

Synthesis and characterisation of a diphosphaalkene, a diphosphaalkyne and the first diphosphavinyl lithium complex

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Received 26 September 2005; received in revised form 4 November 2005; accepted 4 November 2005
Available online 13 December 2005

Abstract

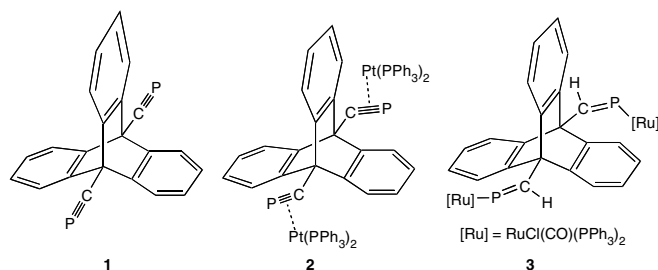
The preparation and characterisation of a diphosphaalkene, $(\text{Me}_3\text{Si})\text{P}=\text{C}(\text{OSiMe}_3)\{\text{C}(\text{C}_2\text{H}_4)_3\text{C}\}\text{C}(\text{OSiMe}_3)=\text{P}(\text{SiMe}_3)$, and the second example of a diphosphaalkyne, $\text{P}=\text{C}\{\text{C}(\text{C}_2\text{H}_4)_3\text{C}\}\text{C}\equiv\text{P}$, are described. In addition, the reaction of another diphosphaalkyne, $\text{P}=\text{C}\{\text{C}(\text{C}_6\text{H}_4)_3\text{C}\}\text{C}\equiv\text{P}$, with MeLi/LiBr in the presence of *tmeda* has given the first diphosphavinyl lithium complex, $[\text{MeP}=\text{C}\{\text{Li}_2\text{Br}(\text{tmeda})_2\}\{\text{C}(\text{C}_6\text{H}_4)_3\text{C}\}\text{C}\{\text{Li}_2\text{Br}(\text{tmeda})_2\}=\text{PMe}]$, which is stable at room temperature and has been crystallographically characterised. © 2005 Elsevier B.V. All rights reserved.

Keywords: Diphosphaalkyne; Diphosphaalkene; Diphosphavinyl lithium; Low coordination; Crystal structure

1. Introduction

Since the first room temperature stable example of a phosphalkyne, $\text{P}\equiv\text{CBu}^t$, was prepared in 1981 [1], these compounds have proved to be invaluable as synthons in the preparation of a wide variety of organophosphorus cage, heterocyclic and acyclic compounds; phospho-organometallics and coordination complexes [2]. Throughout this work, and in line with the now established analogy between P and the valence isoelectronic CR fragment, the chemistry of phosphalkynes has been shown to more closely mimic that of alkynes than nitriles [2]. We have recently added to this field with the preparation of the first diphosphaalkyne, **1** [3]. Preliminary investigations into the reactivity of this compound have led to the η^2 -complex, **2**, and the P-diphosphaalkenyl complex, **3**, the formation of which suggests that diphosphaalkynes will have similar chemistry to monophosphaalkynes. The possibility exists, however, that the bifunctional nature of diphosphaalkynes could lend them to the formation of unsaturated covalent

or coordination polymers. In order to examine this possibility, there is a need to develop routes to other diphosphaalkynes and metallo-diphosphavinyl complexes which could be used as building blocks in the synthesis of such polymers. Our efforts in this direction are reported herein.



2. Results and discussion

Although **1** has much synthetic potential, the bulky nature of its triptycenediyl spacer does limit its reactivity to some extent. Therefore, it would be useful to develop

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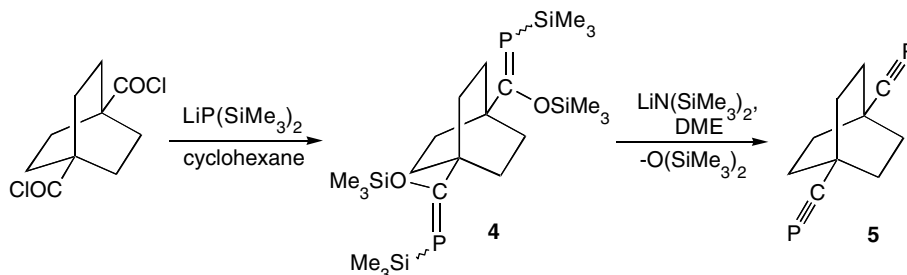
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less bulky, yet stable diphosphaalkynes. However, for diphosphaalkynes to be thermally stable, their spacer units will probably need to be sufficiently rigid to circumvent the possibility of intramolecular coupling reactions between the phosphoalkyne moieties. Accordingly, the bicyclo[2.2.2]octanediyl spacer was chosen for this study. The reaction of bicyclo[2.2.2]octane-1,4-dicarbonylchloride with 2 equivalents of $[\text{LiP}(\text{SiMe}_3)_2(\text{DME})]$ afforded the new diphosphaalkene, **4**, in moderate yield (Scheme 1). Subsequent treatment of **4** with $[\text{LiN}(\text{SiMe}_3)_2]$ in DME led to a based catalysed elimination of hexamethyldisiloxane and the formation of the air and moisture stable diphosphaalkyne, **5**, in 30% yield as a colourless crystalline solid after purification by column chromatography (kieselgel/hexane).

The $^3\text{1P}\{^1\text{H}\}$ NMR spectrum of **4** displays four singlet resonances at low field (δ 124.3, 123.6, 112.8 and 108.5 ppm) which implies that it is prepared as a mixture of its *Z,Z*-, *Z,E*- and *E,E*-isomers. One isomer predominates in this mixture, and this can be fractionally crystallised from hexane. The spectroscopic and X-ray crystal structure data (vide infra) for this material reveal it to be the *Z,Z*-isomer. Compound **5** exhibits a singlet resonance (δ -60.8 ppm) in its $^3\text{1P}\{^1\text{H}\}$ NMR spectrum, which is in the known range

for phosphoalkynes [2]. Similarly, the chemical shift of its alkyne carbon centres ($^{13}\text{C}\{^1\text{H}\}$: δ 181.9 ppm, $^1J_{\text{PC}} = 40.3$ Hz) is normal for phosphoalkynes, as is the frequency of its $\text{P}=\text{C}$ stretching absorption, IR: ν 1538 cm^{-1} (cf. $^3\text{1P}\{^1\text{H}\}$: δ -15.7 ppm; $^{13}\text{C}\{^1\text{H}\}$: δ 164.0 ppm, $^1J_{\text{PC}} = 47.1$ Hz; IR: ν 1558 cm^{-1} for **1** [3]). The molecular structure of **4** is depicted in Fig. 1 and confirms it to exist as its *Z,Z*-isomer. Its P–C distances (1.703 Å avge.) are slightly longer than those in related diphosphaalkenes [4] and the mean for all crystallographically characterised phosphoalkenes (1.69 Å) [5]. These distances are, however, still suggestive of largely localised double bonds. All other geometrical features of the structure are unremarkable.

C-Phosphavinyl lithium and magnesium complexes, $\{\text{RP}=\text{C}(\text{R})\text{M}\}$, M = Li or MgX, R = alkyl, aryl, silyl halide, etc., have proved versatile reagents for organophosphorus and phosphoorganometallic chemistry [6]. To the best of our knowledge there are no known examples of related diphosphavinyl main group metallates. If these could be prepared they may find use in the formation of unsaturated polymers via metathesis reactions with, for example, metal or metalloid dihalide complexes. It has been shown by us and others that Grignard reagents [7] and lithium alkyls [8] can undergo 1,2-addition reactions



Scheme 1.

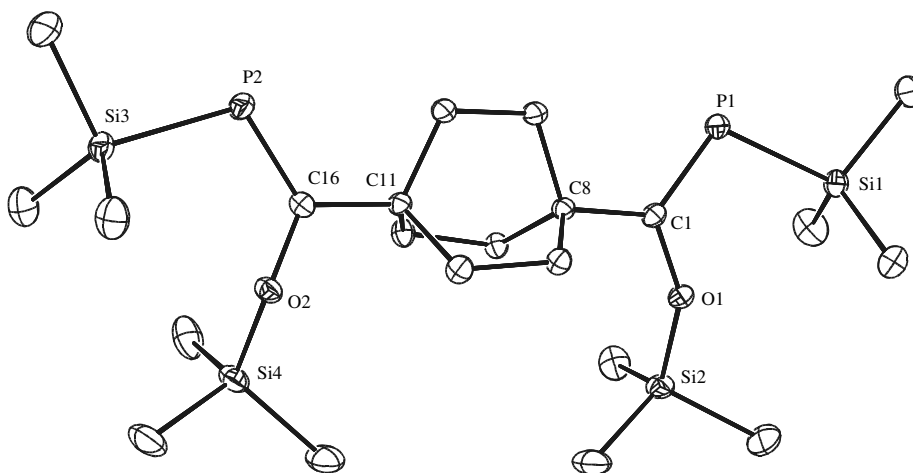
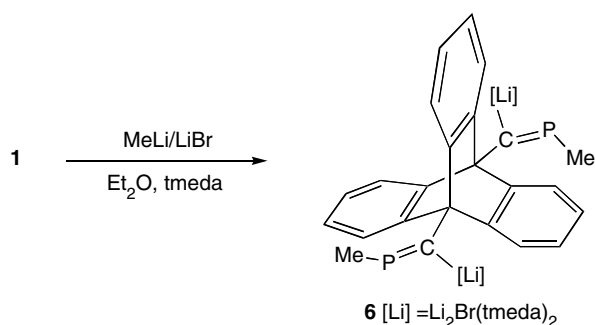


Fig. 1. Molecular structure of **4** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): P(1)–C(1) 1.7049(18), P(1)–Si(1) 2.2573(8), P(2)–C(16) 1.7008(18), P(2)–Si(3) 2.2681(10), Si(2)–O(1) 1.6619(13), Si(4)–O(2) 1.6630(13), C(1)–P(1)–Si(1) 102.73(6), C(16)–P(2)–Si(3) 105.97(6), O(1)–C(1)–C(8) 115.41(14), O(1)–C(1)–P(1) 122.81(12), C(8)–C(1)–P(1) 121.64(12), O(2)–C(16)–C(11) 114.18(14), O(2)–C(16)–P(2) 123.81(12), C(11)–C(16)–P(2) 121.92(12).

with phosphalkynes to give phosphavinyl metallates. We reasoned that similar reactions should occur with diphosphalkynes to give diphosphavinyl metallates.

To this end, **5** was reacted with ethereal solutions of either CyMgCl , Cy = cyclohexyl, or MeLi . The ^{31}P NMR spectra of the reaction mixtures at $-30\text{ }^\circ\text{C}$ displayed low field singlets (δ 322 and 264 ppm, respectively) which suggested that the target complexes had been formed. However, upon warming the samples to room temperature, a multitude of signals in each spectrum resulted, implying that the products are thermally unstable. As a result, attention shifted to the more hindered diphosphalkyne, **1**. Contrastingly, this was found to be unreactive towards a variety of Grignard reagents, RMgCl , R = Cy, Ph, Et or Me, presumably because of the steric protection afforded its $\text{P}\equiv\text{C}$ functionalities. Similarly, its treatment with either MeLi or MeLi/LiBr solutions in diethyl ether led to no reaction. However, when the lithium alkyl reactions were repeated in the presence of excess tmeda (which is known to lower the degree of association and increase the reactivity of MeLi), the former reaction led to an intractable mixture of phosphorus containing products whilst the latter gave the first example of a diphosphavinyl lithium complex, **6** (Scheme 2). It seems, therefore, that the presence of LiBr in the MeLi reactant is essential to obtain a stable diphosphavinyl metallate product. The reason for this is obvious from the crystal structure of the complex (vide infra) which shows it to exist as an “-ate” complex, the carbanionic centres of which are sterically protected by $\text{Li}_2(\text{tmeda})_2\text{Br}$ fragments.

The orange crystalline complex, **6**, is extremely air sensitive but indefinitely stable at room temperature. Although it is difficult to re-dissolve in non-coordinating solvents, its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (C_6D_6) was obtained and showed a low field singlet at δ 248.2 ppm, in the known range for



Scheme 2.

phosphalkenes (cf. δ 181.1 ppm for $\text{MeP}=\text{C}(\text{Li})\text{Mes}^*$, $\text{Mes}^* = \text{C}_6\text{H}_2\text{Bu}_3^t$ -2, 4, 6 [8a]). The molecular structure of **6** is depicted in Fig. 2. Its P-centres are 2-coordinate and its $\text{P}=\text{C}$ double bonds appear to be fully localised [1.662(5) Å]. The carbanionic centres, C(2), have distorted tetrahedral geometries with C–Li bond lengths [2.294 Å avge.] that are markedly longer than that in the only other structurally characterised phosphavinyl lithium complex, $[\text{Mes}^*\text{P}=\text{C}(\text{Cl})\{\text{Li}(\text{DME})_2\}]$ 2.128(3) Å [9]. The difference here can be attributed to the more sterically crowded, 4-coordinate carbanionic centre in **6**, compared to the 3-coordinate carbanion in $[\text{Mes}^*\text{P}=\text{C}(\text{Cl})\{\text{Li}(\text{DME})_2\}]$.

3. Conclusion

In summary, the preparation and characterisation of a diphosphalkene and the second example of a diphosphalkyne have been described. Furthermore, the first example of a diphosphavinyl lithium reagent has been prepared and structurally characterised. We are currently examining the preparation of other diphosphalkynes

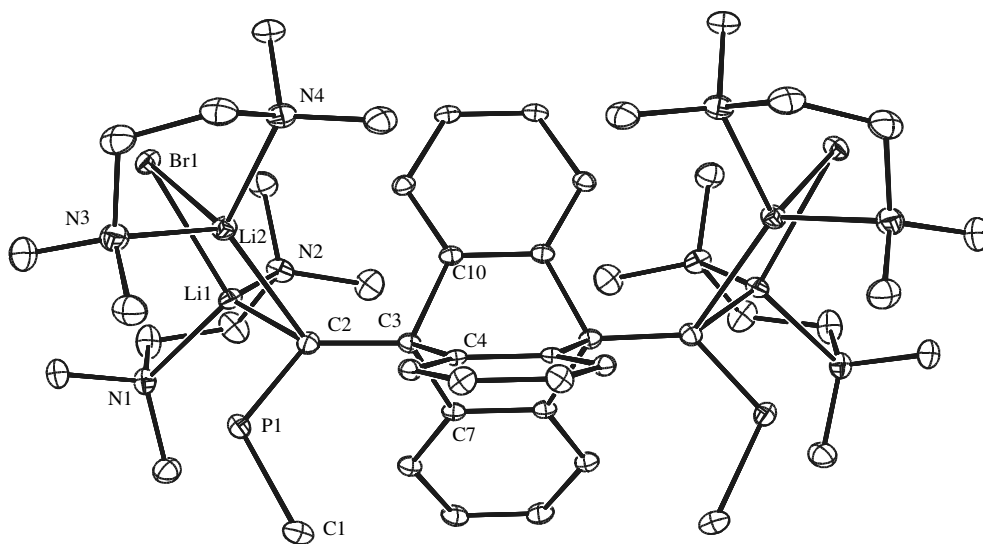


Fig. 2. Molecular structure of **6**. (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles ($^\circ$): C(2)–P(1) 1.662(5), C(2)–Li(2) 2.273(10), C(2)–Li(1) 2.315(10), Li(1)–Br(1) 2.553(9), Br(1)–Li(2) 2.523(9), C(2)–P(1)–C(1) 114.1(3), C(3)–C(2)–P(1) 127.2(4), C(3)–C(2)–Li(2) 121.9(4), P(1)–C(2)–Li(2) 96.5(3), C(3)–C(2)–Li(1) 123.5(4), P(1)–C(2)–Li(1) 96.3(3), Li(2)–Br(1)–Li(1) 70.2(3).

and diphosphavinyl metallates, in addition to exploring the utility of **6** as a precursor to polymers containing phosphalkenyl functionalities.

4. Experimental section

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon. Cyclohexane, DME and hexane were distilled over potassium, whilst diethyl ether was distilled over Na/K then freeze/thaw degassed prior to use. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on either a Bruker DXP400 or Jeol Eclipse 300 spectrometer, and were referenced to the residual ^1H or ^{13}C resonances of the solvent used or external 85% H_3PO_4 , δ 0.0 ppm (^{31}P NMR). The low solubility of **6** in common organic solvents precluded the acquisition of meaningful ^{31}C NMR data for this compound. Mass spectra were obtained from the EPSRC National Mass Spectrometry Service at Swansea University. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. Microanalyses were obtained from Medac Ltd. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. Compound **1** [3], $[\text{LiP}(\text{SiMe}_3)_2(\text{DME})_2]$ [10] and bicyclo[2.2.2]octane-1,4-dicarbonylchloride [11] were synthesised by literature procedures. All other chemicals were obtained commercially and used as received.

4.1. Z,Z -(Me_3Si) $\text{P}=\text{C}(\text{OSiMe}_3)$ - $\{C(\text{C}_2\text{H}_4)_3\}C(\text{OSiMe}_3)=\text{P}(\text{SiMe}_3)$ **4**

To a suspension of $[\text{LiP}(\text{SiMe}_3)_2(\text{DME})_2]$ (1.40 g, 7.6 mmol) in cyclohexane (30 mL) at 5°C was added a solution of bicyclo[2.2.2]octane-1,4-dicarbonylchloride (1.0 g, 3.8 mmol) in cyclohexane (50 mL) over 5 min. The resultant yellow suspension was warmed to 25°C and stirred for 1 h, whereupon it was filtered and volatiles removed in vacuo to leave a beige solid. This was extracted into hexane (ca. 10 mL), filtered and the filtrate placed at -30°C overnight to give **4** as colourless crystals (1.02 g, 53%). M.p. 148 – 150°C ; ^1H NMR (400 MHz, C_6D_6 , 298 K): δ 0.12 (s, 18H, PSiMe_3), 0.27 (s, 18H, OSiMe_3), 1.78 (s, 12H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 298 K): δ -0.1 (d, $^2J_{\text{PC}} = 19.4$ Hz, PSiMe_3), 1.0 (s, OSiMe_3), 30.1 (d, $^3J_{\text{PC}} = 13.7$ Hz, CH_2), 44.9 (d, $^2J_{\text{PC}} = 22.8$, CCH_2), $\text{P}=\text{C}$ resonance not observed; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.7 MHz, C_6D_6 , 298 K): δ 124.3 (s, $\text{P}=\text{C}$); MS/EI: m/z (%) 518 [M^+ , 35], 445 [$\text{M}^+ - \text{SiMe}_3$, 100]; IR (Nujol, cm^{-1}): ν 1254 m, 1212 m, 956 m, 844 m, 722 s; Accurate mass MS (ES^+) Calc. for M^+ : $\text{C}_{22}\text{H}_{48}\text{O}_2\text{P}_2\text{Si}_4$: 518.2201; found: 518.2200; $\text{C}_{22}\text{H}_{48}\text{O}_2\text{P}_2\text{Si}_4$ requires C, 50.92; H, 9.32. Found: C, 50.47; H, 8.98%.

4.2. $\text{PC}\{C(\text{C}_2\text{H}_4)_3\}\text{CP}$ **5**

To a solution of **4** (0.40 g, 0.77 mmol) in DME (5 mL) at -20°C was added a solution of $[\text{LiN}(\text{SiMe}_3)_2]$ (30 mg,

0.20 mmol) in DME (4 mL). The resultant yellow suspension was warmed to 25°C and stirred for 3 h. Volatiles were then removed in vacuo and the residue treated with hexane (10 mL) to give a suspension which was chromatographed (silica gel/hexane), yielding **5** as a colourless crystalline solid after removal of volatiles from the fraction containing this compound (46 mg, 30%). M.p. 64 – 66°C ; ^1H NMR (400 MHz, C_6D_6 , 298 K): δ 0.84 (s, 12H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 298 K): δ 32.1 (d, $^3J_{\text{PC}} = 6.9$ Hz, CH_2), 35.1 (d, $^2J_{\text{PC}} = 22.8$, CCH_2), 181.9 (d, $^1J_{\text{PC}} = 40.3$ Hz, $\text{P}=\text{C}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.7 MHz, C_6D_6 , 298 K): δ -60.8 (s, $\text{P}=\text{C}$); MS/EI: m/z (%) 194 [M^+ , 55], 163 [$\text{M}^+ - \text{P}$, 100]; IR (Nujol, cm^{-1}): ν 1538 m ($\text{P}=\text{C}$), 1260 m, 1097 m, 1021 m, 801 m, 722; Accurate mass MS (ES^+) Calc. for M^+ : $\text{C}_{10}\text{H}_{12}\text{P}_2$: 194.0409; found: 194.0411; $\text{C}_{10}\text{H}_{12}\text{P}_2$ requires C, 61.86; H, 6.23. Found: C, 61.70; H, 6.11%.

4.3. $[\text{MeP}=\text{C}\{\text{Li}_2\text{Br}(\text{tmeda})_2\}\{C(\text{C}_6\text{H}_4)_3\}C\{\text{Li}_2\text{Br}(\text{tmeda})_2\}=\text{PMe}]$ **6**

To a solution of **1** (170 mg, 0.50 mmol) and TMEDA (0.5 mL) in diethyl ether (40 mL) at -78°C was added a solution of methyllithium as a 1:1 complex with lithium bromide (1 mmol, ca. 0.7 mL of a 1.5 M solution in diethyl ether). After 30 min the reaction mixture was allowed to warm to room temperature and stirred for 1 h, during which time a colour change to orange was observed. Volatiles were removed in vacuo and the residue extracted with diethyl ether (20 mL). Concentration and slow cooling to -30°C overnight yielded orange crystals of **6** (96 mg, 51%). M.p. 137 – 139°C (dec.); ^1H NMR (400 MHz, C_6D_6 , 298 K): δ 0.44 (d, 6H, $^2J_{\text{PH}} = 8.6$ Hz, PMe), 1.92 (s, 16H, CH_2), 2.16 (s, 48H, NMe), 7.46–7.52 (m, 12H, ArH); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.7 MHz, C_6D_6 , 298 K): δ 248.2 (s, $\text{P}=\text{C}$); MS/EI: m/z (%) 370 [$\text{MeP}=\text{C}(\text{H})\{C(\text{C}_6\text{H}_4)_3\}C(\text{H})=\text{PMe}^+$, 24]; IR (Nujol, cm^{-1}): ν 1603 w, 1372 s, 1292 m, 1035 s, 950 m, 830 m.

Table 1
Crystal data for compounds **4** and **6**

	4	6
Chemical formula	$\text{C}_{22}\text{H}_{48}\text{O}_2\text{P}_2\text{Si}_4$	$\text{C}_{48}\text{H}_{82}\text{Br}_2\text{Li}_4\text{N}_8\text{P}_2$
Formula weight	518.90	1020.74
T (K)	150(2)	150(2)
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pnma$
a (Å)	9.1850(18)	11.049(2)
b (Å)	11.918(2)	29.131(6)
c (Å)	14.956(3)	17.828(4)
α ($^\circ$)	100.27(3)	90
β ($^\circ$)	106.35(3)	90
γ ($^\circ$)	93.58(3)	90
V (Å 3)	1534.8(5)	5738(2)
Z	2	4
μ (Mo $K\alpha$) (mm^{-1})	0.314	1.505
Reflections	11204	8697
Collected (R_{int})	(0.0262)	(0.0704)
Unique reflections	6151	5016
R_1 ($I > 2\sigma(I)$)	0.0373	0.0779
wR_2 (all data)	0.0918	0.1860

4.4. Crystallographic studies

Crystals of **4** and **6** suitable for X-ray crystal structure determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97) [12] using all unique data. Crystal data, details of data collections and refinement are given in Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures of **4** and **6** have been deposited with the Cambridge Crystallographic Data Centre **4**: CCDC no. 284861; **6**: CCDC no. 284862. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgement

We gratefully acknowledge financial support from the EPSRC (part funded studentship for MB) and the ERASMUS scheme of the European Union (travel grants for FB and CS). Thanks also go to the EPSRC Mass Spectrometry Service.

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