Organophosphorus Compounds, 155[‡]

1,2-Additions of Organomagnesium Halides to Phosphaalkynes: Synthesis of 2-Phospha-1-vinylmagnesium Halides and a Novel Type of Magnesium-Phosphorus Cage Compound

Jens Renner,[a] Uwe Bergsträßer,[a] Paul Binger,*[a] and Manfred Regitz*[a]

Dedicated to Professor Marianne Baudler on the occasion of her 80th birthday

Keywords: Additions / Phosphaalkynes / Grignard reagents / Phosphavinylmagnesium halides / Cage compounds

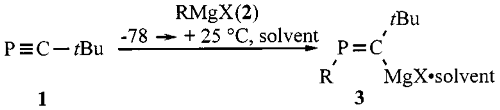
Grignard reagents such as isopropyl- and *tert*-butylmagnesium halide (**2a:** X = Cl; **2b:** X = Br) react with *tert*-butylphosphaacetylene **(1)** in a regio- and stereoselective 1,2-addition process at –78 °C to give the 2-phospha-1-vinylmagnesium halides **3a,b** in high yields. At elevated temperatures, the phosphavinylmagnesium chloride **3a** reacts with two more equivalents of **1** to afford the previously unknown magnesium-phosphorus cage compound **4**, the structure of which has been confirmed by X-ray-analysis.

Introduction

The recent report on the synthesis of phosphavinyl-Grignard compounds by way of a regio- and stereospecific 1,2-addition of Grignard reagents to *tert*-butylphosphaacetylene **(1)**[2] prompted us to report our results in this field.

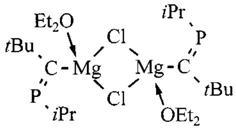
Results and Discussion

In the course of our investigations on the use of metallocene[3] and η^8-cyclooctatetraene trunk complexes[4] of zirconium and hafnium in the synthesis of new heterocyclic organophosphorus compounds, we attempted to use the di(isopropoxy)(η^2-propene)titanium complex[5] − readily accessible from titanium tetraisopropoxide and isopropylmagnesium chloride **(2a)** − as a starting material in an appropriate cyclooligomerization protocol of, for example, *tert*-butylphosphaacetylene **(1)**. In these experiments we found that the Grignard reagent reacts with **1** at least as rapidly as with titanium tetraisopropoxide with the result that an inseparable mixture was obtained from the reaction. As a logical consequence, we then performed the reaction of **1** with isopropylmagnesium chloride **(2a)** in the absence of the titanium complex in diethyl ether at −78 °C and found that the metal−carbon bond in **2a** underwent stereo- and regioselective addition to the triple bond of **1** (Scheme 1). As described by Jones et al. for other organomagnesium halides,[2] the 2-phospha-1-vinylmagnesium chloride monoetherate **(3a)** (colorless) was obtained in this case in 100% yield. In the crystalline form the compound exists as the dimer. The phosphaalkyne **1** reacted analogously with one equivalent of *tert*-butylmagnesium bromide **(2b)** to furnish orange crystals of the THF adduct **3b** in 74% yield.



1 **3**

2,3	a	b
R	*i*Pr	*t*Bu
X	Cl	Br
solvent	Et_2O	THF



3a

Scheme 1. Synthesis of some phosphavinyl Grignard reagents

The NMR spectroscopic data of the novel phospha-1-vinylmagnesium halides are in good agreement with the values previously reported.[2] Thus, the ^{31}P NMR spectra show signals at δ = 339.4 **(3a)** and 355.1 **(3b)**. These signals, considered together with the low-field ^{13}C NMR signals of the olefinic carbon atoms at δ = 262.1 (d, $^1J_{C,P}$ = 72.1 Hz, **3a**) and 258.9 (d, $^1J_{C,P}$ = 69.6 Hz, **3b**), unambiguously illustrate the presence of the phosphaalkene moiety. An X-ray crystallographic analysis of **3a** demonstrates in this case also the regio- and stereochemistry of the 1,2-addition of isopropylmagnesium chloride, as well as the dimeric structure in the solid state.[6] As already shown by Jones and coworkers, the preparation of phosphavinylmagnesium halides is a general method with regard to the originally em-

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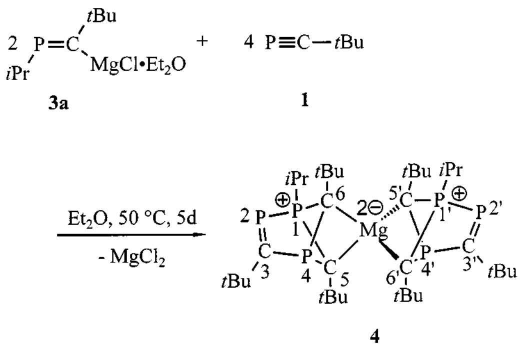
[a] Fachbereich Chemie der Universität Kaiserslautern,
Erwin-Schrödinger-Straße, 67663 Kaiserslautern, Germany
Fax: (internat.) + 49-(0)631/205-3921
Email: regitz@rhrk.uni-kl.de



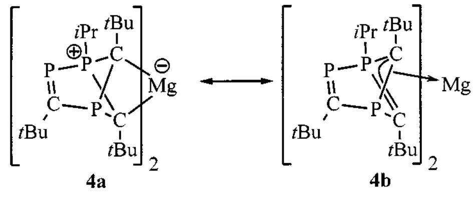
Scheme 2. Synthesis of the new magnesium phosphorus cage compound **4**

ployed Grignard reagent.[2] Preliminary experiments in our laboratory have confirmed this aspect and have also revealed that other kinetically stabilized phosphaalkynes are also amenable to this reaction.

Some phosphavinyl Grignard reagents of the type *trans*-Mes*P=C(R)MgBr (Mes* = C_6H_2-*t*Bu_3-2,4,6; R = halogen, $SiMe_3$) have previously been prepared, albeit only in situ, by other routes and used in synthesis.[7]

Compounds **3a** and **3b** are not only stable at room temperature in the solid state but also in solution. In the presence of at least two equivalents of **1**, however, **3a** undergoes further reaction even at room temperature (Scheme 2, as can be seen from the change from colorless to red. At 50 °C the reaction is complete after five days. The novel magnesium complex **4** formed by the incorporation of two equivalents of **1** is obtained as dark red crystals in 72% yield.

The structure of the complex **4** was unequivocally demonstrated by X-ray crystallography (Figure 1). This shows that the magnesium is in a tetrahedral environment linked by two Mg−C-σ bonds to each of the two 1,2,4-triphosphabicyclo[2.1.1]hexenediyl units. Compound **4** crystallizes without incorporation of solvent molecules and no longer contains chlorine atoms. Both of the bicyclic units contain a four-coordinated phosphorus atom, and accordingly the complex must have a betaine structure in which the bicyclic units each bear a formal positive charge, leaving the magnesium atom with two formal negative charges. To the best of our knowledge, organomagnesium compounds of this type have not been described before.[8] The individual atomic separations found are mostly in agreement with previously reported values. Thus, the bond lengths of between 2.247 and 2.284 Å found for the four Mg−C bonds are in agreement with the reported characteristic values for known organomagnesium compounds.[9] The two bicyclic ligands exhibit P−C, P=C, and P−P bond lengths of 1.878−1.943, 1.663−1.682, and 2.2637−2.2702 Å, respectively, which can be considered as normal.[10,11] The only exceptions are the P1−C6 and P1−C5 (as well as the P1′−C6′ and P1′−C5′) bond lengths of 1.778−1.793 Å, which are considerably shortened in comparison with the values for normal P−C single bonds. From these findings, we can deduce that the structure of the complex **4** must involve not only the betaine structure **4a** but also the η^3-structure **4b** (Scheme 3).



Scheme 3. Mesomeric structures of compound **4**

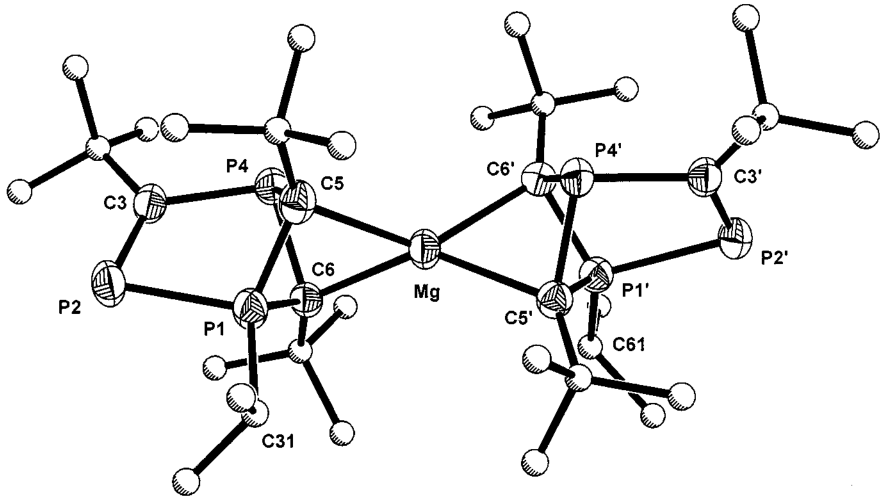
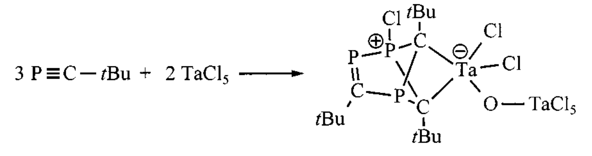


Figure 1. Molecular structure of **4**; selected bond lengths [Å] and angles [°]; H omitted for clarity, displacement ellipsoids at 50% probability: Mg−C5 2.284(3), Mg−C5′ 2.252(3), Mg−C6 2.247(3), Mg−C6′ 2.271(3), C5−P4 1.885(3), C5−P1 1.793(4), C6−P4 1.889(3), C6−P1 1.788(3), P1−P2 2.2637(14), P1−C31 1.850(3), P2−C3 1.682(3), C3−P4 1.932(3), C5′−P4′ 1.888(3), C5′−P1′ 1.778(3), C6′−P4′ 1.877(3), C6′−P1′ 1.779(3), P1′−P2′ 2.2702(12), P1′−C61 1.836(4), P2′−C3′ 1.664(4), C3′−P4′ 1.943(3); C5−Mg−C6 65.18(12), C5−Mg−C6′ 132.52(13), C5−Mg−C5′ 134.90(12), C6−Mg−C5′ 138.80(13), C6−Mg−C6′ 135.06(12), C5′−Mg−C6′ 64.71(11), Mg−C5−P4 82.08(13), Mg−C5−P1 89.3(2), Mg−C6−P4 83.01(13), Mg−C6−P1 90.60(14), Mg−C5′−P4′ 82.24(12), Mg−C5′−P1′ 91.08(13), Mg−C6′−P4′ 81.95(12), Mg−C6′−P1′ 90.42(13), P1−C5−P4 82.45(14), C5−P4−C6 80.6(2), C5−P4−C3 101.0(2), C6−P4−C3 99.10(14), P4−C6−P1 82.46(14), C6−P1−C5 85.9(2), C6−P1−P2 105.14(10), C5−P1−P2 105.50(11), P1−P2−C3 86.05(11), P2−C3−P4 115.8(2), P1′−C5′−P4′ 82.72(14), C5′−P4′−C6′ 79.99(14), C5′−P4′−C3′ 99.17(14), C6′−P4′−C3′ 100.96(14), P4′−C6′−P1′ 82.99(13), C6′−P1′−C5′ 85.7(2), C6′−P1′−P2′ 105.35(11), C5′−P1′−P2′ 104.72(11), P1′−P2′−C3′ 86.65(11), P2′−C3′−P4′ 115.5(2)

On the basis of the crystal structure analysis we were also able to assign the NMR spectroscopic data of complex **4**. As a result of the C_2-symmetry of **4**, only three signals are observed in the ^{31}P NMR spectrum for the six phosphorus atoms. The two olefinic P-atoms give a double doublet signal at $\delta = 174.1$ with $^1J_{P,P} = 284.8$ and $^2J_{P,P} = 14.2$ Hz. The neighboring, four-coordinated P-atoms give a signal at $\delta = 67.2$ with a $^2J_{P,P}$ coupling constant of 38.7 Hz. Finally, the two $\sigma^3\lambda^3$ P-atoms produce a signal (also a double doublet) at $\delta = 27.0$ (see Experimental Section). The ^{13}C NMR spectrum reveals a signal for the vinylic C-atoms at $\delta = 262.0$. This signal appears as a doublet of doublets of doublets and confirms the magnetic equivalence of the respective atoms in the two ligands. The carbon atoms bonded to magnesium give rise to two doubled, pseudo-triplet signals at $\delta = 110.1$ and 109.9 with $^1J_{C,P}$ couplings of 57.1 Hz (56.2 Hz) and small $^2J_{C,P}$ couplings of 4.0 Hz each. Similarly, the ^1H NMR spectrum of **4** contains three signals for the six *tert*-butyl groups at $\delta = 1.57$, 1.12 and 1.10, while the two isopropyl groups produce a complicated multiplet at $\delta = 2.76-2.58$ for the two CH groups and two signals at $\delta = 1.71$ and 1.63 for the four methyl groups.

The skeleton of the two ligands at magnesium is already known: it was first observed in the monomeric tantalum complex **5** obtained from the reaction of tantalum pentachloride with three equivalents of **1** (Scheme 4).[12] The mechanism of formation of **4** is still unknown as it has not yet been possible to isolate or identify any intermediates. It is possible that the mechanism proposed by Becker and coworkers [12] for the formation of **5** is also applicable to **4** even though other routes are feasible.



1 **5**

Scheme 4. Synthesis of the tantalum phosphorus compound **5**[12]

We are currently investigating the synthetic potential of these phosphavinylmagnesium compounds as well as the reactivity of complexes of the type **4**.

Experimental Section

All experiments were carried out under argon in anhydrous solvents. − MS: Finnigan MAT 90. − ^1H and ^{13}C NMR: Bruker AC 200 and Bruker AMX 400; chemical shifts were determined relative to solvent signals and converted into the TMS scale. − ^{31}P NMR: Bruker AC 200 (80.8 MHz); external standard H_3PO_4. − Chemicals: 2,2-dimethylpropylidynephosphane [*tert*-butylphosphaacetylene, **(1)**] was prepared according to a published procedure;[13] the Grignard reagents are commercially available.

(*Z*)-1-*tert*-Butyl-2-isopropyl-2-phosphavinylmagnesium Chloride (3a): To a solution of **1** (0.1 mL, 90% solution in hexamethyldisiloxane, 0.72 mmol) in Et_2O (2 mL) cooled to −78 °C was added dropwise a 2 M solution of isopropylmagnesium chloride **(2a)** in Et_2O (0.36 mL, 0.72 mmol). The color of the reaction solution changed spontaneously from colorless to yellow and **3a** precipitated. After stirring for 2.5 h at this temperature and a further 12 h at room temperature, a yellow solution was obtained from which **3a** crystallized out at +4 °C. − Yield 200 mg (100%) **3a** as monoetherate. − m.p. > 295 °C (dec.). − ^1H NMR (400.1 MHz, CD_2Cl_2): $\delta = 3.94$ (q, $^3J_{H,H} = 7.0$ Hz, 4 H, OCH_2-CH_3), 1.91 [sept, $^3J_{H,H} = 6.9$ Hz, 1 H, $CH(CH_3)_2$], 1.29 (t, $^3J_{H,H} = 7.0$ Hz, 6 H, OCH_2-CH_3), 1.21 [d, $^4J_{H,P} = 2.2$ Hz, 9 H, $C(CH_3)_3$], 1.14 [dd, $^3J_{H,P} = 11.8$ Hz, $^3J_{H,H} = 6.9$ Hz, 6 H, $CH(CH_3)_2$]. − $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): $\delta = 262.1$ (d, $^1J_{C,P} = 72.1$ Hz, P=*C*), 65.7 (s, OCH_2CH_3), 43.4 [d, $^2J_{C,P} = 13.4$ Hz, $C(CH_3)_3$], 36.5 [d, $^1J_{C,P} = 34.8$ Hz, $CH(CH_3)_2$], 33.8 [d, $^3J_{C,P} = 19.1$ Hz, $C(CH_3)_3$], 22.9 [d, $^2J_{C,P} = 15.3$ Hz, $CH(CH_3)_2$], 14.2 (s, OCH_2-CH_3). − $^{31}P\{^1H\}$ NMR (80.8 MHz, C_6D_6): $\delta = 339.4$ (s). − MS (EI, 35 eV); *m/z* (%): 277 (5) [M^+], 144 (39) [M^+ − MgCl − Et_2O], 101 (19) [PC*t*BuH$^+$], 87 (18) [*i*PrPCH$^+$], 74 (30) [Et_2O], 70 (30) [CH*t*Bu$^+$], 69 (55), 59 (34), 57 (71) [*t*Bu$^+$], 43 (96), 41 (100), 31 (96).

(*Z*)-1,2-Di-*tert*-butyl-2-phosphavinylmagnesium Bromide (3b): In analogy to the preparation of **3a** a solution of **1** (0.1 mL, 90% solution in hexamethyldisiloxane, 0.72 mmol) in THF (2 mL) was treated dropwise with a 1.57 M solution of **2b** in THF (0.46 mL, 0.72 mmol) to obtain 154 mg (74%) of **3b** as a solvate complex in the form of orange crystals. − m.p. > 295 °C (dec.). − ^1H NMR (400.1 MHz, CD_2Cl_2): $\delta = 3.95$ (m, 4 H, THF), 1.90 (m, 4 H, THF), 1.26 [d, $^4J_{H,P} = 2.5$ Hz, 9 H, $C(CH_3)_3$], 1.18 [d, $^3J_{H,P} = 9.3$ Hz, 9 H, $C(CH_3)_3$]. − $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): $\delta = 258.9$ (d, $^1J_{C,P} = 69.6$ Hz, P=*C*), 69.6 (s, THF), 44.1 [d, $^2J_{C,P} = 16.7$ Hz, $C(CH_3)_3$], 34.1 [d, $^1J_{C,P} = 20.5$ Hz, $PC(CH_3)_3$], 32.2 [d, $^3J_{C,P} = 15.7$ Hz, $C(CH_3)_3$], 31.2 [d, $^2J_{C,P} = 12.4$ Hz, $C(CH_3)_3$], 25.6 (s, THF). − $^{31}P\{^1H\}$ NMR (80.8 MHz, C_6D_6): $\delta = 355.1$ (s).

Bis[3,5,6-tri-*tert*-butyl-1-isopropyl-1,2,4-triphosphabicyclo[2.1.1]hex-2-ene-5,6-diyl]-magnesium (4): To a solution of **1** (0.2 mL, 90% solution in hexamethyldisiloxane, 1.44 mmol) in Et_2O (2 mL) cooled to −78 °C was added a 2 M solution of isopropylmagnesium chloride **(2a)** in Et_2O (0.72 mL, 1.44 mmol). After the mixture had been stirred for 1 h at −78 °C and a further hour at room temperature, the ^{31}P NMR spectrum of the mixture showed the presence of **3a** as the sole product. The reaction mixture was transferred to a pressure Schlenk tube, a further 2 equivalents of **1** (0.4 mL, 2.88 mmol) were added, and the mixture heated at 50 °C for 5 days. During this time a white precipitate formed and the color of the reaction solution changed to red. The solution was separated by decantation and the precipitate washed with several 1-mL portions of ether. The volume of the collected solutions was reduced under vacuum to ca. 4 mL. Cooling to +4 °C resulted in the precipitation of **4** in the form of red crystals suitable for X-ray crystallography. − Yield 740 mg (72%). − m.p. 238 °C (dec.). − ^1H NMR (200.1 MHz, CD_2Cl_2): $\delta = 2.76-2.58$ [m, 1 H, $CH(CH_3)_2$], 1.71 [dd, $^3J_{H,P} = 6.9$ Hz, $^3J_{H,H} = 5.2$ Hz, 3 H, $CH(CH_3)_2$] and 1.63 [dd, $^3J_{H,P} = 7.1$ Hz, $^3J_{H,H} = 5.3$ Hz, 3 H, $CH(CH_3)_2$], 1.57 [d, $^4J_{H,P} = 1.5$ Hz, 9 H, $C(CH_3)_3$], 1.12 [s, 9 H, $C(CH_3)_3$], 1.10 [s, 9H, $C(CH_3)_3$]. − ^{13}C NMR (100.6 MHz, C_6D_6, 55 °C): $\delta = 262.0$ (ddd, $^1J_{C,P} = 94.8$ Hz, $^1J_{C,P} = 47.4$ Hz, $^2J_{C,P} = 40.5$ Hz, P=*C*), 110.1 (dpt, $^1J_{C,P} = {}^1J_{C,P} = 57.1$ Hz, $^2J_{C,P} = 4.0$ Hz, Mg−*C*) and 109.9 (dpt, $^1J_{C,P} = {}^1J_{C,P} = 56.2$ Hz, $^2J_{C,P} = 4.0$ Hz, Mg−*C*), 44.3 [pt, $^2J_{C,P} = {}^2J_{C,P} = 13.8$ Hz, Mg−C−$C(CH_3)_3$] and 44.1 [pt, $^2J_{C,P} = {}^2J_{C,P} = 13.8$ Hz, Mg−C−$C(CH_3)_3$], 40.5 [dd, $^2J_{C,P} = 7.8$ Hz, $^2J_{C,P} = 6.0$ Hz, P=C−$C(CH_3)_3$], 39.1 [ddd, $^1J_{C,P} = 21.6$ Hz, $^2J_{C,P} = 8.6$ Hz, $^3J_{C,P} = 5.2$ Hz, $CH(CH_3)_2$], 36.0−35.7 [m, Mg−C−$C(CH_3)_3$], 32.7 [dd, $^3J_{C,P} = 10.4$ Hz, $^3J_{C,P} = 6.9$ Hz, P=C−$C(CH_3)_3$], 20.2 [d, $^3J_{C,P} = 9.5$ Hz, $CH(CH_3)_2$]. − $^{31}P\{^1H\}$ NMR (80.8 MHz, CD_2Cl_2): $\delta = 174.1$ (dd, $^1J_{P,P} = 284.8$ Hz, $^2J_{P,P} = 14.2$ Hz, P2 and P2′), 67.2 (dd,

${}^1J_{P,P} = 284.8$ Hz, ${}^2J_{P,P} = 38.7$ Hz, P1 and P1′), 27.0 (dd, ${}^1J_{P,P} = 38.7$ Hz, ${}^2J_{P,P} = 14.2$ Hz, P4 and P4′). − MS (EI, 35 eV), m/z (%): [M^+] not observed; 345 (42) [$C_{18}H_{36}P_3^+$], 245 (14) [$C_{13}H_{27}P_2^+$], 231 (18) [$C_{10}H_{18}P_3^+$], 169 (49) [$C_{10}H_{18}P^+$], 131 (60) [$C_5H_9P_2^+$], 101 (18), 99 (14), 69 (47) [$C_5H_9^+$], 57 (100) [tBu$^+$], 43 (38) [iPr$^+$], 41 (49).

Crystal Structure Analysis of 4: STOE Imaging Plate Diffraction System, graphite monochromator, Mo-K_α radiation ($\lambda = 0.71073$ Å), cell determination and refinement by STOE programs Ver. 2.75, structure solution by direct methods (SHELXS-86[14]) and structure refinement by SHELXL-93,[15] hydrogen atoms were included in the refinement using riding models. $C_{36}H_{68}MgP_6$; $M = 711.0$ g·mol^{-1}; monoclinic; space group $P2_1/c$ (No. 14), lattice constants $a = 11.276(2)$, $b = 17.599(4)$, $c = 21.888(4)$ Å, $\beta = 102.47(3)°$, $V = 4241(2)$ Å^3; $Z = 4$; $D_{calcd.} = 1.114$ Mg/m^3; $\mu = 2.91$ cm^{-1}; $T = 293(2)$ K; crystal size 0.35 × 0.20 × 0.15 mm^3; $1.85 \le \Theta \le 24.16°$. 29644 reflections collected, 6344 independent reflections ($R_{int.} = 0.1222$); 388 parameters; $w^{-1} = [\sigma^2(F_o^2) + (0.0253P)^2]$, $P = [(F_o^2) + 2F_c^2]/3$; $R^1 = 0.0485$, $wR^2 = 0.0933$ for 3999 reflections with $I > 2\sigma(I)$ and $R^2 = 0.0844$, $wR^2 = 0.1037$ for all data; residual electron density 428 e·nm^{-3} and −271 e·nm^{-3}, $S = GOF$ (on F^2)= 1.017.

Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-148262. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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[6] We have not presented a detailed discussion of the molecular structure with numerical data because the crystal structure analysis of an analogue of **3a** (cyclopentyl in place of isopropyl) has already been published, see. ref.[2]

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