

The Preparation, Variable-temperature Nuclear Magnetic Resonance Spectra, and Behaviour under Reflux Conditions of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-ER})_2]$ (E = S, R = Me, Ph, or CH_2Ph ; E = Se, R = Ph)

By Peter V. Broadhurst, Brian F. G. Johnson, and Jack Lewis,* University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The cluster $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ reacts with the compounds R_2E_2 (E = S, R = Me, Ph, or CH_2Ph ; E = Se, R = Ph) to give the clusters $[\text{Os}_3(\text{CO})_{10}(\mu\text{-ER})_2]$ which have been fully characterised on the basis of their spectroscopic properties. In each case, only one of the three possible isomers of these compounds is produced. On heating, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SMe})_2]$ converts to a second isomeric form which is isostructural with the known compound $[\text{Os}_3(\text{CO})_{10}(\mu\text{-OMe})_2]$, whereas the compounds $[\text{Os}_3(\text{CO})_{10}(\mu\text{-ER})_2]$ (E = S, R = Ph or CH_2Ph ; E = Se, R = Ph) give small yields of $[\text{Os}_3(\text{CO})_9\text{E}_2]$ (E = S or Se) and $[\text{Os}_3(\text{CO})_9(\text{SR})_2]$ (E = S or Se, R = Ph).

THE trimetallic cluster carbonyls $[\text{M}_3(\text{CO})_{12}]$ (M = Ru or Os) have been reported to undergo reaction with either R_2S_2 or R_2Se_2 (R = alkyl or aryl) to produce the dimeric compounds $[\text{M}_2(\text{CO})_6(\mu\text{-ER})_2]$ (E = S or Se) ¹⁻⁸ and in some cases ²⁻⁸ the related polymeric compounds $[\text{M}_2(\text{CO})_2(\text{ER})_2]_n$. Single-crystal X-ray crystallographic studies of compounds containing $\text{M}_2(\mu\text{-SR})_2$ cores, for example $[\text{Rh}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-SPh})_2]$ ⁹ or $[\text{Fe}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-SPh})_2]$, ¹⁰ have revealed a puckered arrangement (Figure 1). It has also been established that, depending on the



FIGURE 1 Representations of the puckered $\text{M}_2(\mu\text{-SR})_2$ core

stereochemistry about the bridging sulphur ligand, up to three isomers of these compounds [Figure 2, (A)–(C)] are possible; however only isomers (A) and (B) have been observed to date. Various isomer interconversion and fluxional processes have also been established. ^{9,11-13}

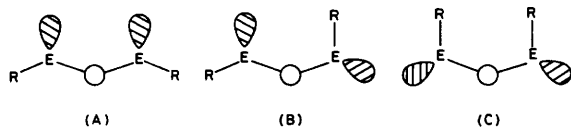


FIGURE 2 The isomers of the $\text{M}_2(\mu\text{-ER})_2$ core, as a view along the $\text{M}\cdots\text{M}$ axis

In this paper, we report the synthesis and study of the cluster compounds $[\text{Os}_3(\text{CO})_{10}(\mu\text{-ER})_2]$ (E = S, R = Me, Ph, or CH_2Ph ; E = Se, R = Ph), in which the Os_3 has been retained and the new isomeric form (C) established.

RESULTS AND DISCUSSION

The cluster $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ reacts with the compounds R_2E_2 in dichloromethane to produce the trimetallic compound $[\text{Os}_3(\text{CO})_{10}(\mu\text{-ER})_2]$ [E = S, R = Me (1a), Ph (1b), or CH_2Ph (1c); E = Se, R = Ph (2)] in yields of ca. 50% [except for $(\text{PhCH}_2)_2\text{S}_2$ where yields are closer to 20%]. The i.r. spectra of these compounds in the $\nu(\text{CO})$ region are similar to those of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-X})_2]$ (X = Cl, Br, or I) ¹⁴ indicating a related molecular geometry, *i.e.* a triangle of three osmium atoms with one

long (non-bonded) edge which is spanned by two RE bridging groups.

In addition to these products, for the reaction when E = S, small yields of the hydrido-compounds $[\text{Os}_3(\text{CO})_{10}\text{H}(\text{ER})]$ were also obtained. These compounds were readily identified on the basis of their mass spectra (Tables 1 and 2) and by a comparison of their i.r. spectra with those previously reported for these compounds. ¹⁵

Yields of the new compounds were highest when between a five- and ten-fold excess of R_2E_2 was employed. It has been proposed previously ^{9,11-13} that under the reaction conditions employed to produce the dimers $[\text{M}_2(\text{CO})_6(\mu\text{-ER})_2]$ (*i.e.* heat or photolysis) the compounds R_2E_2 undergo homolytic cleavage to produce the radical species $\dot{\text{E}}\text{R}$ and that it is these radicals which are the reactive species. In the reactions reported here, we believe that a different mechanism operates. In this alternative mechanism, we consider that the donor R_2E_2 molecule initially displaces the MeCN from $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ to produce $[\text{Os}_3(\text{CO})_{11}(\text{E}_2\text{R}_2)]$ which then undergoes rearrangement and CO loss to form the observed product. The observation that the yield of the product is increased in the presence of excess R_2E_2 tends to support our view that the addition of R_2E_2 is reversible.

With Bu^t_2S_2 reaction does not take place to yield the desired trimetallic product. Presumably the large bulk of the Bu^tS ligand encourages further fragmentation of the Os_3 cluster. In support of this view, it is worth noting that the large PhCH_2S ligand only gives relatively poor yields of the trimeric product.

As observed with the bimetallic compounds discussed above, the compounds $[\text{Os}_3(\text{CO})_{10}(\mu\text{-ER})_2]$ may exist in three different isomeric forms depending on the stereochemistry about the ER bridging groups. These isomeric possibilities are shown in Figure 3, where a representative view of the molecule along the non-bonded osmium–osmium edge supported by the two ER ligands is given. In all cases the ^1H n.m.r. spectra of the compounds $[\text{Os}_3(\text{CO})_{11}(\mu\text{-ER})_2]$ are consistent with the presence of only one isomer, namely isomer (B), with two different R environments. For compounds (1a) and (1c) the spectra at 30 °C exhibited two sets of signals in

each case τ 7.00 (1) and 7.55 (1) for (1a) and at τ 5.81 (1) and 6.41 (1) for (1c) (relative intensities are in parentheses). Compounds (1b) and (2) exhibited a complex spectrum in the phenyl region. However, a comparison of these spectra with that of free Ph_2E_2 revealed that they resembled two superimposed patterns of the organic ligand consistent with the idea that there are two different phenyl environments.

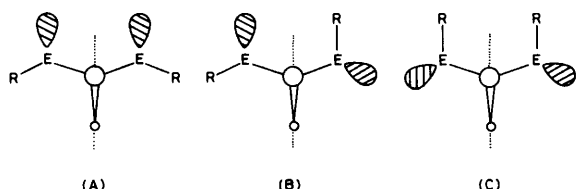


FIGURE 3 The isomers of the $\text{Os}_3(\mu\text{-ER})_2$ core, showing the plane of the Os_3 triangle

These spectra show little or no change over the temperature range 30–100 °C indicating that no fluxional process or isomer interconversion occurs. However, with $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SMe})_2]$ (1a) the spectrum shows two resonances at τ 7.00 and 7.55 of relative intensities 1 : 1 at 30 °C but as the temperature is raised, line broadening and coalescence occurs until at 95 °C a single resonance at τ 6.92 is observed. This change is not reversible and is time dependent suggesting that isomer interconversion is taking place. In agreement, the i.r. spectrum $[\nu(\text{CO})]$ of the final solution is different to that of the original (Table 1). Isolation of the final product shows, on the basis of its mass spectrum, that it has the same composition as (1a). From this information, together with the fact that the i.r. spectrum of the new compound (3) is closely related to that of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-OMe})_2]$ which is known¹⁶ to possess the geometry given for isomer (C), we believe (3) also to possess the isomer structure (C). The formation of isomer (C) rather than the alternative (A), which is favoured for $[\text{M}_2(\text{CO})_6(\mu\text{-ER})_2]$, presumably results from the unfavourable steric interactions between the SMe bridging group and the CO ligands of the third osmium atom expected for isomer (A). The compound $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{Ph})_2]$ also undergoes reaction on heating (in octane). However, in this case, simple isomerisation was not observed; instead small amounts of $[\text{Os}_3(\text{CO})_9\text{S}_2]$ ¹⁷ and a large amount of intractable polymer were obtained. Similar behaviour was also

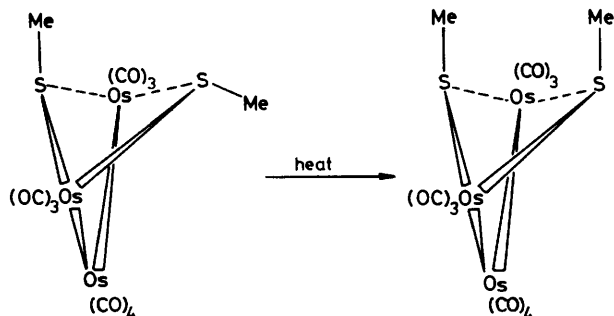


FIGURE 4 The thermal isomerisation of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SMe})_2]$

noted for $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SPh})_2]$ except in this case a small amount (~6%) of $[\text{Os}_3(\text{CO})_9(\mu\text{-SPh})_2]$ (4) was also produced. Spectroscopic data did not permit the molecular structure of this compound to be deduced but three possible structures may be proposed (Figure 4). Structure type (III) has been postulated previously for $[\text{Fe}_3(\text{CO})_9(\text{SBU}^t)_2]$,¹⁸ and triply bridging SR groups have been observed elsewhere as, for example, in $[\text{Co}_3\text{H}(\text{CO})_9(\mu_3\text{-SR})]$ (R = Me or Et).¹⁸

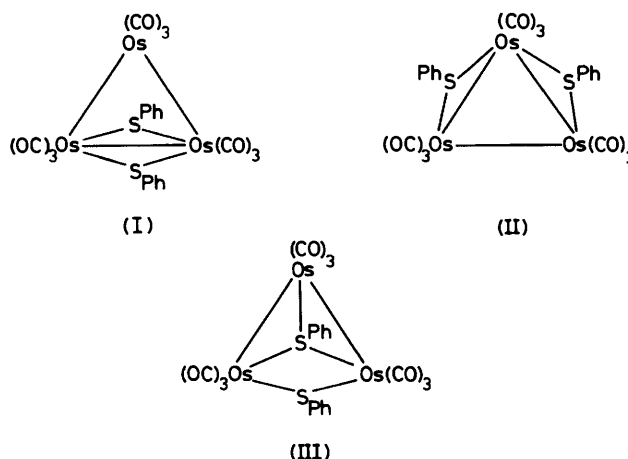


FIGURE 5 Possible structures of $[\text{Os}_3(\text{CO})_9(\text{SPh})_2]$

The compound $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SePh})_2]$ (2) behaves similarly, undergoing thermal decomposition in hot *n*-octane to give low yields of $[\text{Os}_3(\text{CO})_9\text{Se}_2]$ ¹⁷ and a second isomeric form (C) of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SePh})_2]$ which exhibited an i.r. spectrum closely related to that of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-OMe})_2]$ with structure (C).

EXPERIMENTAL

Reactions were performed under N_2 . Solvents for reactions or crystallisations were dried and deoxygenated by distillation under N_2 over CaH_2 , except benzene when AnalaR grade was used. Prior to distillation, unsaturated impurities in the saturated hydrocarbons were removed by stirring over concentrated H_2SO_4 .

A literature preparation was used for $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$,¹⁹ and other reagents were obtained commercially and used without further treatment.

Product separation was achieved using thin layer chromatography (t.l.c.) with plates precoated to 0.25 mm thickness with Merck Kieselgel 60F₂₅₄, supplied by Merck.

Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer using the 2143 cm^{-1} absorption of $\text{CO}(\text{g})$ as calibrant. Mass spectra were recorded with an A.E.I. MS12 spectrometer. Microanalyses were performed by the University Chemical Laboratory microanalytical department.

Proton n.m.r. spectra were recorded on Varian Associates CFT 20 or XL-100-12 spectrometers at 80 and 100 MHz respectively. The latter was used for elevated temperature work. Spectra were recorded in CD_2Cl_2 solution or, at elevated temperature, in $[\text{D}_2\text{H}_8]$ toluene {for $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{Ph})_2]$ } or in CD_3NO_2 .

Spectroscopic and analytical data for new compounds are given in Tables 1 and 2.

Reaction of $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ *with* R_2E_2 .—(a) $\text{R} = \text{Me}$, $\text{E} = \text{S}$. The compound $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ (211 mg, 0.23 mmol) and Me_2S_2 (ca. 200 mg, 2.1 mmol, 0.2 cm^3) in CH_2Cl_2 (30 cm^3) were stirred overnight. T.l.c., eluting with CH_2Cl_2 -hexane (2 : 8), gave a trace of $[\text{Os}_3(\text{CO})_{10}\text{H}(\mu\text{-SMe})]$ (yellow, $R_f = 0.75$) and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SMe})_2]$ (yellow, $R_f = 0.55$) (1a) which gave yellow crystals on cooling in hexane solution (106 mg, 49%).

benzene-hexane (1 : 1) solution by cooling to give yellow crystals (55 mg, 19%).

(d) $\text{R} = \text{Ph}$, $\text{E} = \text{Se}$. The compound $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ (246 mg, 0.27 mmol) and Ph_2Se_2 (500 mg, 1.60 mmol) in CH_2Cl_2 (40 cm^3) were stirred overnight at room temperature. T.l.c., eluting with CH_2Cl_2 -hexane (2 : 8) gave excess Ph_2Se_2 (yellow, $R_f = 0.8$) and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SePh})_2]$ (yellow, $R_f = 0.6$) (2) which crystallised by

TABLE 1
Infrared, ^1H n.m.r., and melting point data for new compounds

Compound	$\nu(\text{CO})$ (cm^{-1}) ^a	^1H n.m.r. (τ) ^b	M.p. ($^\circ\text{C}$)
(1a) $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SMe})_2]$	2 115mw, 2 065s, 2 045ms, 2 042 (sh), 2 037ms, 2 032vs, 2 014w, 1 991m, 1 988 (sh), 1 980m, 1 959mw	7.00 (s, Me), 7.55 (s, Me) Integrate 1 : 1	decomp. ca. 140
(1b) $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SPh})_2]$	2 115mw, 2 069s, 2 045ms, 2 035vs, 2 016w, 1 996m, 1 985mw, 1 978w, 1 966w, 1 959mw	2.39 (m, Ph), 2.52 (m, Ph), 2.68 (m, Ph), 2.74 (m, Ph)	150—153
(1c) $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{Ph})_2]$	2 112m, 2 062s, 2 044ms, 2 039 (sh), 2 031vs, 1 988ms, 1 977m, 1 961w, 1 955w	2.65 (m, Ph) } Integrate 5.81 (s, CH_2) } 10 : 2 : 2 6.41 (s, CH_2) }	144—146
(2) $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SePh})_2]$	2 113m, 2 066s, 2 044ms, 2 033vs, 2 014w, 1 992m, 1 977m, 1 966w, 1 958w	2.41 (m, Ph), 2.69 (m, Ph)	141—143
(3) $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SMe})_2]$	2 106ms, 2 065s, 2 056m, 2 022vs, 2 018 (sh), 1 996vw, 1 988s, 1 978mw	6.92 (s, Me)	decomp. ca. 190
(4) $[\text{Os}_3(\text{CO})_9(\text{SPh})_2]$	2 102ms, 2 039ms, 2 035s, 2 026vs, 2 001mw, 1 974vs, 1 966ms	2.04 (m, Ph), 2.21 (m, Ph) 2.39 (m, Ph), 2.42 (m, Ph)	decomp. ca. 200
(5) $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SePh})_2]$	2 104m, 2 064s, 2 055w, 2 050w, 2 019vs, 2 000w, 1 988m, 1 980w		

^a m = Medium, s = strong, w = weak, (sh) = shoulder; cyclohexane solution. ^b (s) = Singlet, (m) = multiplet.

(b) $\text{R} = \text{Ph}$, $\text{E} = \text{S}$. The complex $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ (250 mg, 0.27 mmol) and Ph_2S_2 (250 mg, 1.15 mmol) in CH_2Cl_2 (20 cm^3) were stirred at room temperature for 6 h. T.l.c., eluting with hexane, gave a yellow band ($R_f = 0.7$) at the head of a broad band visible under u.v. light and a yellow band ($R_f = 0.2$). These were $[\text{Os}_3(\text{CO})_{10}\text{H}(\mu\text{-SPh})]$ (trace), excess Ph_2S_2 , and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SPh})_2]$ (1b) which crystallised by cooling a benzene-hexane (1 : 1) solution to give yellow crystals (150 mg, 52%).

cooling a benzene-hexane (1 : 1) solution to give yellow crystals (156 mg, 50%).

Reflux Reactions of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-ER})_2]$, *Isomer (B)*.—(a) $\text{R} = \text{Me}$, $\text{E} = \text{S}$. The complex $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SMe})_2]$ (1a) (70 mg, 7.3×10^{-2} mmol) was refluxed in n-octane (30 cm^3) for 30 min; t.l.c., eluting with CH_2Cl_2 -hexane (1 : 9), gave $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SMe})_2]$ (yellow, $R_f = 0.6$) (3) which proved to be another isomer, (C). Crystallisation by cooling a hexane solution yielded 37 mg, 53%.

(b) $\text{R} = \text{Ph}$, $\text{E} = \text{S}$. Compound (1b), $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SPh})_2]$ (141 mg, 0.13 mmol), was refluxed in n-octane (40 cm^3) for 25 min. After t.l.c., eluting with CH_2Cl_2 -hexane (15 : 85), the first yellow band ($R_f = 0.9$) was identified as $[\text{Os}_3(\text{CO})_9\text{S}_2]$ and the third yellow band as $[\text{Os}_3(\text{CO})_9(\text{SPh})_2]$ (4). Crystallisation from benzene-hexane (1 : 1) solutions by cooling yielded 1.8 mg (1.5%) and 8.0 mg (6.0%) respectively.

(c) $\text{R} = \text{CH}_2\text{Ph}$, $\text{E} = \text{S}$. Compound (1c) $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{Ph})_2]$ (20 mg, 1.8×10^{-2} mmol) was treated as above. The first yellow band on t.l.c. was identified as $[\text{Os}_3(\text{CO})_9\text{S}_2]$ (ca. 5%).

(d) $\text{R} = \text{Ph}$, $\text{E} = \text{Se}$. Compound (2), $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SePh})_2]$ (93 mg, 8.0×10^{-2} mmol), was refluxed in n-octane (30 cm^3) for 15 min. After t.l.c., eluting with CH_2Cl_2 -hexane (1 : 9), the first yellow band ($R_f = 0.75$) was identified as $[\text{Os}_3(\text{CO})_9\text{Se}_2]$ and was crystallised by cooling a hexane solution (10 mg, 13%). The fourth band, visible under u.v. light, was identified spectroscopically as $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SePh})_2]$ (5), isomer (C) (ca. 3%).

Variable-temperature ^1H N.M.R. *Experiments*.—Samples were sealed under N_2 . Spectra were run at 30, 50, 70, and 90 $^\circ\text{C}$ for all samples, and at 100 $^\circ\text{C}$ for $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{Ph})_2]$ (1c) but showed no indication of any fluxional behaviour. Some coalescence of peaks occurred for $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SePh})_2]$ due to increased thermal motion.

For $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SMe})_2]$ (1a), a series of spectra at 95 $^\circ\text{C}$ over 2.5 h showed an isomerisation to $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SMe})_2]$

TABLE 2
Microanalytical,^a mass spectral, and yield data for new products

Compound	Analysis (%)		m/e ^b
	C	H	
(1a) $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SMe})_2]$	15.35 (14.95)	0.80 (0.65)	950
(1b) $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SPh})_2]$	24.85 (24.70)	1.20 (0.95)	1 074
(1c) $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{Ph})_2]$	26.50 (25.80)	1.35 (1.25)	1 102
(2) $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SePh})_2]$	22.75 (22.35)	0.90 (0.85)	1 168
(3) $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SMe})_2]$	15.05 (14.95)	0.90 (0.65)	950
(4) $[\text{Os}_3(\text{CO})_9(\text{SPh})_2]$	24.40 (23.75)	1.10 (0.95)	1 046
(5) $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SePh})_2]$			1 168

^a Calculated values in parentheses. ^b ^{192}Os , ^{79}Se .

(c) $\text{R} = \text{CH}_2\text{Ph}$, $\text{E} = \text{S}$. The cluster $[\text{Os}_3(\text{CO})_{11}(\text{NCMe})]$ (247 mg, 0.27 mmol) and $(\text{PhCH}_2)_2\text{S}_2$ (500 mg, 2.03 mmol) in CH_2Cl_2 (40 cm^3) were stirred overnight. T.l.c., with hexane eluant gave two yellow bands ($R_f = 0.55$ and 0.25) and a heavy band (u.v. visible) in between. Repeated t.l.c. may be needed to separate the central band of excess $(\text{PhCH}_2)_2\text{S}_2$. The yellow bands are a trace of $[\text{Os}_3(\text{CO})_{10}\text{H}(\mu\text{-SCH}_2\text{Ph})]$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SCH}_2\text{Ph})_2]$ (1c) which crystallised from

(3), which was followed by the decay of the two methyl signals of (1a) and concurrent growth of the one methyl signal of (3).

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