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Phosphorus Activation

Selective Functionalization of P_4 by Metal-Mediated C−P Bond Formation**

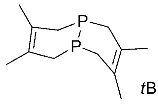
*Sebastian Heinl, Sabine Reisinger, Christoph Schwarzmaier, Michael Bodensteiner, and Manfred Scheer**

Dedicated to Professor Helmut Werner on the occasion of his 80th birthday

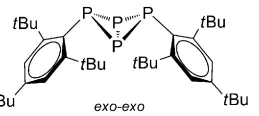
Abstract: *A new and selective one-step synthesis was developed for the first activation stage of white phosphorus by organic radicals. The reactions of NaCp^R with P_4 in the presence of CuX or $FeBr_3$ leads to the clean formation of organic substituted P_4 butterfly compounds $Cp^R{}_2P_4$ (Cp^R: Cp^{BIG} = $C_5(4\text{-}nBuC_6H_4)_5$ (**1a**), Cp′′′ = $C_5H_2tBu_3$ (**1b**), Cp* = C_5Me_5 (**1c**) und Cp^{4iPr} = C_5HiPr_4 (**1d**)). The reaction proceeds via the activation of P_4 by Cp^R radicals mediated by transition metals. The newly formed organic derivatives of P_4 have been comprehensively characterized by NMR spectroscopy and X-ray crystallography.*

Based on the search for atom-efficient processes and direct activation ways of the P_4 tetrahedron, the activation of white phosphorus with transition metals[1] and main-group elements[2] has become an active research area over the last decade. Especially a catalytic process for the direct C−P bond formation is a clear objective, but it is presently far from being achieved. To date only a few reactions are known in which carbon reagents react with P_4 selectively to yield organophosphorus compounds, among them a UV-light-promoted degradation to P_2-containing organophosphorus derivatives, such as **A**.[3]

Early results were achieved by the reaction of P_4 with organolithium or organomagnesium compounds to yield complex mixtures of organophosphanides.[2a,4] The reactions are not selective, and the degradation/reaggregation pathway of the P_n fragments is not well understood. Recently, Bertrand et al. showed the potential of stable carbenes for the activation of white phosphorus.[5] However, in these cases the P_4 tetrahedron is fragmented or re-aggregated. In means of a targeted, carbon-based activation of white phosphorus, it would be of interest to understand every step of its degradation. The first step is the cleavage of one P−P bond, yielding a butterfly-like tetraphosphabicyclo[1.1.0]butane unit.[2b] Only three examples of P_4 butterfly moieties with carbon substituents are known so far that are derived from white phosphorus. In the 1980s, Fluck et al. presented the synthesis of [Mes*$_2P_4$] (**B**) (Mes* = 2,4,6-tBu-(C_6H_2)) in 4% yield by the reaction of LiMes* with Mes*Br in the presence of P_4.[6] More recently Power et al. reported on the formation of [{Ar^{Dipp}}$_2P_4$] (**C**) (Ar^{Dipp} = C_6H_3-2,6-(C_6H_3-2,6-iPr$_2$)$_2$) in a two-step synthesis in moderate yields.[7] While the formation of **B** and **C** involves a nucleophilic attack at the P_4 tetrahedron, Cummins and Cossairt presented the formation of [Dmp$_2P_4$] (**D**) (Dmp = 2,6-Mes$_2C_6H_3$) by a radical reaction.[8] However, all of these reactions use substituted aromatic compounds with a sp^2-hybridized carbon atom as the reactive site.[9] Direct C−P bond formation reactions involving sp^3-hybridized carbon atoms and white phosphorus have not been reported to date.



A



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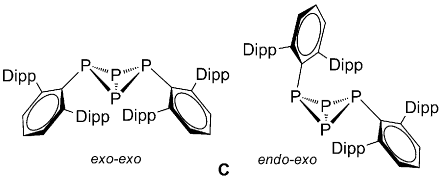

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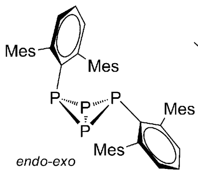

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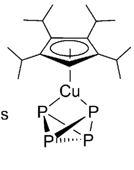

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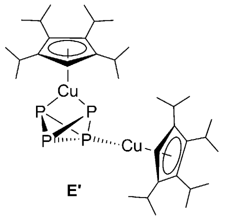

E'

Herein we report on the selective formation of Cp$^R{}_2P_4$ (Cp^R: Cp^{BIG} = $C_5(4\text{-}nBuC_6H_4)_5$ (**1a**), Cp′′′ = $C_5H_2tBu_3$ (**1b**), Cp* = C_5Me_5 (**1c**), Cp^{4iPr} = C_5HiPr_4 (**1d**)) using P_4 as the phosphorus source. The metal-mediated selective conversions leading to **1a**–**1d** feature radical reactions.

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[*] S. Heinl, S. Reisinger, Dr. C. Schwarzmaier, Dr. M. Bodensteiner, Prof. Dr. M. Scheer
Institute of Inorganic Chemistry, University of Regensburg
93040 Regensburg (Germany)
E-mail: Manfred.Scheer@chemie.uni-regensburg.de

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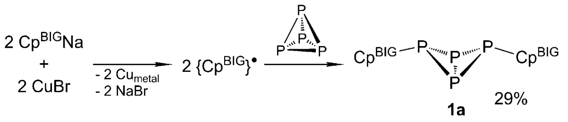
Supporting information for this article, including full synthetic, spectroscopic and crystallographic, details, is available on the WWW under http://dx.doi.org/10.1002/anie.201403295.

Initially, we were interested in the synthesis of copper complexes with unsubstituted P_n ligands, a class of compounds for which Scherer and Akbayeva reported the complex **E** and **E′** obtained by the reaction of $[Cp^{4iPr}Cu(CO)]$ with white phosphorus.[10] However, the products were only characterized by ^{31}P NMR spectroscopy. To enhance the stability of such complexes, we used the sterically more demanding Cp^{BIG} ligand. We tried to generate $[Cp^{BIG}Cu(CO)]$ in situ by adding a solution of $Cp^{BIG}Na$ in THF to a CuBr suspension in THF and subsequently discharging CO gas into the solution. However, already with the first drop of the $Cp^{BIG}Na$ solution, the mixture turns into dark blue and metallic Cu precipitates. The intense color indicates the initial formation of $\{Cp^{BIG}\}^{\bullet}$ radicals, which was confirmed by EPR spectroscopy. The characteristic color together with the obtained EPR data fit well with the known $\{C_5Ph_5\}^{\bullet}$ radical.[11] Upon discharging CO gas into the solution, the color does not change, a hint that the desired complex $[Cp^{BIG}Cu(CO)]$ is not formed. However, following the procedure for $[Cp^{4iPr}Cu(\eta^2\text{-}P_4)]$,[10] white phosphorus was added. After column chromatographic work-up, yellow cube-shaped crystals were obtained. The X-ray structure analysis did not show the desired copper complex $[Cp^{BIG}Cu(\eta^2\text{-}P_4)]$ but rather the metal-free compound **1a**, exhibiting two newly formed C−P bonds. To exclude $[Cp^{BIG}Cu(CO)]$ as potential intermediate, the reaction was repeated without the CO discharge step, again leading to **1a** as the only product. Thus, based on the EPR measurements, a radical mechanism including the formation of $\{Cp^{BIG}\}^{\bullet}$ radicals together with elemental copper can be suggested. These radicals react with P_4 to afford the butterfly compound **1a** in moderate isolated yields [Eq. (1)].



1a

(1)

In the $^{31}P\{^1H\}$ NMR spectrum of **1a**, two coupled triplets of an A_2M_2 spin system are observed at $\delta = -181.0$ ppm ("wing-tip") and $\delta = -308.2$ ppm (bridgehead; $^1J_{PP} = 192$ Hz), which is characteristic for a P_4 butterfly structural motif. The ^1H and $^{13}C\{^1H\}$ NMR spectra show several superimposed signals because of the nonequivalent 4-nBuC$_6$H$_4$ moieties of the Cp^{BIG} ligands in **1a**. The FD mass spectrometry exclusively reveals the molecular ion peak at $m/z = 1576.2$. As for **B**, but in contrast to **C**, the X-ray structure of **1a** (Figure 1) shows only the *exo-exo*-configuration of the organic substituents in the solid state. The P−P and P−C distances (2.1814(8)–2.2279(8) Å and 1.935(2)–1.954(2) Å, respectively) are in the range of similar P_4 butterfly compounds, such as **B** and **C**.[12]

To verify the possible generality, reaction (1) was repeated with other Cp^R salts, including CpNa, Cp*Na, Cp‴Na, and $Cp^{4iPr}Na$. However, no formation of $Cp^R{}_2P_4$ could be observed at all. A reason for this might be the lower $\{Cp^R\}^{\bullet}$ radical stability compared to the aryl-substituted $\{Cp^{BIG}\}^{\bullet}$ radical. For the latter, its high steric demand and the possible mesomeric stabilization lead to a less-reactive radical species and a hindered radical coupling, allowing the reaction with the P_4 molecule. In case of the smaller and more reactive $\{Cp^R\}^{\bullet}$ derivatives, the radical decomposition (for example, Cp^RH formation) seems to be faster than the reaction with white phosphorus, and therefore the formation of the desired P_4 butterfly molecules does not proceed.

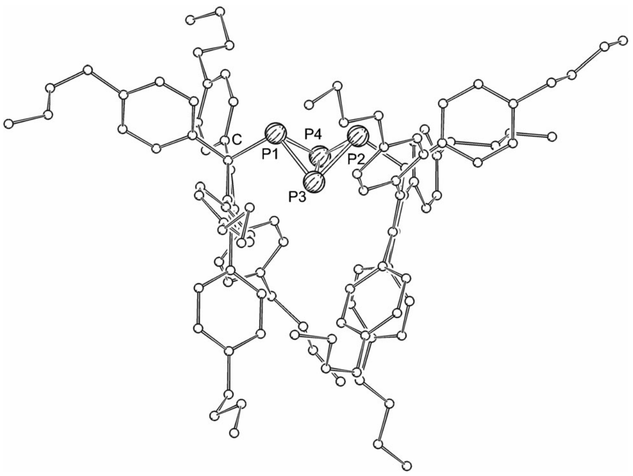
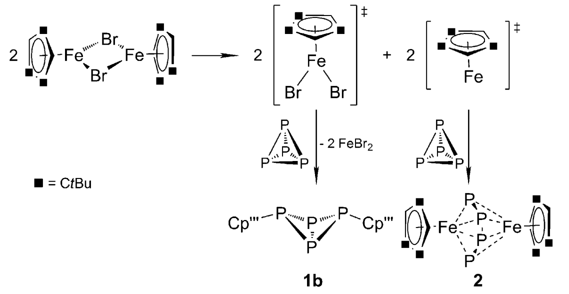


Figure 1. Molecular structure of **1a** in the crystal (molecule A; H atoms are omitted for clarity).

As the key step in the formation of **1a** is the oxidation of $\{Cp^{BIG}\}^-$ to $\{Cp^{BIG}\}^{\bullet}$ by Cu^+ (together with the formation of Cu). A possibility of avoiding the formation of short-lived stable $\{Cp^R\}^{\bullet}$ radicals would be the use of a more flexible redox system with a broader variety of oxidation states. Thus, we chose the system Fe^{II}/Fe^{III}, as Sitzmann et al. reported on the synthesis of a $\{Cp^{5iPr}\}^{\bullet}$ radical ($Cp^{5iPr} = C_5iPr_5$) from the reaction of the corresponding sodium salt and $FeCl_2$.[13] Thus, the dimeric iron(II) complex $[\{Cp^{5iPr}Fe(\mu\text{-}Cl)\}_2]$ might be a potential intermediate during this reaction. As the related derivatives $[\{Cp'''Fe(\mu\text{-}Br)\}_2]$ and $[\{Cp^{4iPr}Fe(\mu\text{-}Br)\}_2]$ are known[14] and coordinatively unsaturated, we proposed that they could be able to interact with P_4 molecules, allowing a direct C−P bond formation in the coordination sphere of the iron centers.

The reaction of $[\{Cp'''Fe(\mu\text{-}Br)\}_2]$ with one equivalent of P_4 in toluene at room temperature leads to the formation of $[\{Cp'''Fe\}_2(\mu,\eta^{4:4}\text{-}P_4)]$[15] (**2**) as well as the carbon-substituted butterfly compound **1b** (Scheme 1) together with a brownish precipitate of $FeBr_2$. The $^{31}P\{^1H\}$ NMR spectrum of the



Scheme 1. Proposed reaction pathway for the formation of **1b** and **2** from $[\{Cp'''Fe(\mu\text{-}Br)\}_2]$ and P_4.

reaction mixture shows a total conversion of P_4 into the two products in a 1:1 ratio. However, after chromatographic workup, **1b** is obtained as pure material only in 14% yield. The $^{31}P\{^1H\}$ NMR spectra of **1b** show some coupled sets of signals. This can be explained by the presence of four different constitutional isomers (Figure 2). By $^{31}P\{^1H\}$–$^{31}P\{^1H\}$ COSY NMR spectroscopy, all signals could be assigned to the four isomers **1b-A**, **1b-B**, **1b-C**, and **1b-D**, showing a ratio of circa. 4:1:7:7.[12]

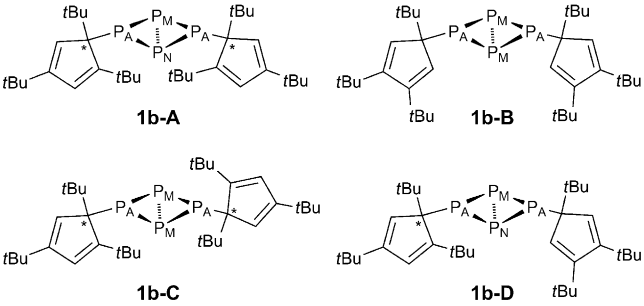
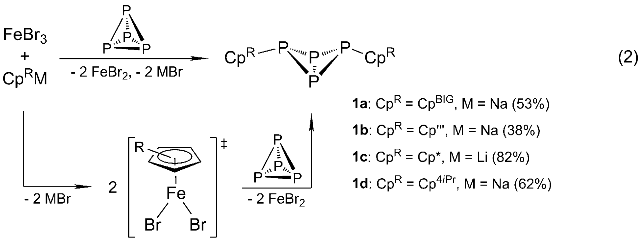


Figure 2. Isomers of **1b** monitored by $^{31}P\{^1H\}$ NMR spectroscopy. P atoms are assigned to the corresponding spin system. Isomers **1b-A** and **1b-C** are diasteriomeric, and **1b-A** represents the *meso* compound.

The respective chemical shifts and coupling constants clearly indicate the formation of butterfly compounds in which the "wing-tip" P atoms of the bicyclic P_4 framework are only bound to tertiary P atoms. This gives a hint on the underlying reaction mechanism involving Cp''' moieties. For the $\{\mathrm{Cp}'''\}^{\bullet}$ radical, several mesomers are possible in which the single electron is either located on a tertiary or on a secondary carbon atom of the ring. As the stability of tertiary radicals is higher than that of secondary radicals, their formation is favored, leading to the formation of the observed isomers. In contrast, an ionic mechanism requires the formation of an aromatic cyclopentadienyl anion with a delocalized 6π-electron system. Thus, the tertiary carbon atoms are no longer preferred reaction sites and the formation of C–P bonds to secondary carbon atoms should be observed to a certain extent. As that is not observed experimentally, a mechanism with radicals is most likely.

The 1:1 ratio of the two products **1b** and **2** in combination with the formation of a brownish precipitate of $FeBr_2$ gives further indication for the reaction pathway (Scheme 1). In solution, a disproportionation of $[\{\mathrm{Cp}'''\mathrm{Fe}(\mu\text{-Br})\}_2]$ into the two complex fragments $\{\mathrm{Cp}'''\mathrm{Fe}^{\mathrm{I}}\}$ and $\{\mathrm{Cp}'''\mathrm{Fe}^{\mathrm{III}}\mathrm{Br}_2\}$ is most likely. Two of the $\{\mathrm{Cp}'''\mathrm{Fe}^{\mathrm{I}}\}$ fragments react with one equivalent of P_4 to form compound **2** with a cisoid P_4^{2-} ligand. The remaining two 16VE $\{\mathrm{Cp}'''\mathrm{Fe}^{\mathrm{III}}\mathrm{Br}_2\}$ complex fragments are able to interact with white phosphorus. The coordination of a P_4 molecule to iron enables a transfer of a radical $\{\mathrm{Cp}'''\}^{\bullet}$ onto the P_4 tetrahedron to give **1b**. As a consequence, the reduced $\mathrm{Fe}^{\mathrm{III}}$ species precipitates as brownish $FeBr_2$ from the reaction mixture.

To verify whether $[\mathrm{Cp}'''\mathrm{FeBr}_2]$ is the key intermediate on the way to **1b**, we studied the reaction of $[\mathrm{Cp}'''\mathrm{FeBr}_2]$ generated in situ (from $\mathrm{Cp}'''\mathrm{Na}$ and $FeBr_3$) with white phosphorus [Eq. (2)]. In fact, the Cp'''-substituted compound **1b** is obtained with an identical isomer distribution as observed before. Moreover, the intrinsic loss of 50% of the material by the formation of **2** is also avoided. Furthermore, workup by column chromatography is not necessary for purification and the yields of isolated product are therefore significantly increased.



(2)

By applying this procedure to other Cp^R ligands [Eq. (2); $Cp^R = Cp$, Cp^{BIG}, Cp^*, Cp^{4iPr}], it was also possible to synthesize the compounds $Cp^{BIG}{}_2P_4$ (**1a**), $Cp^*{}_2P_4$ (**1c**), and $Cp^{4iPr}{}_2P_4$ (**1d**) in good yields. Unfortunately, the parent compound Cp_2P_4 was still not accessible. The reason for this might be the minimized stabilizing effects of the small Cp ring for the reaction intermediates as well as for the potential product.

However, this metal-mediated mechanism seems to be different to the above-mentioned formation of $Cp^{BIG}{}_2P_4$ (**1a**) by the "copper route", in which a free and stable radical has to be formed to successfully attack P_4. This explains why this method succeeded for Cp^{BIG} but not for Cp^*, Cp''', or Cp^{4iPr}. The related complex fragment $[\mathrm{Cp}^R\mathrm{Fe}^{\mathrm{III}}\mathrm{Br}_2]$ might provide enough stability to transfer $\{Cp^R\}^{\bullet}$ radicals to P_4, which were indeed detected by EPR spectroscopy.[12] The fact that the "copper route" is only suitable for Cp^{BIG} for the reaction with P_4 but with iron halides also other Cp^R moieties can be transferred is an indication that in the latter case a metal-mediated process takes place. However, the radical formation proceeds via a metal for the "copper route" as well, but the stability of the radical is much higher in the case of Cp^{BIG}.[16] The presented new iron-mediated method allows the fast and clean conversion of white phosphorus into the carbon-substituted butterfly compounds in only one step in good yields.

As already observed for **1a**, compounds **1b–d** show two characteristic groups of signals in the $^{31}P\{^1H\}$ NMR spectrum at $\delta \approx -134$–-163 ppm ("wing-tip") and $\delta \approx -307$–-367 ppm (bridgehead). In case of the pentasubstituted Cp^* moiety and its isomers with high molecular symmetry (for example, **1b-B** and **1b-C**), two triplets of an AM_2 spin system with $^1J_{PP}$ coupling constants of 173–193 Hz are observed.[12] However, if Cp^R is tri- or tetra-substituted ($Cp^R = \mathrm{Cp}'''$, Cp^{4iPr}), isomers with low molecular symmetry (Cp^R ligands are non-equivalent; see Figure 2) are also formed, leading to more complicated $^{31}P\{^1H\}$ NMR spectra with A_2MN or ABMN spin systems with signal groups in a 1:1 ratio.[12] In the case of **1d**, even though several isomers are possible, only two of them are observed in the $^{31}P\{^1H\}$ NMR spectrum with an A_2M_2 and A_2MN spin system, respectively. The reason could be a random superimposition of signals of different isomers, or the steric hindrance might lead exclusively to the formation of selected isomers.

The molecular structures of **1b–d** were examined by single-crystal X-ray structure analysis (Figure 3). The P–P bond lengths vary in the range of 2.178(6) and 2.244(7) Å, and the C–P bond lengths from 1.884(4) to 1.911(8) Å. The structural parameters compare well with those of known R_2P_4 butterfly compounds.[12] All of the four derivatives **1a–d** show a *exo-exo* configuration. Interestingly and in contrast to **1a**, **1b**, and **1d**, in **1c**, the two Cp* substituents are pointing upwards, which might be explained by packing effects.

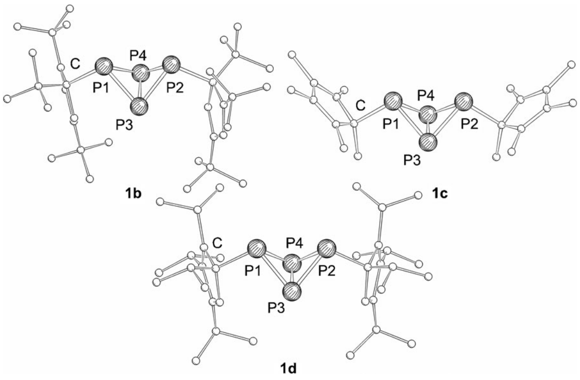


Figure 3. Molecular structures of **1b** (left), **1c** (right), and **1d** (bottom) in the crystal. H atoms are omitted for clarity.

The chemical shifts and coupling constants of the two isomers of **1d** are nearly identical to those published by Scherer and Akbayeva for the proposed copper complexes $[\mathrm{Cp}^{4i\mathrm{Pr}}\mathrm{Cu}(\eta^2\text{-}\mathrm{P}_4)]$ **E** and $[\{\mathrm{Cp}^{4i\mathrm{Pr}}\mathrm{Cu}\}_2(\mu,\eta^{2:1}\text{-}\mathrm{P}_4)]$ **E′**.[10] Furthermore, in the FD mass spectrum of the corresponding crude reaction mixture (2), only the molecular ion peak of **1d** (45%) was detected along with some phosphorus-free $\mathrm{Cp}^{4i\mathrm{Pr}}$Fe complex fragments. As our preparation of **1d** was performed without using copper, we assume that the NMR data in Ref. [10] were misinterpreted, and that they obtained $\mathrm{Cp}^{4i\mathrm{Pr}}{}_2\mathrm{P}_4$ (**1d**) accidentally and unfortunately did not recognize their discovery. The crystal structure of **1d** supports this fact considerably. Thus, the quest for copper complexes of the type $[\mathrm{LCu}(\eta^2\text{-}\mathrm{P}_4)]$ is still open.

In conclusion, we have shown that stable $\{\mathrm{Cp}^{\mathrm{BIG}}\}^{\bullet}$ radicals are suitable to selectively activate one P–P bond of the P_4 tetrahedron to form the bicyclic butterfly compound **1a**. Further attempts to transfer the procedure to other Cp^{R} derivatives, such as Cp′′′, Cp*, or $\mathrm{Cp}^{4i\mathrm{Pr}}$, failed. Therefore, a new synthesis was developed that uses the generation of $\{\mathrm{Cp}^{\mathrm{R}}\}^{\bullet}$ radicals in the coordination sphere of $\mathrm{Fe}^{\mathrm{III}}$ complexes. This unique metal-mediated transfer of carbon-centered radicals to the P_4 tetrahedron allows a simple and selective synthesis of novel $\mathrm{Cp}^{\mathrm{R}}{}_2\mathrm{P}_4$ compounds (**1a–d**). These unprecedented butterfly molecules exhibit a bond between sp^3 hybridized carbon atoms and phosphorus, which could not be realized before by using white phosphorus as a P source in other systems.[9] As the synthesis works with different Cp^{R} derivatives, independently from their steric demand, it provides a general access to this fascinating class of compounds and reveals the first step of the P_4 activation process. Future studies will focus on the carbon-based fragmentation of the P_4 tetrahedron, which might open the way to catalytic phosphorus activation.

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[1] a) B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* **2010**, *110*, 4164–4177; b) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.* **2010**, *110*, 4178–4235.

[2] a) M. Scheer, G. Balázs, A. Seitz, *Chem. Rev.* **2010**, *110*, 4236–4256; b) N. A. Giffin, J. D. Masuda, *Coord. Chem. Rev.* **2011**, *255*, 1342–1359; c) S. Khan, S. S. Sen, H. W. Roesky, *Chem. Commun.* **2012**, *48*, 2169–2179.

[3] D. Tofan, C. C. Cummins, *Angew. Chem.* **2010**, *122*, 7678–7680; *Angew. Chem. Int. Ed.* **2010**, *49*, 7516–7518.

[4] M. M. Rauhut, A. M. Semsel, *J. Org. Chem.* **1963**, *28*, 471–473.

[5] a) O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2009**, *121*, 5638–5641; *Angew. Chem. Int. Ed.* **2009**, *48*, 5530–5533; b) J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2007**, *119*, 7182–7185; *Angew. Chem. Int. Ed.* **2007**, *46*, 7052–7055; c) J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2007**, *129*, 14180–14181; d) C. L. Dorsey, B. M. Squires, T. W. Hudnall, *Angew. Chem.* **2013**, *125*, 4558–4561; *Angew. Chem. Int. Ed.* **2013**, *52*, 4462–4465; e) C. D. Martin, C. M. Weinstein, C. E. Moore, A. L. Rheingold, G. Bertrand, *Chem. Commun.* **2013**, *49*, 4486–4488.

[6] E. Fluck, R. Riedel, H. D. Hausen, G. Heckmann, *Z. Anorg. Allg. Chem.* **1987**, *551*, 85–94.

[7] A. R. Fox, R. J. Wright, E. Rivard, P. P. Power, *Angew. Chem.* **2005**, *117*, 7907–7911; *Angew. Chem. Int. Ed.* **2005**, *44*, 7729–7733.

[8] B. M. Cossairt, C. C. Cummins, *New J. Chem.* **2010**, *34*, 1533–1536.

[9] If CyBr is used, Cy_3P and Cy_4P_2 are obtained as products of a complete P_4 degradation.

[10] D. N. Akbayeva, O. J. Scherer, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1429–1430.

[11] For spectra of $\{\mathrm{Cp}^{\mathrm{R}}\}^{\bullet}$, see the Supporting Information; a) K. Ziegler, B. Schnell, *Justus Liebigs Ann. Chem.* **1925**, *445*, 266–282; b) W. Broser, P. Siegle, H. Kurreck, *Chem. Ber.* **1968**, *101*, 69–83; c) C. Janiak, R. Weimann, F. Görlitz, *Organometallics* **1997**, *16*, 4933–4936.

[12] See the Supporting Information for the details of the NMR and EPR spectroscopy and the X-ray structural analysis, including the comparisons of NMR parameters and atom distances (**1a–d**, **A**, **B**, and **C**).

[13] H. Sitzmann, R. Boese, *Angew. Chem.* **1991**, *103*, 1027–1029; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 971–973.

[14] a) H. Sitzmann, T. Dezember, W. Kaim, F. Baumann, D. Stalke, J. Kärcher, E. Dormann, H. Winter, C. Wachter, M. Kelemen, *Angew. Chem.* **1996**, *108*, 3013–3016; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2872–2875; b) M. Wallasch, G. Wolmershäuser, H. Sitzmann, *Angew. Chem.* **2005**, *117*, 2653–2655; *Angew. Chem. Int. Ed.* **2005**, *44*, 2597–2599.

[15] O. J. Scherer, T. Hilt, G. Wolmershäuser, *Organometallics* **1998**, *17*, 4110–4112.

[16] There are some remote relations to ATRP protocols, cf.: K. Matyjaszewski, *Macromolecules* **2012**, *45*, 4015–4039.