166$ Hz, Cp), 97.6 (d of q, 2C, $J = 170, 6$ Hz, Cp), 93.8 (dd, 2C, $J = 159, 10$ Hz, C-2,4), 51.8 (tm, 2C, $J = 146$ Hz, C-1,5), 19.2 (qm, 3C, $J = 131$ Hz, $P(CH_3)_3$), 14.6 (q, 1C, $J = 126$ Hz, CH_3Cp).

Mass Spectrum (EI, 80 eV) m/z (relative intensity): 194 (31), 193 (21), 192 (100), 191 (15), 190 (20), 126 (26), 76 (24), 61 (21), 59 (13), 57 (24).

2.2. '[Ti(CH_3C_5H_4)(C_5H_7)(C_3H_6O)_2]_2'

To a stirred solution of $Ti(CH_3C_5H_4)(C_5H_7)[P(CH_3)_3]$ (0.500 g, 1.85 mmol) in 50 ml THF at $-78°C$ under a nitrogen atmosphere was added acetone (0.330 ml, 4.49 mmol). Upon warming to room temperature, a color change from orange to dark red occurred and the mixture was stirred for 12 h. The solvent was removed in vacuo to give a red-orange solid which was extracted with two 50 ml portions of pentane and filtered through a Celite pad on a coarse frit to give a red solution. The solution was concentrated to ca. 20 ml and cooled to $-30°C$ to give the product as an orange solid (0.15 g, 25%, m.p. 195–200°C).

Anal. Calc. for $C_{17}H_{26}O_2Ti$: C, 65.80; H, 8.44. Found: C, 65.58; H, 8.40.

^{1}H-NMR (benzene-d_6, ambient): δ 6.00 (q, 1H, $J = 2$ Hz, Cp), 5.87 (q, 1H, $J = 2$ Hz, Cp), 5.71 (q, 1H, $J = 2$ Hz, Cp), 5.64 (q, 1H, $J = 2$ Hz, Cp), 5.45 (t, 1H, $J = 10$ Hz, H-3), 4.98 (qt, 1H, $J = 9, 1$ Hz, H-2), 2.53 (d, 1H, $J = 14$ Hz, H-5), 2.51 (t, 1H, $J = 10$ Hz, H-4), 2.20 (dd, 1H, $J = 8, 12$ Hz, H-1), 2.11 (s, 3H, CH_3Cp), 1.82 (dd, 1H, $J = 9, 14$ Hz, H-5'), 1.66 (dd, 1H, $J = 9, 12$ Hz, H-1'), 1.52 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.15 (s, 3H,

CH_3), 0.94 (s, 3H, CH_3)—see **2** for numbering scheme.

^{13}C-NMR (benzene-d_6, ambient): δ 141.8 (d, 1C, $J = 144$ Hz), 125.0 (s, 1C, Cp), 113.7 (d, 1C, $J = 145$ Hz), 111.5 (d, 1C, $J = 175$ Hz, Cp), 110.2 (d, 1C, $J = 171$ Hz, Cp), 109.9 (d, 1C, $J = 168$ Hz, Cp), 109.2 (d, 1C, $J = 170$, Cp), 92.4 (s, 1C, C–O), 86.4 (s, 1C, C–O), 70.8 (d, 1C, $J = 124$ Hz), 53.2 (t, 1C, $J = 122$ Hz), 41.8 (t, 1C, $J = 128$ Hz), 34.0 (q, 1C, $J = 128$ Hz, CH_3), 32.0 (q, 1C, $J = 125$ Hz, CH_3), 28.4 (q, 1C, $J = 126$ Hz, CH_3), 28.1 (q, 1C, $J = 125$ Hz, CH_3), 15.6 (q, 1C, $J = 118$ Hz, CH_3Cp).

Mass spectrum (EI, 70 eV) m/z (relative intensity): 620 (3), 562 (9), 310 (13), 287 (10), 286 (18), 253 (13), 252 (52), 207 (10), 195 (17), 194 (84), 193 (27), 192 (100), 191 (13), 190 (13), 143 (17), 126 (10), 80 (15), 79 (23), 59 (12), 43 (21), 41 (10), 39 (12), 27 (8).

2.3. '[Ti(C_5H_5)(C_5H_7)(C_3H_6O)_2]_2'

A solution of $Ti(C_5H_5)(C_5H_7)(PMe_3)$ (0.20 g, 0.78 mmol) in 30 ml THF was prepared and stirred at room temperature under a N_2 atmosphere. Acetone (130 μl, 1.7 mmol, 2.2 equivalents) was added via a syringe and the resulting red solution was allowed to stir for 12 h. The solvent was removed in vacuo to give a red foam. The foam was redissolved in two 30 ml portions of pentane or hexanes and filtered through a Celite pad on a coarse frit to give a red solution. The solution was concentrated to ca. 10 ml and cooled to $-80°C$ for 12 h. The product was obtained as small red crystals in 27% yield (63 mg).

^{1}H-NMR (C_6D_6): δ 5.93 (s, 5H, Cp), 5.53 (t, 1H, $J = 10.2$ Hz, H-3), 5.02 (qt, 1H, $J = 9.0, 1.2$ Hz, H-2), 2.81 (t, 1H, $J = 9.8$ Hz, H-4), 2.27 (dd, 1H, $J = 12.3, 7.8$ Hz, H-1), 2.11 (d, 1H, $J = 13.4$ Hz, H-5), 1.91 (dd, 1H, $J = 12.2, 9.1$ Hz, H-1'), 1.55 (dd, 1H, $J = 13.6, 9.6$ Hz, H-5'), 1.40 (s, 3H), 1.25 (s, 3H), 1.18 (s, 3H), 0.97 (s, 3H).

^{13}C-NMR (C_6D_6): δ 142.2 (d, 1C, $J = 144$ Hz), 113.9 (d, 1C, $J = 156$ Hz), 109.8 (d of quintets, 5C, $J = 172, 7$ Hz), 92.1 (s, 1C), 87.6 (s, 1C), 71.5 (d, 1C, $J = 126$ Hz), 52.4 (t, 1C, $J = 124$ Hz), 41.7 (t, 1C, $J = 125$ Hz), 32.2 (q, 1C, $J = 126$ Hz), 32.0 (q, 1C, $J = 126$ Hz), 28.7 (q, 1C, $J = 126$ Hz), 28.1 (q, 1C, $J = 126$ Hz).

HRMS: Calc. for $C_{16}H_{24}TiO_2$, 296.1256; Found: 296.1237.

2.4. Crystallographic structural determination

As slow cooling of the acetone coupling product with the regular Cp complex tended to yield rather small crystals, a $C_5H_4CH_3$-containing coupling product was prepared, and found to crystallize more readily. A crystal of this complex was quickly immersed in oil, and then placed on a glass fiber on a goniometer head in a nitrogen cold stream, which thereby held the crystal fixed and protected from the air. Crystal data collection and refinement parameters are given in Table 1. The

systematic absences in the diffraction data are uniquely consistent for the reported space group. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. The asymmetric unit of the molecule lies on an inversion center. A semi-empirical absorption correction was not required because of the $< 10\%$ variation in the integrated ψ-scan intensities. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (5.03) program library (G. Sheldrick, Siemens XRD, Madison, WI).

3. Results and discussion

The reaction of $Ti(C_5H_4R)(C_5H_7)(PMe_3)$ (R = H, CH_3) complexes with acetone led to the incorporation and coupling of two equivalents of acetone, along with expulsion of phosphine, as had been observed earlier for the $Ti(C_5H_5)(2,4-C_7H_{11})$ ($C_7H_{11} =$ dimethylpentadienyl) fragment 2b, which yielded complex **1**.
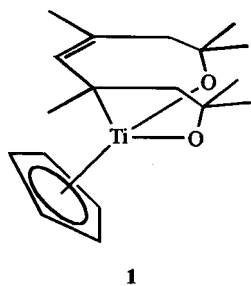
1

Table 1
Crystallographic data for $C_{34}H_{52}O_4Ti_2$

Formula	$C_{34}H_{52}O_4Ti_2$
Formula weight	310.28
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.52020(10)
b (Å)	8.6487(2)
c (Å)	17.9525(5)
β (°)	91.3920(10)
V (Å^3)	1632.95(6)
Z	2
Crystal color, habit	Red block
D_{calc} (g cm^{-3})	1.262
μ(Mo–K$_\alpha$) (cm^{-1})	5.23
Temperature (K)	173(2)
Diffractometer	Siemens P4/CCD
Radiation	Mo–K$_\alpha$ ($\lambda = 0.71073$ Å)
$R(F)$ (%) [a]	3.36
$R(wF^2)$ (%) [a]	12.13

[a] Quantity minimized $= R(wF^2) = \Sigma \left[w(F_o^2 - F_c^2)^2 \right] / \Sigma \left[(wF_o^2)^2 \right]^{1/2}$; $R = \Sigma \Delta / (\Sigma F_o)$, $\Delta = |(F_o - F_c)|$.
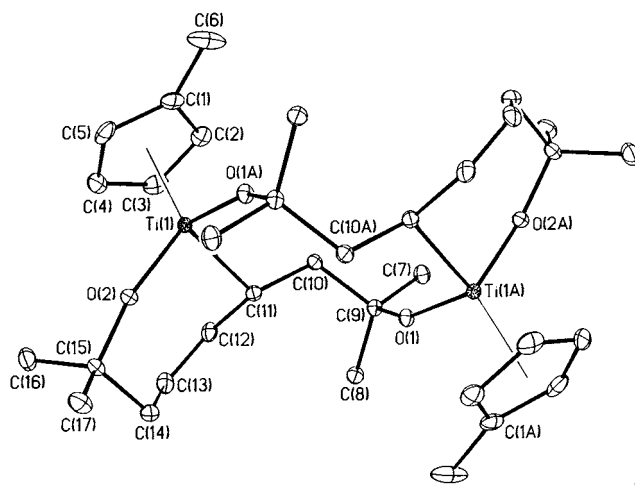
Fig. 1. Perspective view of the solid state structure of '[Ti$(C_5H_4CH_3)(C_5H_7)(C_3H_6O)_2]_2$'.

The ^{1}H- and ^{13}C-NMR spectra of the newer (C_5H_7-derived) products revealed that, as expected, the couplings had taken place at the dienyl termini, whose $J(^{13}C–H)$ values dropped from ca. 146 to 125 Hz, clearly reflecting their conversion from formal sp^2 to sp^3 hybridization. However, unlike the situation for **1**, the NMR spectra in this case showed that the dienyl fragments were no longer symmetric, suggesting that a *U* conformation was not being adopted. In the ^{1}H-NMR spectra, two vinylic resonances were apparent, revealing a static, localized σ-allyl coordination mode, as opposed to the dynamic, σ-allyl mode observed for **1** even at low temperatures. The coupling constant of 9–10 Hz between these two resonances indicated a *cis* olefin, thus precluding a *W* conformation, and based on the expected unfavorability of the *U* conformation, thereby suggesting a sickle conformation for the original dienyl fragment, with the metal attached to the handle end, as in **2** (dashed lines indicate couplings to the acetone molecules).

2
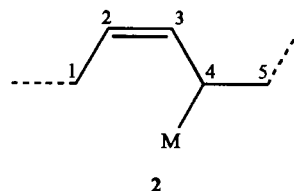
Indeed, a sickle conformation was adopted, which then apparently led to another notable difference relative to **1**—the adoption of a dimeric structure, as indicated by mass spectroscopy. Presumably due to the more extended framework, chelation to a single metal center could not be effectively maintained.

The structure of the coupling product of acetone with the $Ti(C_5H_4CH_3)(C_5H_7)$ fragment is presented in Fig. 1, while important positional and bonding parameters are contained in Tables 2 and 3. In accord with mass

spectroscopic data, the complex can be seen to be dimeric, with the halves related through a center of inversion. In contrast, the ketone coupling products derived from related 2,4-C_7H_{11} complexes were found to be monomeric, a likely consequence of the adoption of the favored U conformation by the 2,4-C_7H_{11} fragment. As can be seen in Fig. 1, the dienyl fragment has instead adopted more of a sickle conformation which, along with a W conformation, would be favored for the isolated fragment in the absence of substituents in the 2 and 4 positions. The titanium centers are bound to an oxygen atom at an end of each coupled fragment, and to C(11), leading to formal $Ti(C_5H_4CH_3)(\sigma$-allyl$)(OR)_2$ coordination spheres, as in **3**.
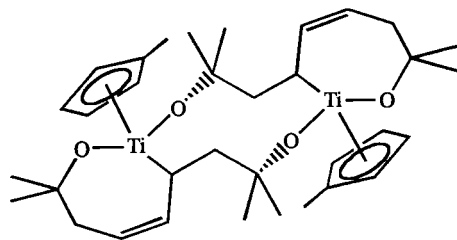
3

As a result, C(11) has become a chiral center, whose configuration was selectively fixed once the second acetone coupling step had taken place. As for the 2,4-C_7H_{11} analog (**1**), an 18 electron configuration could be attained were one of the alkoxides to serve as a five electron donor, while the other served as a three elec-

Table 2
Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for '[$Ti(C_5H_4CH_3)(C_5H_7)(C_3H_6O)_2]_2$' [a]

Atom	x	y	z	U_{eq}
Ti(1)	2108.9(3)	3596.5(3)	9328.2(2)	14(1)
O(1)	−1900(1)	5843(2)	9715(1)	18(1)
O(2)	3038(1)	5077(1)	8904(1)	18(1)
C(1)	2457(2)	981(2)	9802(2)	25(1)
C(2)	1379(2)	923(2)	9329(2)	26(1)
C(3)	1734(2)	1270(2)	8593(2)	30(1)
C(4)	3041(2)	1584(2)	8612(2)	31(1)
C(5)	4585(2)	1447(2)	9351(2)	30(1)
cent	2419(2)	1241(2)	9138(2)	28(1)
C(6)	2492(3)	652(3)	10618(2)	50(1)
C(7)	−3292(2)	3792(2)	9287(2)	23(1)
C(8)	−2282(2)	5649(2)	8396(1)	20(1)
C(9)	−2102(2)	4747(2)	9124(1)	16(1)
C(10)	−924(2)	3666(2)	9116(1)	16(1)
C(11)	311(2)	4415(2)	8860(2)	17(1)
C(12)	487(2)	4440(2)	8052(2)	22(1)
C(13)	1213(2)	5423(3)	7655(2)	26(1)
C(14)	2003(2)	6693(2)	7988(2)	27(1)
C(15)	3302(2)	6131(2)	8319(1)	21(1)
C(16)	4078(2)	5303(3)	7726(2)	30(1)
C(17)	4029(2)	7502(2)	8657(2)	30(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Pertinent bond distances and angles for '[$Ti(C_5H_4CH_3)(C_5H_7)(C_3H_6O)_2]_2$'

Bond distances

Ti(1)–O(1)	1.803(2)	C(1)–C(6)	1.491(4)
Ti(1)–O(2)	1.7916(13)	O(1)–C(9)	1.436(3)
Ti(1)–C(1)	2.441(2)	O(2)–C(15)	1.423(3)
Ti(1)–C(2)	2.436(2)	C(7)–C(9)	1.534(2)
Ti(1)–C(3)	2.433(2)	C(8)–C(9)	1.529(3)
Ti(1)–C(4)	2.388(2)	C(9)–C(10)	1.552(2)
Ti(1)–C(5)	2.356(2)	C(10)–C(11)	1.533(2)
Ti(1)–C(11)	2.170(2)	C(11)–C(12)	1.467(3)
C(1)–C(2)	1.400(4)	C(12)–C(13)	1.356(3)
C(1)–C(5)	1.425(3)	C(13)–C(14)	1.494(3)
C(2)–C(3)	1.415(4)	C(14)–C(15)	1.555(3)
C(3)–C(4)	1.401(4)	C(15)–C(16)	1.534(3)
C(4)–C(5)	1.402(4)	C(15)–C(17)	1.528(3)

Bond angles

O(1)–Ti–O(2)	107.03(7)	Ti(1)–C(11)–C(10)	118.88(14)
O(1)–Ti–C(11)	99.00(7)	Ti(1)–C(11)–C(12)	104.97(12)
O(2)–Ti–C(11)	94.66(7)	C(10)–C(11)–C(12)	115.5(2)
Ti(1)–O(1)–C(9)	149.64(12)	C(11)–C(12)–C(13)	128.0(2)
Ti(1)–O(2)–C(15)	152.8(2)	C(12)–C(13)–C(14)	124.4(3)
O(1)–C(9)–C(10)	107.5(2)	C(13)–C(14)–C(15)	113.5(2)
C(9)–C(10)–C(11)	115.52(14)	C(14)–C(15)–O(2)	107.3(2)

tron donor. Some evidence for this sort of contribution was provided for complex **1** from a structural study, which revealed differing Ti–O–C angles (142.0(3) vs. 116.5(3)°), the larger of which was associated with a slightly shorter Ti–O distance (1.809(3) vs. 1.846(3) Å). While one could attribute some of the bond shortening simply to an increase in s character for the sigma component of the Ti–O bond, the fact that related imine coupling products have been found to contain π rather than σ allyl coordination[8] suggests that some extra electron donation is provided by the alkoxide ligand beyond what is possible for an amide ligand. For **3**, the dimeric nature seems to impose fewer constraints on its geometry, and one can note that this is accompanied by significantly larger Ti–O–C bond angles, 149.6(1) and 152.8(2)°, along with respective Ti–O distances of 1.803(2) and 1.792(1) Å. These parameters continue the trend observed for **1**, in that further expansion of the angle about an oxygen center is correlated with ever decreasing Ti–O bond distance. In contrast, in at least some other systems, such correlations have not been observed, thereby seeming to render the case for alkoxide five electron donation questionable [9]. However, further support for at least partial contributions of five electron alkoxide donation comes from the fact that the current Ti–O–C angles are significantly greater than the value of ca. 133° believed to be optimal for three electron donation[10] (as well as the 120° value formal sp^2 hybridization would suggest). Of course, both alkoxides could not serve as five electron donors, as a formal 20 electron

configuration would result, so that partial contributions from each could be involved.

The Ti–C bonding parameters are quite similar to those of **1**, for which Ti–C(σ-allyl) and average Ti–C(Cp) distances of 2.170(6) and 2.385(10) Å were observed (2.170(2) and 2.411(1) Å for **3**). From these values it would appear that the enhanced π donation by the alkoxide ligands has primarily led to a compensating weakening of the Ti–Cp interactions. This is perhaps better reflected by the respective Ti–Cp (centroid) distances of 2.072(5) and 2.093(2) Å. Overall, the Ti–C(σ or π) distances are similar to those observed in other mixed species [11–13]. The C–C bonding parameters are reasonable, with the C(11)–C(12) and C(12)–C(13) values (1.467(3) and 1.356(3) Å) reflecting the clear presence of localized σ-allyl coordination (cf. 1.451(7) and 1.355(8) Å for **1**). It can finally be noted that the C–C–C angles about atoms C(10–14) are all greater than expected based upon their formal (sp^2 or sp^3) hybridization. This would appear to be due to an attempt to optimize the geometric arrangement of the ligand atoms about the titanium centers. Even so, however, the C(11)–Ti(1)–O(2) angle is still anomalously small, and there is some asymmetry in the Ti–C(11)–C(10,12) bond angles.

The dimeric nature of the acetone coupling products reported herein reveals a profound effect that substitution patterns (especially 2,4-disubstitution) can have on the course of these reactions. However, in cases in which coupling reactions lead to products whose frameworks are held rigidly in place (e.g. with α,ω-diynes [2,14]), it has proven possible to isolate coupled dienyl products retaining the U configuration, regardless of the dienyl substitution pattern, thus demonstrating the important possibility that multiple couplings can be achieved in some cases rapidly enough that rotational isomerization may be prevented. Furthermore, it has proven possible to remove the acetone coupling products by hydrolysis [14], yielding the expected enediol as a mixture of *cis* and *trans* isomers. The results of these studies will be reported in due course.

4. Supplementary materials available

Anisotropic thermal parameters, hydrogen atom co-ordinates, and structure factor tables may be obtained from the authors.

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