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Investigation of novel and reinvestigation of known cyclopentadienylphosphanes: News on [1,5] sigmatropic rearrangements

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ABSTRACT

$Ph_2P(C_5HMe_4)$ (**1**) was found to undergo a prototropic rearrangement contrary to previous reports. The first detailed investigation of a cyclopentadienylphosphane to undergo such a reaction is presented. One of the two tautomers of **1** which were observed represents the kinetic product, the other one is the thermodynamic product. The two isomers exhibit pronounced differences with respect to their chemical reactivity. Thermodynamic and kinetic data of the isomerisation process were determined. A novel, electron rich cyclopentadienylphosphane, the phosphorus diamide $(Me_2N)_2P(C_5HMe_4)$ (**2**), was synthesised and was also found to undergo a prototropic rearrangement. The characteristics of the isomerisation process are fully consistent with the findings on **1**. The molecular structure of the kinetic product of **2** was established by means of single crystal X-ray diffraction analysis. $Me_2P(C_5H_4tBu)$ (**3**) is presented as another novel cyclopentadienylphosphane. The mixture of isomers of **3** in thermodynamic equilibrium was investigated in detail with respect to the molecular structures of the tautomers. The results of this study suggested a reinvestigation of the parent compound $Ph_2P(C_5H_4tBu)$ (**4**) and findings differing from an earlier report in some details are presented.

1. Introduction

Cyclopentadienylphosphanes have found manifold use as synthetic building blocks in organometallic chemistry. On the one hand this is due to the fact that the monoanions derived from these molecules can act as bidentate ligands with the two coordination sites being in close proximity. This characteristic has frequently been taken advantage of for the syntheses of dihetero metallic [1–7] as well as tri- [8–10] and multimetallic [11,12] compounds. On the other hand cyclopentadienylphosphanes can easily be derivatised via oxidative addition at the phosphorus atom with group 14, 15 or 16 electrophiles opening up synthetic routes to many different classes of chelating ligands [13–15]. Beside the importance of cyclopentadienylphosphanes as synthetic building blocks, these molecules have also been subjects of academic research, when the fluxional behaviour of cyclopentadienes was investigated [16]. After the first example of a cyclopentadienylphosphane to exhibit fluxional behaviour due to the migration of a phosphanyl moiety had been reported [17], the kinetic parameters [18] as well as the stereochemical aspects of phosphatropic shifts in such molecules [19,20] have been studied in detail. Different isomers of cyclopentadienylphosphanes resulting from prototropic rearrangements have been described and in some cases the course of these reactions could be monitored [21–23]. However, a detailed investigation of the kinetic parameters of such a reaction has not been reported yet. Also, there is no evidence in the literature of different isomers of cyclopentadienylphosphanes to show pronounced differences in their chemical reactivity. During our studies involving oxidative addition reactions with diphenyltetramethylcyclopentadienylphosphane, $Ph_2PCp^{\#}$ (**1**) ($Cp^{\#} = C_5HMe_4$), we found that this phosphane is a suitable substrate for closing this gap of knowledge. In addition, our findings on the isomerisation of **1** – a molecule which is known to the literature since 1990 [24,25] and has been used in numerous derivatisation reactions [1,2,5,7,8,26–32] – are not fully consistent with earlier reports, which in turn are not in congruency with each other (see section 2.1). Moreover we would like to report the synthesis of two novel cyclopentadienylphosphanes, $(Me_2N)_2PCp^{\#}$ (**2**) and Me_2PCp^{tBu} (**3**) ($Cp^{tBu} = C_5H_4tBu$), and the detailed NMR spectroscopic analysis of the isomers present in thermodynamic equilibrium. The results obtained on **3** prompted us to reinvestigate the mixture of tautomers of the parent compound Ph_2PCp^{tBu} (**4**) [33] with respect to the molecular structures of the single isomers.

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2. Results and discussion

2.1. Diphenyltetramethylcyclopentadienylphosphane, $Ph_2PCp^{\#}$ (**1**)

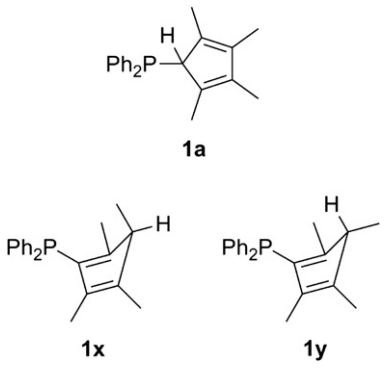
$Ph_2PCp^{\#}$ (**1**) has been described by two different groups independently in 1990 [24,25]. Their conclusions concerning the structure of this molecule differed. The results we obtained are not fully consistent with either one of these reports. In order to clarify the differences the results published earlier shall very briefly be summarised.

2.1.1. Results on $Ph_2PCp^{\#}$ (**1**) obtained by other groups

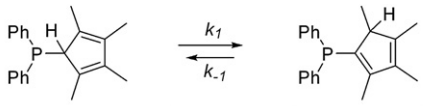
Szymoniak et al. presented the first synthesis of **1** [24], which authors usually refer to when using **1** as a synthetic building block. They reported **1a** to be the only isomer present and classified **1** to be unstable under inert gas atmosphere at ambient temperature, which was why they suggested a straightforward derivatisation. Wong et al. described $Ph_2PCp^{\#}$ as a 1:1 mixture of two isomers, **1x** and **1y** (Scheme 1) [25]. They did not mention the number of signals obtained in ^1H NMR spectra of **1**. ^{13}C NMR or two dimensional NMR spectra were not reported. According to their interpretation, the sp^3 hybridised carbon atom, which is part of the five-membered ring, is not in plane with the other four carbon atoms forming this cycle, which would let **1x** and **1y** be diastereomers, and the transfer of this carbon atom from the *re* to the *si* side of the molecule (and vice versa) is slow on the NMR time scale. In another publication two isomers of $Ph_2PCp^{\#}$ have briefly been mentioned without any details concerning their number, structures, molar ratio or analytical data given [8].

2.1.2. Isomerisation of $Ph_2PCp^{\#}$ and investigations concerning the kinetics thereof

1 was synthesised with minor modifications to Szymoniak's protocol resulting in a simplification of the synthesis. The cyclopentadienylphosphane **1** was obtained as a single isomer (**1a**) in congruency with Szymoniak's results [24]. Upon storage at ambient temperature under inert gas atmosphere the formation of another substance was observed via NMR spectroscopic measurements. However, this substance proved not to be a product of decomposition processes as suggested earlier [24], but a product of an isomerisation process with the molecular structure **1b** (Scheme 2). This isomerisation takes place when **1** is stored as a neat product as well as in solution of diethylether or pentane. The equilibrium of this slow isomerisation process is reached at a molar ratio of **1a**:**1b** = 30:70 (Scheme 2), i. e. the isomer **1b** is thermodynamically more stable. This can be ascribed to the fact that the π-system of the cyclopentadienyl ring in **1b** is extended by a phosphanyl moiety,



Scheme 1. Structures of $Ph_2PCp^{\#}$ (**1**) according to earlier publications; Szymoniak et al. reported **1a** to be the only isomer present [24]; Wong et al. described the structures **1x** and **1y** [25].



t / d	[**1a**] / mol%	[**1b**] / mol%
0.17	94	6
3	80	20
9	50	50
19	30	70
40	30	70

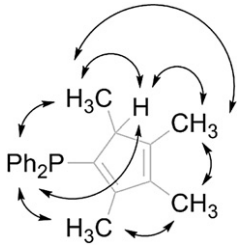
Scheme 2. Isomerisation of $Ph_2PCp^{\#}$ (**1**) via a prototropic rearrangement.

which can act as an electron donor with its lone pair or as an electron acceptor with its $\sigma^*_{P-C(Ph)}$-orbitals.

The molecular structure of **1b** was established on the basis of one and two dimensional NMR spectroscopic experiments. Especially the NOE spectrum provides evidence for the structure suggested. In this spectrum, the resonance due to the proton, which is directly bonded to the five-membered ring, shows a cross peak to the resonances which were assigned to the methyl groups in 5- and in 4-position of the cyclopentadienyl fragment. A cross peak to a third resonance arising from a methyl group could not be observed, which rules out the molecular structures **1x** and **1y** which have been suggested earlier (Scheme 1) [25]. The other cross peaks arising in the NOE spectrum of **1** are fully consistent with the molecular structure of **1b** and are graphically summarised in Scheme 3. The full NOE spectrum of **1b** can be found in the electronic supplement.

In order to find further evidence for **1b** to be an isomer of $Ph_2PCp^{\#}$, an equimolar mixture of **1a** and **1b** was dissolved in benzene and deprotonated using *n*BuLi as a base in eightfold excess. As expected both isomers were transformed into the lithium organyl $Li(PPh_2(C_5Me_4))$ (**5**), which was observed via ^1H and ^{31}P NMR spectroscopy. However, the kinetics of this deprotonation reaction, which was also monitored by ^1H and ^{31}P NMR spectroscopic measurements, differed significantly for the two isomers **1a** and **1b**. Whereas **1a** was completely deprotonated after a reaction time of $t \leq 15$ min, a reaction time as high as $t = 35$ h was necessary to achieve the deprotonation of 98% of the isomer **1b**. This is the first example of two isomers of a cyclopentadienylphosphane differing significantly in their chemical reactivity, namely their kinetic basicity. The course of the reaction is visualised by the graph shown in Fig. 1.

When less than eight equivalents of *n*BuLi are used, the result does not change within the estimated range of error (±5% for integrals in NMR spectra). These observations lead to the conclusion that under the chosen reaction conditions the deprotonation of **1b** is first order with respect to **1b** and zero order with respect to the base. The situation described in Scheme 4 gives a possible explanation for these results: the deprotonation of **1a** is significantly faster than the isomerisation of **1**, whereas the deprotonation of **1b** is significantly slower than the isomerisation of **1**. In



Scheme 3. Cross peaks in the NOE spectrum of **1b** (indicated by arrows between the relevant substituents).

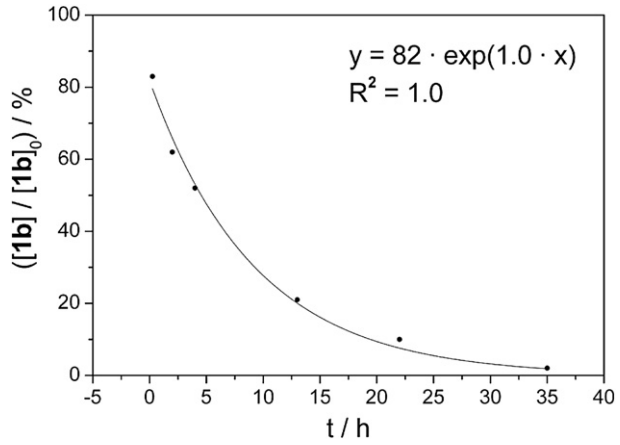
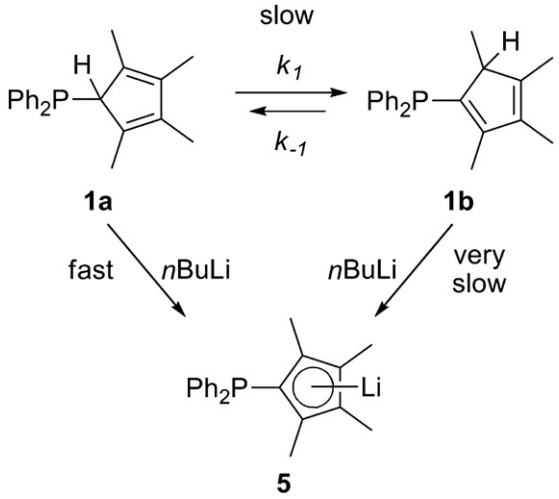


Fig. 1. Plot of the relative concentration of **1b** versus time in the deprotonation of an equimolar mixture of **1a** and **1b** with eight equivalents of *n*BuLi in C_6D_6 at ambient temperature.

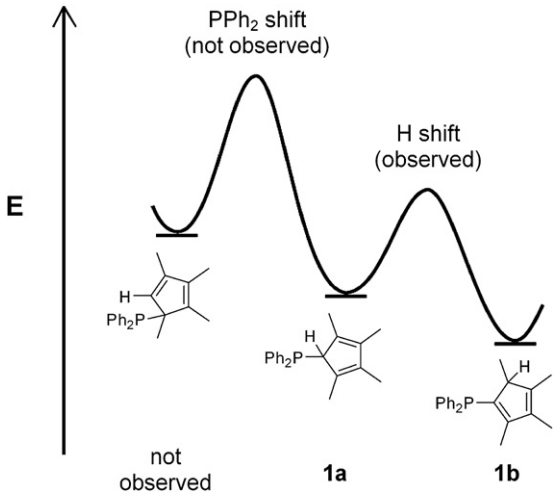
other words, the isomerisation of **1b** to **1a** is the rate determining step of the deprotonation of **1b** under the chosen reaction conditions.

The difference in chemical reactivity of the isomers **1a** and **1b** in this deprotonation reaction can only arise from different kinetic barriers, as the product **5** is the same in both cases, which rules out thermodynamic reasons. The height of kinetic barriers of reactions with lithiated compounds acting as nucleophilic reagents are known to be strongly affected by precoordination effects in some cases [34–36]. In the deprotonation of **1** with *n*BuLi, a precoordination of the lithium atom by the lone pair of the phosphorus atom is a plausible initiating reaction step. In the isomer **1b**, electron density from this lone pair can also be donated into the π-system of the cyclopentadienyl moiety. This would result in a decreased coordination ability of **1b** compared with **1a** offering a possible explanation for the differences of these two isomers with respect to their chemical reactivity.

The data on the deprotonation of **1** (Fig. 1) do not only reveal the differences of **1a** and **1b** in their chemical reactivity, but also allow for the kinetic parameters of the isomerisation of **1** to be determined (details of these procedures can be found in the electronic supplement). The rate constant k_{-1} can be obtained from the slope of the halflogarithmic plot of the graph shown in Fig. 1; the



Scheme 4. Kinetics of the isomerisation of $Ph_2PCp^{\#}$ (**1**) relative to those of the deprotonation of **1a** and **1b**.



Scheme 5. Schematic energy diagram for phosphatropic and prototropic shift in $Ph_2PCp^{\#}$ (**1**).

margin of error given for k_{-1} is due to the error determined in the linear regression analysis:

$$k_{-1} = (2.8 \pm 0.1) \cdot 10^{-5}\ s^{-1}.$$

The equilibrium constant, *K*, can be calculated from the data listed in Scheme 2; in this case, the margin of error is due to the estimated range of error (5% for integrals in NMR spectra). For completeness, the Gibbs energy can also be determined from *K*:

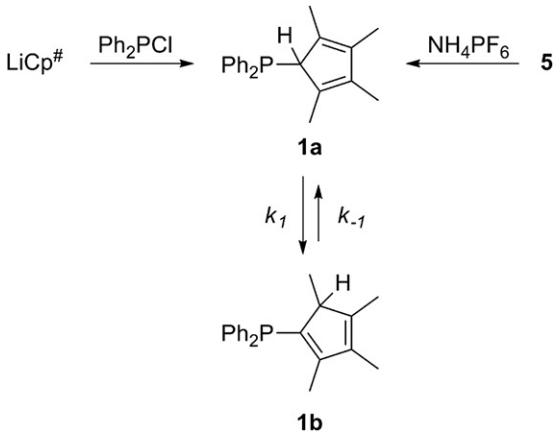
$$K = 2.3 \pm 0.2$$

$$\Delta G = (-2.1 \pm 0.3)\ \text{kJ}.$$

When the relation between the equilibrium constant and the rate constants of the isomerisation of **1**, $K = k_1/k_{-1}$, is taken into account, the second rate constant, k_1, can also be determined:

$$k_1 = (6.4 \pm 0.8) \cdot 10^{-5}\ s^{-1}.$$

This is the first report of kinetic data on a prototropic shift in a cyclopentadienylphosphane. The values of the rate constants are by approximately 17 orders of magnitude lower than the value which has been determined for the prototropic shift in cyclopentadiene [37]. The fact that a phosphatropic shift was not observed in $Ph_2PCp^{\#}$ is not surprising as in all reported cases of



Scheme 6. Highly selective formation of the isomer **1a** via two different synthetic routes; in both cases **1a** isomerises to form **1b** until the thermodynamic equilibrium is reached.

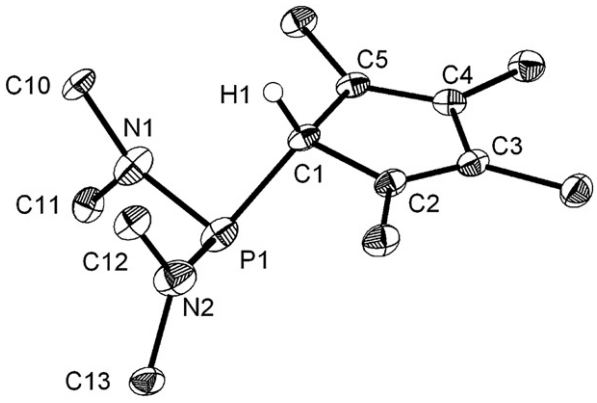


Fig. 2. ORTEP drawing of the molecular structure of **2a**; the thermal ellipsoids are drawn at the 30% probability level. All hydrogen atoms except for H1 are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.869(3), P1–N1 1.690(3), P1–N2 1.686 (3), C1–C2 1.522(4), C2–C3 1.340(5), C3–C4 1.477(5), C4–C5 1.338(5), C1–C5 1.520(5), C1–H1 0.967(35), C1–P1–N1 101.1(1), C1–P1–N2 100.5(2), N1–P1–N2 109.9(1), C1–C2–C3 109.2(3), C2–C3–C4 109.6(3), C3–C4–C5 109.3(3), C4–C5–C1 109.5(3), C2–C1–C5 102.3(3), P1–N1–C10 126.5(2), P1–N1–C11 118.2(2), C10–N1–C11 113.2(3), P1–N2–C12 127.8(2), P1–N2–C13 117.5(2), C12–N2–C13 111.8(3).

such a rearrangement one of two criteria was met, which do not apply to $Ph_2PCp^{\#}$. Either at least one strongly electronegative substituent was bonded to the phosphorus atom of the posphanyl moiety [17,38] or five sterically demanding substituents were bonded to the cyclopentadienyl core in addition to the phosphanyl fragment [18,39]. In $Ph_2PCp^{\#}$ there are no highly electronegative substituents and only four sterically demanding substituents bonded to the cyclopentadienyl core apart from the phosphanyl moiety. In addition, a phosphatropic rearrangement in **1** would result in a geminally methyl and phosphanyl substituted product, which would be sterically highly unfavourable. On the basis of these findings a schematic energy diagram describing the fluxional behaviour of $Ph_2PCp^{\#}$ can be formulated (Scheme 5).

As pointed out above, **1a** is formed as the kinetic product in the synthesis of $Ph_2PCp^{\#}$, when the protocol established by Szymoniak et al. [24] or minor modifications thereof are applied (left part, Scheme 6). A different synthetic approach to the cyclopentadienylphosphane **1** was investigated in an attempt to synthesise the isomer **1b** in high selectivity prior to isomerisation. In this respect, $Li(PPh_2(C_5Me_4))$ (**2**) was protonated using ammonium hexafluorophosphate as a Brønsted acid. However, **1a** was again exclusively formed (right part, Scheme 6) prior to the beginning slow isomerisation process (middle part, Scheme 6). So the carbon atom in 1-position of the lithium cyclopentadienide **5** is the kinetically most basic site of this molecule.

2.2. Synthesis and isomerisation of $(Me_2N)_2PCp^{\#}$ (2) ($Cp^{\#} = C_5HMe_4$)

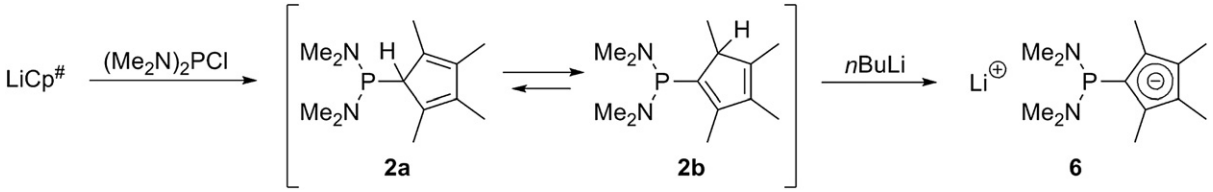
$(Me_2N)_2PCp^{\#}$ (**2**), the second tetramethylcyclopentadienyl substituted phosphane we would like to report on, was synthesised in order to enrich the spectrum of this small class of compounds. Within this ligand family, the outstanding characteristic of **2** is its electron richness which is induced by the two dimethylamino moieties. This characteristic is of interest as electron rich phosphanes proved to be superior when used in some derivatisation reactions [40,41] or as ligands in catalytic applications [42,43]. When the cyclopentadienylphosphane **2** was synthesised, the isomer **2a** was obtained exclusively.

The molecular structure of **2a** was established via one and two dimensional NMR experiments and confirmed by single crystal X-ray analysis (Fig. 2). In solid state, the bulky $Cp^{\#}$ substituent is oriented away from the two dimethylamino moieties, which was ascribed to steric interactions. The bond lengths within the cyclopentadienyl unit exhibit the typical pattern of two short (C2–C3, C4–C5), one medium (C3–C4) and two long (C1–C2, C1–C5) C–C distances. These values provide evidence for C1 to be sp^3 hybridised and to bear the proton H1. In addition, H1 was found in the final density map and refined with isotropic displacement parameters. By means of this analysis, the isomer **2a** with H1 in α-position relative to the phosphanyl substituent was unambiguously established as the product primarily formed in the synthesis of **2**. The lengths of the phosphorus nitrogen bonds (P1–N1, P1–N2) and the phosphorus carbon bond (P1–C1) were found to lie within the range of values typical for diaminoarylphosphanes [44–48]. The P–C and P–N bonds in other diaminocyclopentadienylphosphanes and the P–C bonds in iminocyclopentadienylphosphanes, which have been characterised by means of single crystal X-ray analyses, are slightly longer [49,50], but of comparable length when such molecules are coordinated to a transition metal [51,52]. Remarkably, both of the nitrogen atoms in compound **2a**, N1 and N2, are centres of a trigonal planar configuration with angle sums (C–N–C/P) of 357.1(7)° and 357.9(7)° respectively. This allows for more effective n_N-σ^*_{P-C} interactions, which provides experimental evidence for the high potential donor ability of the phosphorus atom P1.

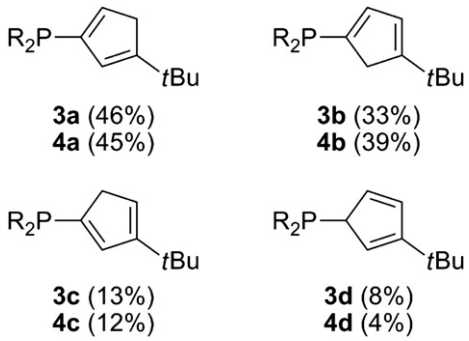
In the light of our results on the isomerisation of $Ph_2PCp^{\#}$ (**1**) (see section 2.1) it was not surprising, that **2a** is partially transformed into the isomer **2b** via a prototropic shift upon storage at room temperature in a solution of toluene. The molecular structure of **2b** was established by one and two dimensional NMR spectroscopic experiments, a detailed analysis of which can be found in the electronic supplement. The two isomers **2a** and **2b** were found to be in thermodynamic equilibrium at a ratio of **2a**:**2b** = 40:60. From these data can be concluded, that **2a** is formed as the kinetic product in the synthesis of **2**. The isomer **2b**, in which the π-system of the cyclopentadienyl group is in conjugation with a phosphanyl moiety, represents the thermodynamic product. A phosphatropic rearrangement was not observed. These results are in good agreement with our findings on $Ph_2PCp^{\#}$ (**1**) (see section 2.1), i.e. the schematic energy diagram shown in Scheme 5 also holds for **2**.

The lithiated species $Li(P(NMe_2)_2(C_5Me_4))$ (**6**) was prepared as a useful building block for further derivatisation reactions or coordination of the $(P(NMe_2)_2(C_5Me_4))^-$ anion to one or more metal centres (Scheme 7).

Having found evidence for slow prototropic shifts in $Ph_2PCp^{\#}$ (**1**) and $(Me_2N)_2PCp^{\#}$ (**2**) – two tetramethylcyclopentadienylphosphanes which differ significantly in their electronic characteristics –



Scheme 7. In the synthesis of **2**, the isomer **2a** is exclusively formed prior to the beginning slow isomerisatin process; lithiation of **2** yields $Li(P(NMe_2)_2(C_5Me_4))$ (**6**).



Scheme 8. Tautomers which were observed in the mixture of isomers of R_2PCp^{tBu}; in parenthesis: molar percentage of each single isomer present in the mixture of isomers; **3**: R = Me, **4**: R = Ph.

this type of rearrangement is likely to be a viable reaction pathway for the entity of this small class of compounds. The C_S-symmetric isomers, **1a** and **2a**, are formed exclusively prior to the beginning isomerisation processes.

2.3. Synthesis of Me_2PCp^{tBu} (3) and reinvestigation of Ph_2PCp^{tBu} (4) ($Cp^{tBu} = C_5H_4tBu$)

When there are less than five sterically demanding substituents bonded to the five-membered ring of a cyclopentadienylphosphane, a mixture of isomers is usually obtained in the syntheses of these compounds. This also proved to be the case when the novel cyclopentadienylphosphane Me_2PCp^{tBu} (**3**) was synthesised in analogy to the protocol which was established for the parent compound Ph_2PCp^{tBu} (**4**) [33]. All isomers of **3** exhibit the typical substitution pattern, in which the two bulky substituents are separated by a C1-bridge, which is attributed to steric repulsion. With this restriction in mind five isomers of **3** could possibly be formed, four of which were actually observed (Scheme 8). The molecular structures of these compounds were established by means of one and two dimensional NMR spectroscopic methods. The detailed analysis of the NMR data is presented in the electronic supplement. The molecular structures established for **3** differ in some points from those which were reported for the parent compound **4** [33]. In the course of our studies we also synthesised **4** for further derivatisation reactions. The analysis of the tautomeric mixture of compound **4** let us suggest the molecular structures shown in Scheme 8 for the four isomers observed (details can be found in the electronic supplement). These findings are in full congruency with our results on Me_2PCp^{tBu} (**3**). However, they deviate in some points from the conclusions drawn in an earlier publication [33], in which the same number of isomers and similar molar percentages of the single isomers were reported, but different molecular structures were proposed for the isomers **4b** and **4c**.

3. Conclusion

In the synthesis of the cyclopentadienylphosphane $Ph_2PCp^{\#}$ (**1**) ($Cp^{\#} = C_5HMe_4$) the symmetric isomer **1a** is – at first – exclusively formed, independent of the synthetic route chosen. In contrast to earlier reports [24,25] **1a** was found to undergo a prototropic rearrangement yielding **1b** as a thermodynamically more stable isomer. A mixture of these two isomers in a ratio of **1a**:**1b** = 30:70 was found to be present in thermodynamic equilibrium. The rate constants of this slow isomerisation process, k_1 and k_{-1}, were determined and are in the order of $5\cdots10^{-5}$ s^{-1}. Unexpectedly, the isomers **1a** and **1b** differ significantly with respect to their chemical reactivity towards *n*BuLi. **1b** is much more inert towards this base than **1a**, which makes the isomerisation of **1b** to **1a** the rate limiting step of this reaction.

$(Me_2N)_2PCp^{\#}$ (**2**) is presented as a novel highly nucleophilic cyclopentadienylphosphane. In general, the observations concerning the isomerisation processes of **1** also hold for **2**; i. e. the symmetric isomer **2a** is exclusively formed as the kinetic product independent of the synthetic approach to compound **2** and **2a** undergoes a prototropic rearrangement to form the thermodynamically more stable isomer **2b** (**2a**:**2b** = 40:60 in thermodynamic equilibrium). The molecular structure of the kinetic product **2a** was established by means of single crystal X-ray analysis.

Me_2PCp^{tBu} (**3**) ($Cp^{tBu} = C_5H_4tBu$) was synthesised as another new cyclopentadienylphosphane. The mixture of isomers of **3** present in thermodynamic equilibrium was studied in detail with respect to the molecular structures of the single tautomers. The results of these studies suggested a reinvestigation of the mixture of isomers of the parent compound Ph_2PCp^{tBu} (**4**). Deviations from an earlier report [33] with respect to the molecular structures of two of the four the isomers of **4** were found.

4. Experimental

4.1. General considerations

All experimental procedures were carried out in an atmosphere of purified argon or nitrogen using standard Schlenk techniques or a glovebox. The solvents used were dried and degassed according to standard protocols. Chemicals were purchased from Alfa Aesar or Aldrich and used without further purification. $PClMe_2$ [53], $LiCp^{\#}$ ($Cp^{\#} = C_5HMe_4$) [54], $PCl(NMe_2)_2$ [55] and $LiCp^{tBu}$ [56] were synthesised according to literature procedures. NMR measurements were performed using a Bruker AVANCE 300, DRX 400 or DRX 500 spectrometer at 25 °C. Elemental analyses were carried out at the Analytical Laboratory of the Department of Chemistry/Philipps-Universität Marburg. EI mass spectra were recorded using a Finnigan MAT CH7 instrument (E = 70 eV). ATR FT IR spectra were obtained using a Bruker Alpha-P spectrometer.

4.1.1. Synthesis of $Ph_2PCp^{\#}$ (1) [24]

$LiCp^{\#}$ (1.95 g, 15.2 mmol) was suspended in pentane (80 mL) and chlorodiphenyl phosphane (3.14 g, 14.2 mmol) was added at ambient temperature. The liquid phase slowly turned yellow. After 7 h the suspension was filtered. The solid was washed with pentane (3 × 15 mL) and the solvent was removed from the filtrate under reduced pressure yielding a yellow oil, which was dried in vacuo for 2 h. The product **1** consisting exclusively of the isomer **1a** was obtained as a yellow oil in quantitative yield (4.35 g, 14.2 mmol). A mixture of the isomers **1a** and **1b** (**1a**:**1b** = 30:70) was obtained upon storage of **1** under inert gas atmosphere at ambient temperature as a neat substance or in a solution of diethylether or pentane for at least 19 d.

^{1}H NMR (300.1 MHz, C_6D_6): **1a**: δ = 1.53 (s, 6H, 3,4-Cp*Me*$_2$), 1.79 (s, 6H, 2,5-Cp*Me*$_2$), 3.67 (d, 1H, $^2J_{HP}$ = 1.1 Hz, H_{Cp}), 7.04–7.07 (m, 6H, *m-, p- Ph*), 7.44–7.48 (m, 4H, *o-Ph*) ppm. **1b**: δ = 0.84 (d, 3H, $^3J_{HH}$ = 6.9 Hz, 5-Cp*Me*), 1.63 (s, 3H, 4-Cp*Me*), 1.65 (s, 3H, 3-Cp*Me*), 2.00 (d, 3H, $^4J_{HP}$ = 1.6 Hz, 2-Cp*Me*), 2.84 (q, 1H, $^3J_{HH}$ = 6.9 Hz, H_{Cp}), 7.07–7.12 (m, 6H, *m-, p- Ph*), 7.51–7.55 (m, 4H, *o-Ph*) ppm.

^{31}P NMR (121.5 MHz, C_6D_6): **1a**: δ = 0.6 ppm. **1b**: δ = –24.8 ppm.

^{13}C NMR (75.5 MHz, C_6D_6): **1a**: δ = 11.2 (s, 3,4-Cp*Me*$_2$), 14.2 (d, $^3J_{CP}$ = 6.7 Hz, 2,5-Cp*Me*$_2$), 57.1 (d, $^1J_{CP}$ = 26.3 Hz, 1-*Cp*), 128.0 (d, $^2J_{CP}$ = 19.5 Hz, *o-Ph*), 128.6 (s, *p-Ph*), 133.5 (d, $^3J_{CP}$ = 19.5 Hz, *m-Ph*), 133.8 (d, $^2J_{CP}$ = 3.5 Hz, 2,5-*Cp*), 136.8 (d, $^1J_{CP}$ = 19.9 Hz, *ipso-Ph*), 137.3 (d, $^2J_{CP}$ = 3.4 Hz, 3,4-*Cp*) ppm. **1b**: δ = 11.1 (s, 3-Cp*Me*), 12.2 (s, 4-Cp*Me*), 14.2 (d, $^3J_{CP}$ = 15.6 Hz, 2-Cp*Me*), 15.3 (d, $^3J_{CP}$ = 2.4 Hz,

5-Cp*Me*), 53.5 (d, $^{2}J_{CP}$ = 3.7 Hz, 5-*Cp*), 128.6 (d, $^{3}J_{CP}$ = 5.5 Hz, *m-Ph*), 133.1 (d, $^{2}J_{CP}$ = 6.3 Hz, *o-Ph*), 133.4 (d, $^{4}J_{CP}$ = 5.8 Hz, *p-Ph*), 134.2 (d, $^{2}J_{CP}$ = 12.7 Hz, 2-*Cp*), 135.0 (d, $^{3}J_{CP}$ = 6.1 Hz, 3-*Cp*), 138.3 (d, $^{1}J_{CP}$ = 11.8 Hz, *ipso-Ph*$^{1/2}$), 139.1 (d, $^{1}J_{CP}$ = 10.6 Hz, *ipso-Ph*$^{2/1}$), 147.1 (d, $^{3}J_{CP}$ = 2.5 Hz, 4-*Cp*), 155.0 (d, $^{1}J_{CP}$ = 15.2 Hz, 1-*Cp*) ppm.

4.1.2. De- [24] and Reprotonation of $Ph_2PCp^{\#}$ (**1a:1b** = 50:50)

A mixture of **1a** and **1b** (**1a**:**1b** = 50:50, 10 mg, 33 μmol) was dissolved in 600 μL of perdeuterated benzene. A solution of *n*BuLi in hexane (2.5 M, 30 μL, 75 μmol) was added at ambient temperature. 98% of the **1** were found to be converted to the product **2** after a reaction time of 36 h (judged by the ^{1}H and ^{31}P NMR spectra) during which the yellow colour of the reaction mixture intensified. Ammonium hexafluorophosphate (46 mg, 282 μmol) was added to the reaction mixture. After ultrasonic treatment for 1 h and an overall reaction time of 6 h the intensity of the yellow colour of the reaction mixture had decreased and a complete conversion of **2** to the starting material **1** was observed with the isomer **1a** being formed exclusively (judged by the ^{1}H and ^{31}P NMR spectra; for NMR spectroscopic data of **1a** see section 4.1.1). After 6 more hours of reaction time the beginning isomerisation of **1a** to **1b** was observed by ^{1}H and ^{31}P NMR spectroscopic analysis (for detailed NMR spectroscopic data of **1b** see section 4.1.2).

2: ^{1}H NMR (300.1 MHz, C_6D_6/Hex (20:1)): δ = 2.00 (bs, 6H, Cp*Me*$_2$), 2.10 (bs, 6H, Cp*Me*$_2$), 7.04–7.12 (m, 6H, *Ph*), 7.43–7.48 (m, 4H, *Ph*) ppm.

^{31}P-NMR (121.5 MHz, C_6D_6/Hex (20:1)): δ = −27.8 ppm.

4.1.3. Synthesis of $(Me_2N)_2PCp^{\#}$ (**2**)

$LiCp^{\#}$ (520 mg, 4.06 mmol) was suspended in diethylether/hexane (1:1, 30 mL). At 0 °C $PCl(NMe_2)_2$ (553 mg, 3.58 mmol) was added dropwise and the resulting reaction mixture was warmed to room temperature over a period of 16 h. The volume of the liquid phase was reduced to half in vacuo, after which the solid was separated by filtration and washed with pentane (2 × 8 mL). All volatiles were removed from the filtrate under reduced pressure yielding a white solid. After drying in vacuo **2** was obtained in 70% yield (601 mg, 2.50 mmol) as a colourless solid. At first **2a** was exclusively formed. After keeping **2** at 100 °C for 24 h in *d8*-toluene, a mixture of **2a** and **2b** was obtained with a ratio of **2a**:**2b** = 40:60, which did not change upon storage at room temperature or further heating at 100 °C.

^{1}H-NMR (300.1 MHz, *d8*-Tol): **2a**: δ = 1.78 (d, $^{4}J_{HP}$ = 2.4 Hz, 6H, 2,5-Cp*Me*$_2$), 1.92 (s, 6H, 3,4-Cp*Me*$_2$), 2.59 (d, $^{3}J_{HP}$ = 8.6 Hz, 12H, N*Me*$_2$), 3.38 (bs, 1H, 1-*H*$_{Cp}$) ppm. **2b**: δ = 1.24 (d, $^{4}J_{HP}$ = 5.4 Hz, 3H, 5-Cp*Me*), 1.72 (s, 3H, 3-Cp*Me*), 1.82 (s, 3H, 4-Cp*Me*), 1.93 (s, 3H, 2-Cp*Me*), 2.66 (d, $^{3}J_{HP}$ = 9.1 Hz, 12H, N*Me*$_2$), 2.86 (m, 1H, 5-*H*$_{Cp}$) ppm.

^{13}C-NMR (100.7 MHz, *d8*-Tol): **2a**: δ = 11.6 (s, 2,5-Cp*Me*$_2$), 12.6 (s, 3,4-Cp*Me*$_2$), 41.7 (d, $^{2}J_{CP}$ = 16.0 Hz, N*Me*$_2$), 57.1 (d, $^{1}J_{CP}$ = 21.1 Hz, *ipso-C*$_{Cp}$), 133.7 (d, $^{2}J_{CP}$ = 9.2 Hz, 2,5-*Cp*), 137.9 (d, $^{3}J_{CP}$ = 5.4 Hz, 3,4-*Cp*) ppm. **2b**: δ = 10.9 (s, 3-Cp*Me*), 11.9 (s, 4-Cp*Me*), 13.4 (d, $^{3}J_{CP}$ = 1.4 Hz, 2-Cp*Me*), 17.2 (d, $^{3}J_{CP}$ = 9.7 Hz, 5-Cp*Me*), 41.7 (d, $^{2}J_{CP}$ = 15.8 Hz, N*Me*$_2$), 42.4 (d, $^{2}J_{CP}$ = 16.2 Hz, N*Me*$_2$), 53.4 (d, $^{2}J_{CP}$ = 9.4 Hz, 5-*Cp*), 135.4 (d, $^{3}J_{CP}$ = 2.8 Hz, 3-*Cp*), 140.8 (d, $^{1}J_{CP}$ = 3.0 Hz, *ipso-Cp*), 144.5 (d, $^{2}J_{CP}$ = 5.8 Hz, 4-*Cp*), 146.5 (d, $^{3}J_{CP}$ = 17.6 Hz, 2-*Cp*) ppm.

^{31}P-NMR (121.5 MHz, *d8*-Toluol): 2a: δ = 100.6 ppm. **2b**: δ = 100.0 ppm.

EI/MS (70 eV): m/z (%) = 240 (8) [M^+], 196 (22.0), 153 (7), 119 (100), 105 (4), 76 (31).HR-EI/MS (70 eV): Calc. for $C_{13}H_{25}N_2P$: 240.1755. Found: 240.1790.

Anal. Calc. for $C_{13}H_{25}N_2P$ (240.32): C, 64.97; H, 10.49; N, 11.66. Found: C, 65.00; H, 10.53; N, 11.29.

IR: 2961 (w), 2912 (w), 2885 (m), 2828 (m), 2781 (w), 1439 (m), 1378 (w), 1257 (m), 1215 (m), 1186 (s), 1135 (w), 1098 (w), 1068 (w), 1054 (w), 953 (s), 800 (w), 764 (w), 661 (s), 632 (m), 504 (s), 452 (m) cm^{-1}.

4.1.4. Synthesis of $Li((Me_2N)_2P(C_5Me_4)$ (**6**)

$(Me_2N)_2PCp^{\#}$ (100 mg, 0.43 mmol) was dissolved in hexane and cooled to 0 °C. A solution of *n*BuLi in hexane (1.6 M, 300 μL, 0.48 mmol) was added. After stirring at ambient temperature for 16 h and at 55 °C for another 24 h a precipitate had formed, which was separated by filtration and washed with pentane (2 × 5 mL). After drying in vacuo **6** was obtained as a yellow solid in 67% yield (72 mg, 0.29 mmol).

^{1}H-NMR (300.1 MHz, *d8*-THF): δ = 1.93 (d, 6H, Cp*Me*$_2$), 2.01 (s, 6H, Cp*Me*$_2$), 2.57 (d, $^{3}J_{HP}$ = 8.5 Hz, 12H, N*Me*$_2$) ppm.

^{13}C-NMR (100.7 MHz, *d8*-THF): δ = 11.4 (s, Cp*Me*$_2$), 12.5 (d, $^{3}J_{CP}$ = 4.7 Hz, Cp*Me*$_2$), 41.4 (d, $^{2}J_{CP}$ = 16.4 Hz, N*Me*$_2$), 103.4 (d, $^{1}J_{CP}$ = 10.4 Hz, 1-*Cp*), 111.9 (d, $^{2}J_{CP}$ = 6.8 Hz, 2,5-*Cp*), 112.9 (d, $^{3}J_{CP}$ = 14.4 Hz, 3,4-*Cp*) ppm.

^{31}P-NMR (121.5 MHz, *d8*-THF): δ = 109.3 ppm.

4.1.5. Synthesis of Me_2PCp^{tBu} (**3**)

A suspension of $LiCp^{tBu}$ (500 mg, 3.90 mmol) in toluene (12 mL) was cooled to −78 °C. A solution of $PClMe_2$ in toluene (3.94 M, 1.04 mL, 4.10 mmol) was added. After warming the reaction mixture up to room temperature over a period of 16 h the solid was separated by filtration and washed with hexane (2 × 6 mL). The solvents were removed from the filtrate under reduced pressure at 0 °C. **3** was obtained as a slightly yellowish oil of low viscosity in 92% yield (650 mg, 3.57 mmol).

^{1}H-NMR (300.1 MHz, C_6D_6): **3a**: δ = 1.06 (d, $^{2}J_{HP}$ = 2.9 Hz, 6H, P*Me*$_2$), 1.17 (s, 9H, C(C*H*$_3$)$_3$), 2.88 (m, 2H, C*H*$_2$), 6.03 (m, 1H, *H*$_{Cp}$), 6.80 (m, 1H, *H*$_{Cp}$) ppm. **3b**: δ = 1.08 (d, $^{2}J_{HP}$ = 2.9 Hz, 6H, P*Me*$_2$), 1.10 (s, 9H, C(C*H*$_3$)$_3$), 2.95 (m, 2H, C*H*$_2$), 6.11 (m, 1H, *H*$_{Cp}$), 6.55 (m, 1H, *H*$_{Cp}$) ppm. **3c**: δ = 1.13 (d, $^{2}J_{HP}$ = 2.8 Hz, 6H, P*Me*$_2$), 1.16 (s, 9H, C(C*H*$_3$)$_3$), 2.84 (m, 2H, C*H*$_2$), 6.23 (m, 1H, *H*$_{Cp}$), 6.32 (m, 1H, *H*$_{Cp}$) ppm. **3d**: δ = 0.86 (d, $^{2}J_{HP}$ = 4.5 Hz, 3H, P*Me*$_2$), 0.88 (d, $^{2}J_{HP}$ = 4.5 Hz, 3H, P*Me*$_2$), 1.10 (s, 9H, C(C*H*$_3$)$_3$), 3.20 (m, 1H, *H*$_{Cp}$), 6.04 (m, 1H, *H*$_{Cp}$), 6.38 (m, 1H, *H*$_{Cp}$), 6.60 (m, 1H, *H*$_{Cp}$) ppm.

^{13}C-NMR (75.5 MHz, C_6D_6): **3a**: δ = 14.6 (d, $^{1}J_{CP}$ = 12.7 Hz, P*Me*$_2$), 30.0 (s, C(*CH*$_3$)$_3$), 32.5 (s, *C*(CH$_3$)$_3$), 42.0 (d, ^{3}J$_{CP}$ = 8.7 Hz, *CH*$_2$), 125.7 (d, $^{2}J_{CP}$ = 3.1 Hz, *CH*$_{Cp}$), 137.2 (d, $^{2}J_{CP}$ = 20.0 Hz, *CH*$_{Cp}$), 150.6 (d, $^{1}J_{CP}$ = 16.1 Hz, *ipso-C*$_{Cp}$), 157.5 (d, $^{3}J_{CP}$ = 5.7 Hz, *CC*(CH$_3$)$_3$) ppm. **3b**: δ = 14.7 (d, ^{1}J$_{CP}$ = 12.8 Hz, P*Me*$_2$), 31.0 (s, C(*CH*$_3$)$_3$), 33.6 (s, *C*(CH$_3$)$_3$), 41.3 (d, $^{2}J_{CP}$ = 9.9 Hz, *CH*$_2$), 125.0 (d, J_{CP} = 6.0 Hz, *CH*$_{Cp}$), 136.9 (d, J_{CP} = 18.9 Hz, *CH*$_{Cp}$), 146.6 (d, $^{1}J_{CP}$ = 15.3 Hz, *ipso-C*$_{Cp}$), 162.4 (d, $^{3}J_{CP}$ = 3.1 Hz, *CC*(CH$_3$)$_3$) ppm. **3c**: δ = 13.5 (d, $^{1}J_{CP}$ = 12.8 Hz, P*Me*$_2$), 30.2 (s, C(*CH*$_3$)$_3$), 33.5 (s, *C*(CH$_3$)$_3$), 41.6 (d, $^{2}J_{CP}$ = 5.5 Hz, *CH*$_2$), 125.1 (d, J_{CP} = 15.0 Hz, *CH*$_{Cp}$), 132.9 (d, J_{CP} = 14.4 Hz, *CH*$_{Cp}$), 148.4 (d, $^{1}J_{CP}$ = 14.4 Hz, *ipso-C*$_{Cp}$), 160.3 (d, $^{3}J_{CP}$ = 4.5 Hz, *CC*(CH$_3$)$_3$) ppm. **3d**: δ = 12.2 (d, $^{1}J_{CP}$ = 18.6 Hz, P*Me*$_2$), 12.4 (d, $^{1}J_{CP}$ = 18.7 Hz, P*Me*$_2$), 31.1 (s, C(*CH*$_3$)$_3$), 32.5 (s, *C*(CH$_3$)$_3$), 54.2 (d, $^{1}J_{CP}$ = 19.9 Hz, *ipso-C*$_{Cp}$), 124.3 (d, J_{CP} = 5.2 Hz, *CH*$_{Cp}$), 132.6 (d, J_{CP} = 3.6 Hz, *CH*$_{Cp}$), 135.0 (d, J_{CP} = 4.8 Hz, *CH*$_{Cp}$) ppm. (The resonance due to *CC*(CH$_3$)$_3$ of the isomer **3d** is overlapped by the resonance arising from *CC*(CH$_3$)$_3$ of the isomer **3a** (157.5 ppm), but could be identified by two dimensional NMR experiments.)

^{31}P-NMR (121.5 MHz, C_6D_6): **3a**: δ = -57.2 (46%) ppm. **3b**: δ = −57.5 (33%) ppm. **3c**: δ = −59.7 (13%) ppm. **3d**: δ = −41.9 (8%) ppm.

EI/MS (70 eV): m/z (%) = 182 (45) [M^+], 167 (100), 126 (16), 111 (18), 57 (23).HR-EI/MS (70 eV): Calc. for $C_{11}H_{19}P$: 182.1224. Found: 182.1224.

Anal. Calc. for $C_{11}H_{19}P$ (182.24): C, 72.50; H, 10.51. Found: C, 68.19; H, 9.85.

IR: 3054 (w), 2959 (s), 2900 (m), 1591 (w), 1426 (w), 1362 (m), 1260 (m), 1127 (m), 1064 (m), 1018 (m), 938 (m), 903 (s), 881 (s), 809 (s), 752 (w), 709 (m), 595 (m), 462 (w) cm^{-1}.

4.2. X-ray crystallographic studies

4.2.1. Crystallography

Crystal data were collected with a Stoe-IPDSIII area-detector diffractometer using graphite-monochromatised Mo-K_α-radiation ($\lambda = 71.073$ pm) at 100 K. Data reduction was carried out by using the IPDS software X-Area (Stoe) [57]. The data were empirically corrected for absorption and other effects by using multiscans [58]. The structures were solved by direct methods (Sir-97) [59] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97) [60]. The programs PLATON [61] and PLUTON [62] were used to check the results of the X-ray analysis. Diamond was used for the structure representation [63]. CCDC-760488 (**2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Storage of an oversaturated solution of **2a** in hexane at -30 °C yielded colourless single crystals of this substance.

4.2.2. Crystal data for *2a*

$C_{13}H_{25}N_2P$, $Mr = 240.32$, triclinic, $P\bar{1}$, a = 5.7450(4) Å, b = 9.3979 (7) Å, c = 13.0274(10) Å, $\alpha = 89.456(6)^\circ$, $\beta = 89.310(6)^\circ$, $\gamma = 88.029$ $(6)^\circ$, $V = 702.87(9)$ Å^3, $Z = 2$, ρ(calc.) = 1.136 g cm^{-3}, $\mu = 0.175$ mm^{-1}, $T = 100$ K. A total of 4923 reflections were collected, 2443 of which were independent. The refinement on all data converged at $R_1 = 5.09\%$, $wR_2 = 18.05\%$ and the goodness of fit was 1.147. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters except for the hydrogen atom H1 bonded to the Cp(ipso)-carbon atom, which was found in the final density map and refined with isotropic displacement parameters.

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Appendix. Supplementary data

CCDC-760488 (**2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.05.001.

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