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Synthesis, structure and fluxional behavior of di-t-butylcyclopentadienyl compounds of group 15 elements

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Abstract

The syntheses of di-t-butylcyclopentadienyldichlorophosphane (I), di-t-butylcyclopentadienyldiisopropylphosphane (II), di-t-butylcyclopentadienyldichloroarsane (III) and di-t-butylcyclopentadienyldichlorostibane (IV) are described. The influence of group 15 elements on the structure and the dynamic behavior (sigmatropic rearrangements) is discussed on the basis of ^{1}H, ^{13}C, and ^{13}P NMR data.

Introduction

In the context of investigations concerning the fluxional behavior of σ-cyclopentadienyl compounds of main-group elements [1], we recently reported on the synthesis and the molecular dynamics of di-t-butylcyclopentadienyl compounds of group 14 elements [2]. These thermally stable species mainly exist in form of the isomer with the group 14 element in the (allylic) 1-position and the t-butyl groups in the 2- and 4-positions. The dynamic behavior is characterized by degenerate 1,2-element shifts (1.5 sigmatropic rearrangements). The activation parameters depend on the nature of the main-group fragment. In continuation of this work, we now report on the synthesis and the fluxional behaviour of some di-t-butylcyclopentadienyl compounds of group 15 elements.

Results and discussion

Di-t-butylcyclopentadienyldichlorophosphane (I), di-t-butylcyclopentadienyldiisopropylphosphane (II), di-t-butylcyclopentadienyldichloroarsane (III) and di-t-butylcyclopentadienyldichlorostibane (IV) were obtained in very good yields as distillable, very air-sensitive, compounds by reaction of di-t-butylcyclopentadienyl-

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lithium, $LiC_5H_3Bu^t_2$, with the corresponding chloro-phosphanes, -arsanes and -stibanes, as shown in eq. 1:

$$t\text{-}Bu_2C_5H_3Li + ElCl \rightarrow t\text{-}Bu_2C_5H_3El + LiCl \quad (1)$$

(I–IV)

Compound	I	II	III	IV
El	PCl_2	$P(^iC_3H_7)_2$	$AsCl_2$	$SbCl_2$

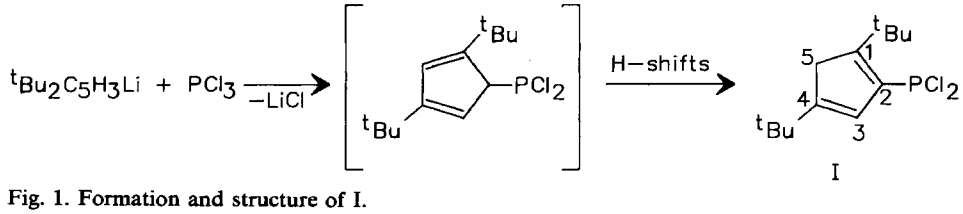
Compounds I–IV were characterized by their ^1H, ^{13}C, ^{31}P NMR data, their mass spectra, and their elemental analyses. The dynamic behavior was investigated by variable temperature ^1H NMR studies. The DNMR spectra were recorded at 300 MHz in toluene-d_8 as solvent.

The ^1H NMR spectrum of compound I recorded at room temperature (+30 °C) shows two signals for the two t-butyl groups (0.98 and 1.19 ppm), a singlet at 3.73 ppm for two protons in the allylic region, and a doublet at 6.16 ppm for a vinyl hydrogen. The singlet at 1.19 ppm appears as a doublet and can be assigned to the t-butyl group adjacent to the PCl_2 group, whereas that at 0.98 ppm is assigned to the remote t-butyl group which is not coupled with the PCl_2 group. The doublet at 6.16 ppm can be assigned to a vinylic proton which couples with the PCl_2 group. In contrast, the two allylic protons are not coupled with the phosphorus atom and appear as a singlet. The ^{13}C NMR spectrum for I shows that the two t-butyl groups are non-equivalent (singlet at 30.9 and doublet at 32.4 ppm), the allylic carbon (C^5) appears at 42.1 ppm, and the unsubstituted vinylic carbon (C^3) as a doublet at 126.5 ppm. The carbon atom bearing the PCl_2 group (C^2) appears as a doublet at 134.0 ppm, whereas the carbon atoms C^4 and C^1, the ones bearing the two t-butyl groups, appear as two doublets at 168.8 and 171.0 ppm respectively. The ^{31}P NMR spectrum of I shows only one signal at 161.2 ppm, indicative for the presence of only one isomer. From all these spectroscopic data, the isomer present must be the one with the PCl_2 group in the vinylic position, as depicted in Fig. 1. This isomer can be formed from the allylic isomer, which must be the first reaction product, by two successive 1,2 hydrogen shifts.

The ^1H NMR spectrum of I is temperature-independent. It can be concluded that the isomer present possesses a rigid structure. This result is in agreement with those obtained for other cyclopentadienylphosphorus compounds [3].

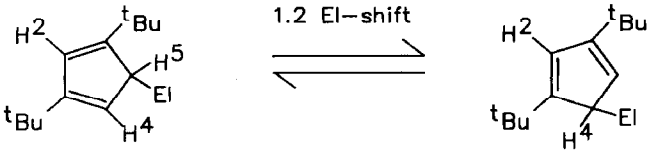
The ^{31}P NMR spectrum of the phosphane II shows the presence of five isomers with signals at −12.9, −11.2, −4.7, −2.4 and +10.8 ppm. The ^1H and ^{13}C NMR spectra of II are rather complicated due to overlapping resonances. Therefore, it was not possible to assign the structures of the different isomers precisely.

The ^1H and ^{13}C NMR spectra of the arsane III indicate the presence of mainly one isomer (about 90%). The ^1H NMR spectrum shows a singlet for the two t-butyl



I

Fig. 1. Formation and structure of I.



III A
IV A

III A'
IV A'

Fig. 2. Degenerate 1,2 element shift in compounds III and IV.

groups at 1.23 ppm, and for the cyclopentadienyl protons a doublet at 5.36 ppm and a triplet at 6.60 ppm. This type of spectrum is typical of a highly fluxional structure. It demonstrates that the isomer IIIA is in equilibrium with the identical isomer IIIA' through a degenerate 1,2-shift (1.5 sigmatropic rearrangement) of the $AsCl_2$ group as indicated in Fig. 2. In the ^{13}C NMR spectrum of III the two t-butyl groups appear equivalent (resonances at 31.0 and 53.1 ppm) as well as the set of vinylic-allylic type carbon atoms at 93.6 ppm. Two further signals for vinylic carbon atoms appear at 129.8 and 159.7 ppm.

It is not possible from ^1H and ^{13}C NMR data to ascertain the structures of the other isomers detected together with the isomer III.

The ^1H and ^{13}C NMR spectra of the stibane IV are comparable to those of compound III. The temperature independence of these spectra is consistent with a high fluxionality caused by a rapid degenerate 1,2 shift of the $SbCl_2$ group in the isomers IVA and IVA' (see Fig. 2).

Conclusion

The air sensitive but thermally stable di-t-butylcyclopentadienyl compounds I–IV of the group 15 elements phosphorus, arsenic, and antimony can be synthesized by the reaction of di-t-butylcyclopentadienyllithium with the corresponding element halide. The dichloroarsenic and antimony compounds III and IV mainly exist in form of the isomers with the group 15 element in the allylic position and the two t-butyl groups in the vinylic 1- and 3-position. These compounds possess fluxional structures due to fast generate 1,2 element shifts. In the diisopropyl phosphorus compound five isomers are present whose structures could not be determined by NMR spectroscopy. The dichlorophosphorus compound I prefers a static structure in an isomer with the PCl_2 group in a vinylic position and the two t-butyl groups adjacent to the allylic CH_2 group.

Experimental

All reactions were performed under dry oxygen-free nitrogen. Solvents and reagents were dried and purified by standard methods. Melting points were determined with a Büchi 510 Capillary melting point apparatus. All NMR spectra were recorded on a Bruker AM 300 (^1H NMR 300 MHz; $^{13}C\{^1H\}$ NMR 75 MHz; ^{31}P NMR 121 MHz). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ and in $C_6H_5CH_3$-d_8 for variable temperature using TMS and C_6D_6 as an internal reference. ^{31}P NMR spectra were recorded in THF, using H_3PO_4 as an external

reference. Chemical shifts are reported as δ-values in ppm followed by peak multiplicities, relative proton intensities (where relevant), and coupling constants in Hz. Mass spectral data (MS) were collected using a Varian 311 A instrument (70 eV, 300 μA emission), only characteristic fragments are listed. Elemental analyses were performed by "Mikroanalytisches Laboratorium Beller" (Göttingen) and the analytical laboratory of the Universität Bielefeld.

Di-t-butylcyclopentadienyldichlorophosphane (I)

To a solution of 1,3-di-t-butylcyclopentadiene (3.56 g, 20 mmol) in 50 ml of THF at 0 °C was added a solution of 1.57 *M* n-BuLi in hexane (12.7 ml, 20 mmol). The mixture was allowed to warm to room temperature, stirred for 6 h, then was added dropwise at 0 °C to a solution of freshly distilled PCl_3 (3.43 g, 25 mmol) in 30 ml of THF. The mixture was stirred at 0 °C for 1 h, allowed to warm to room temperature, and then stirred for further 12 h. After removal of the solvent, 50 ml of petroleum ether was added. The precipitated LiCl was filtered off, the solvent was removed from the filtrate, and the residue was distilled in vacuo at 150 °C (bath temperature) to give compound I, 4.1 g (74%); b.p. 81–83 °C at 0.05 torr. The product solidified at room temperature to give yellow needles, m.p. 43–44 °C. ^{1}H NMR ($C_6H_5CH_3$-d_8): δ 0.98 (s, 9H, Me_3C^4), 1.19 (d, 9H, Me_3C^1, *J* 2 Hz), 3.73 (S, 2H, H^5), 6.16 (d, 1H, H^3, *J* 2 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 30.9 (Me_3C^4), 32.38 (d, Me_3C^1), 42.09 (C^5), 126.5 (d, C^3, *J* 6 Hz), 134.0 (d, C^2, *J* 66 Hz), 168.8 (d, C^4, *J* 2 Hz), 171.1 (d, C^1, *J* 26 Hz) ppm. ^{31}P NMR ($CDCl_3$): δ 161.2 ppm. Anal. Found: C, 55.61; H, 7.93. $C_{13}H_{21}PCl_2$ calcd.: C, 55.91; H, 7.58%. MS: *M/e* 282 ($M^+ + 4$, $C_{13}H_{21}P^{37}Cl_2$, 2), 280 ($M^+ + 2$, $C_{13}H_{21}P^{35}Cl^{37}Cl$, 7), 278 ($M^+$, $C_{13}H_{21}P^{35}Cl_2$, 10), 263 ($M^+ - CH_3$, 3), 243 ($M^+ - {}^{35}Cl$, 7), 207 (3), 177 (4), 162 (10), 135 (29), 57 (Me_3C^+, 100).

Di-t-butylcyclopentadienyldiisopropylphosphane (II)

A solution of 3.0 g (20 mmol) diisopropylchlorophosphane in 30 ml THF was treated with an equimolar amount of di-t-butylcyclopentadienyllithium in 50 ml THF. The mixture was stirred at room temperature for 6 h. After removal of the solvent and addition of 40 ml of petroleum ether, the precipitated LiCl was filtered off. The petroleum ether was removed and the residue was distilled in vacuo to give compound II, 5.0 g (85%); b.p. 85–88 °C at 0.05 torr. ^{1}H NMR ($CDCl_3$): δ 0.77–1.33 (m, $(CH_3)_2CH$, Me_3C), 1.84–2.06 (m, $(CH_3)_2CH$), 2.96 (s), 2.98 (d, *J* 1.5 Hz), 3.00 (d, *J* 1 Hz), 3.44 (t, *J* 1.5 Hz), 3.45 (t, *J* 1.5 Hz), 5.89 (t, *J* 1 Hz), 6.06 (s), 6.09 (s), 6.16 (d, *J* 3 Hz), 6.22 (t, *J* 1 Hz). ^{31}P NMR ($CDCl_3$): δ −12.90, −11.24, −4.70, 2.89 and +10.77 ppm. Anal. Found: C, 77.15; H, 12.02. $C_{19}H_{35}P$ calcd.: C, 77.50, H, 11.98%. MS: *M/e* 295 (M^+, 47), 279 ($M^+ - {}^iPr$, 46), 121 (32), 91 (40), 57 (Me_3C^+, 100).

Di-t-butylcyclopentadienyldichloroarsane (III)

In a similar procedure, a solution of 8.17 g (45 mmol) $AsCl_3$ in 30 ml THF was treated with a 40 mmolar solution of di-t-butylcyclopentadienyllithium in THF to give compound III, 9.2 g (71%); b.p. 100–103 °C at 0.01 torr. ^{1}H NMR ($CDCl_3$): δ 1.23 (s, 18H, Me_3C), 5.36 (d, 2H, $H^{4,5}$, *J* 1 Hz), 6.60 (t, 1H, H^2, *J* 1 Hz). ^{13}C NMR ($CDCl_3$): δ 31.0 (Me_3C), 53.1 (Me_3C), 93.6 ($C^{4,5}$) 129.8 ($C^{1,3}$) 159.7 (C^2) ppm. Anal. Found: C, 48.39; H, 6.87. $C_{13}H_{21}AsCl_2$ calcd.: C, 48.32; H, 6.55%. MS: *M/e*

324 ($M^+ + 2$, $C_{13}H_{21}As^{35}Cl^{37}Cl$, 2) 322 ($M^+C_{13}H_{21}As^{35}Cl_2$, 4), 287 ($C_{13}H_{21}As^{35}Cl_2{}^{35}Cl$, 5), 177 (6), 147 (10), 135 (25), 121 (30), 105 (10), 57 (Me_3C^+, 100).

Di-t-butylcyclopentadienyldichlorostibane (IV)

Similarly, a solution of 10.3 g (45 mmol) $SbCl_3$ in 30 ml THF was treated with a 40 mmolar solution of di-t-butylcyclopentadienyllithium in THF to give compound IV, 11.3 g (76%); b.p. 115–118°C at 0.01 torr. ^1H NMR ($CDCl_3$); δ 1.29 (s, 18H, Me_3C), 5.79 (d, 2H, $H^{4,5}$, J 2 Hz), 6.72 (t, 1H, H^2, J 2 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 31.7 (Me_3C), 53.2 (Me_3C), 95.4 ($C^{4,5}$), 123.7 ($C^{1,3}$) 156.5 (C^2) ppm. Anal. Found: C, 41.86; H, 6.12. $C_{13}H_{21}SbCl_2$ calcd.: C, 42.20; H, 5.72%. MS: *M/e* 372 ($M^+ + 2$, $C_{13}H_{21}Sb^{35}Cl^{37}Cl$, 2), 370 ($M^+$, $C_{13}H_{21}Sb^{35}Cl_2$, 5), 354 (4), 335 (9), 298 (4), 242 (3), 193 ($SbCl_2$, 8) 177 (10), 147 (20), 135 (40), 121 (45), 57 (Me_3C^+, 100).

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