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Decomposition mechanism of a cobalt-coordinated phosphite–olefin ligand under irradiation

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ABSTRACT

We herein report on the different coordination behavior of phosphite–olefin ligands containing either a terminal olefin moiety or a related compound containing an internal olefin moiety to a CpCo(I)-center. While the former coordinates to the metal center via P atom and olefin moiety upon irradiation, photolysis of the latter led to the subsequent formation of the phosphorus-free [CpCo(η^4-1,3-butadiene)] complex (**6**). A mechanistic rational of the decomposition reaction based on an Arbuzov-like rearrangement is suggested.

Introduction

Over the past decades intensive studies on CpCo(I)-complexes (Cp: η^5-cyclopentadienyl) as catalysts for [2 + 2 + 2] cycloaddition reactions have been reported [1]. While their catalytic performances under thermal as well as photochemical conditions have been studied extensively, the degradation or reactivity towards cluster formation of only several olefin-ligated CpCo(I)-complexes has been investigated and various respective cluster complexes have been characterized [2]. The reaction of with alkynes can lead to mononuclear [CpCo(η4-diene)]-complexes, affording highly stable cyclobutadiene complexes, which can however be subject to oxidative degradation with sterically hindered cyclobutadienes [3]. A number of oligonuclear CpCo-cluster complexes has been investigated by Wadepohl et al. [4]. They demonstrated that the reaction of [CpCo(η^2-C_2H_4)$_2$] or in situ generated low-valent complexes starting from cobaltocene/K with various cycloalkenes resulted in the formation of trinuclear CpCo-hydrido cluster complexes. As a result of the dehydrogenation reaction of the cyclic olefin, the corresponding cycloalkyne is coordinated by three CpCo-fragments. The formation of a tetrameric cluster from [CpCo($H_2C{=}CHSiMe_3$)$_2$], affording a butterfly-type coordination of the derived trimethylsilylacetylene has been described by our group [2e]. There are only two further reports on this kind of degradation, resulting in tetrameric CpCo-clusters [5].

Reactions of CpCo(I)-sources with phosphine and phosphite ligands leading to oligonuclear Co-complexes have been described occasionally. One example is the report of the reactivity of [CpCo(CO)$_2$] (**1**) with free phosphines yielding phosphorus-bridged clusters as described by Lal De and Maiti [6]. An interesting example for the decomposition of a phosphorus compound is delivered by the reaction of *tert*-butylphosphaethyne with [ω-(di-*tert*-butyl)phosphanyl (ethylcyclopentadienyl)cobalt]-complexes, where the C≡P bond was split completely and a trinuclear μ_3-carbyne-μ_3-phosphidotricobalt cluster formed [7].

Therefore, the decomposition of phosphorus ligands poses a serious problem in catalysis [8]. Depending on the ligands of the transition metal complexes various routes of decomposition can be envisioned [9]. Since our group recently focussed on the synthesis of CpCo(I)-bisphosphite as well as CpCo(I)-phosphite–olefin complexes, the decomposition of coordinated phosphite ligands was especially interesting. While phosphites are more stable towards oxidation compared to phosphines, a number of different other reaction pathways is possible including hydrolysis, alcoholysis, *trans*-esterification, O–C and P–O bond cleavage as well as the Arbuzov rearrangement. There are few reports on CpCo(I)- [10] as well as CpRh(I)-complexes [9] with phosphite ligands undergoing an Arbuzov rearrangement leading to phosphite decomposition and an alkylated metal center (Scheme 1).

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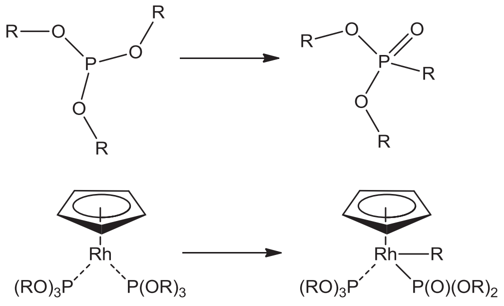


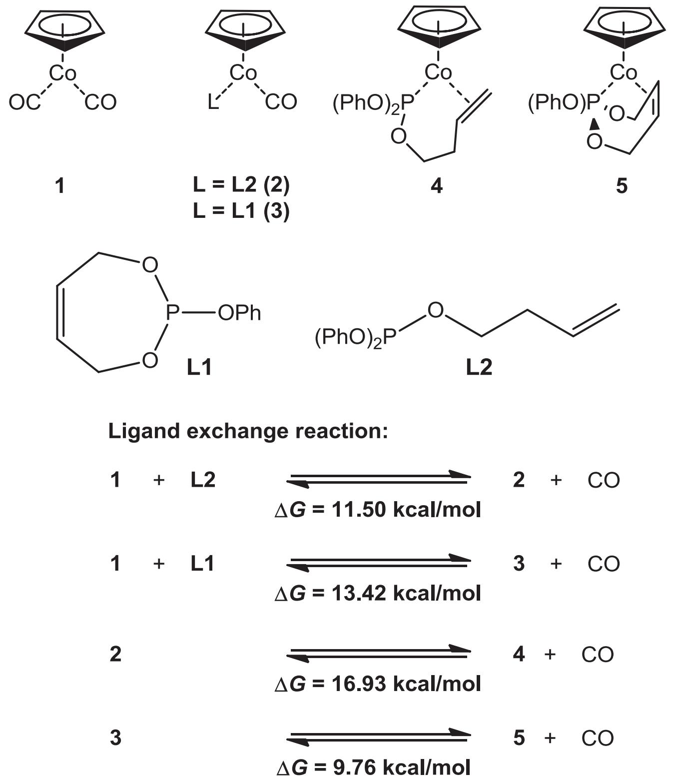
Scheme 1. Documented Arbuzov rearrangements in the coordination sphere of a transition metal.

In general aliphatic phosphites are found to be more prone to the Arbuzov rearrangement than arylphosphites. To the best of our knowledge these rearrangement reactions have exclusively been reported for conventional trialkylphosphites and there has not been any account of decomposition of a coordinated phosphorus-olefin ligand. We herein report on the degradation of a cobalt-bound phosphite–olefin ligand under irradiation with light, resulting in the phosphorus-free and purely olefin-ligated [CpCo(η^4-1,3-butadiene)] (**6**) complex.

Results and discussion

We recently described the synthesis of the first CpCo(I)-complex with a chelating phosphite–olefin ligand [11]. Interestingly in this specific case no stabilizing effect due to the chelatisation effect was observed. To investigate the influence of the ligands into more detail the application of a different chelating phosphite–olefin ligand seemed to be promising. We chose to compare the cyclic phosphite **L1** and the linear phosphite **L2** (Scheme 2). DFT calculations suggested – after carrying out BP86 density functional theory computations to examine the thermal stability – that the coordination of **L1** and **L2** via the phosphite group leading to the formation of both **4** as well as **5** were endothermic but possible under reaction conditions. Starting from [CpCo(CO)$_2$] (**1**) as well as the cyclic phosphite **L1** and linear phosphite **L2**, the formation of the corresponding complexes [CpCo(CO)(**L2**)] (**2**) and [CpCo(CO)(**L1**)] (**3**) have been computed to be endergonic by 13.42 and 11.50 kcal/mol, respectively, indicating that the formation of complexes **2** and **3** is thermodynamically not favorable.

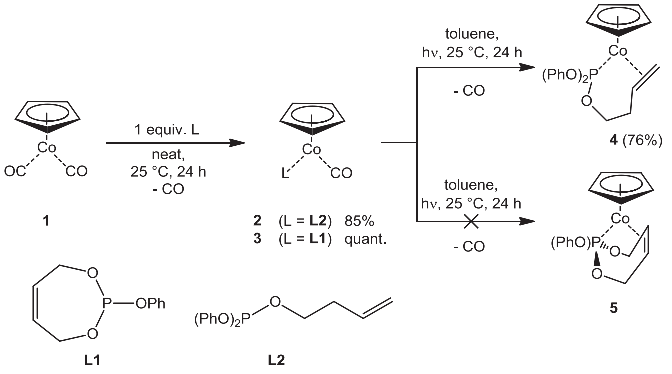
Since the formed CO gas molecule can be removed from the reaction mixture to the gas-phase, the chemical potential of the possible equilibrium of the system is changed and the reaction shifted to favor the formation of complexes **2** and **3**. This has indeed been observed since the synthesis of **2** and **3** respectively proceeded smoothly at room temperature. Thus, starting from [CpCo(CO)$_2$] (**1**) the first carbonyl ligand could easily be replaced by a phosphite at room temperature and the respective complexes with one CO ligand were prepared in very good yields (Scheme 3). Crystals of **3** suitable for X-ray analysis were obtained from a *n*-pentane solution at 4 °C. As shown in Fig. 1 the phosphite–olefin ligand is only coordinated via the phosphorus atom and one CO ligand is still attached to the cobalt center.



Scheme 2. Calculations on the formation of the new complexes **2**–**5** from **1**–**3** at BP86/TZVP.

Starting from complexes **2** and **3** we further computed the possible intramolecular substitution reaction of the CO ligand with the olefin unit within **L2** and **L1**. As expected, these substitution reactions with the formation of complexes **4** and **5** are also thermodynamically not favorable and endergonic by 16.93 and 9.76 kcal/mol, respectively. Since the same equilibrium shift due to the release of the second CO ligand applies, we were hopeful for the reaction to yield the chelating complexes **4** and **5** anyway. However, the irradiation with light and the release of the second CO ligand only led to a successful chelation in the case of ligand **L2** and the generation of **4**. Irradiation of **3** led to no chelating compound **5** despite the fact that the formation of complex **5** is less endergonic than that of complex **4**.

If **3** was irradiated with light at 25 °C or even at temperatures as low as −20 °C a black solid precipitated and no ^{31}P NMR signal could be detected in the red solution. Filtration of the solution over neutral aluminum oxide and removal of the solvent afforded a red, highly volatile solid in 41% yield. NMR and MS analysis provided evidence for the formation of [CpCo(η^4-1,3-butadiene)] (**6**). Pruett and Myers already described **6** as a volatile red solid prepared from **1** and excess 1,3-butadiene at elevated temperatures [12], but only Bergman et al. published a full characterization of **6**, the NMR data being in accordance with our findings [13].



Scheme 3. Synthesis of chelating CpCo(I)-phosphite–olefin complexes.

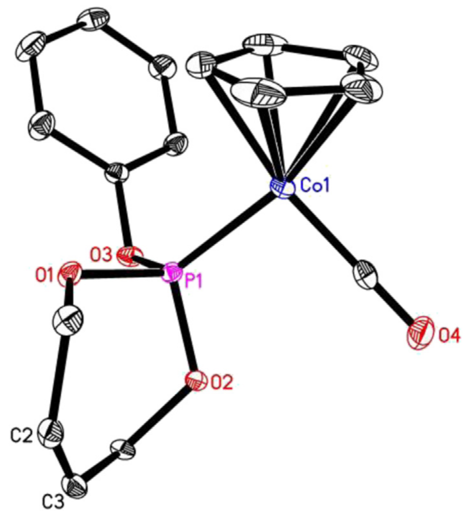


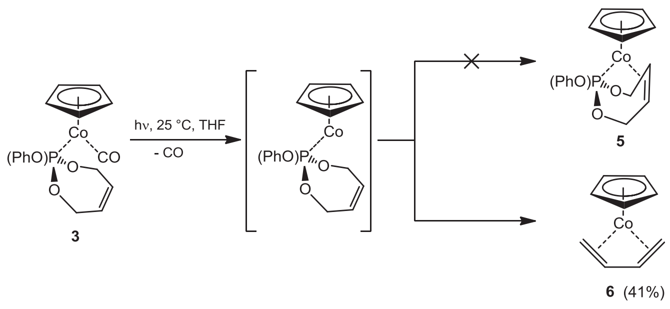
Fig. 1. ORTEP drawing of the molecular structure of **3**. Ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity.

Vollhardt et al. reported on **6** in their investigation of the isomerization reaction of late transition metal-1,3-butadiene-derived complexes [14,15].

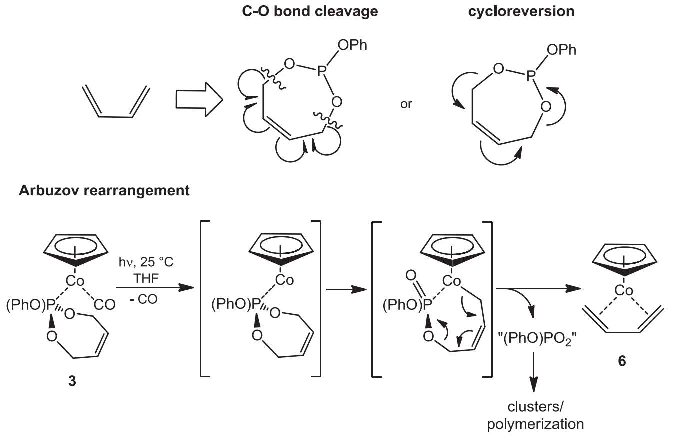
The degradation mechanism of **3** is not yet fully understood (Scheme 4). It seems that the cleavage of the C—O bond is preferred over the P—O bond although both bond energies are very similar (C—O: 85.5 kcal/mol; P—O: 80 kcal/mol) [16]. A similar observation has been made by McDonald et al. [17], who reported on the same effect of a CO_2-laser on phosphite compounds describing the decomposition of various alkyl phosphites when subjected to this CO_2 laser for 20 s. Alcohols, which are the decomposition products from normal, thermal pyrolysis, were never found therefore hinting at a C—O bond cleavage leaving the P—O bond intact.

A number of degradation pathways for **L1** in **3** is conceivable, involving for example homolytic C—O bond cleavage or a formal cycloreversion (Scheme 5).

However, we believe that an Arbuzov-like rearrangement with a subsequent second rearrangement causes the formation of 1,3-butadiene and complex **6** respectively (Scheme 5). Arbuzov rearrangements of coordinated phosphite ligands have been reported for a number of different metal complex fragments such as CpRh [9,18], CpNi [19], CpRu [20], CpFe [10], but also CpCo [10]. In our case we postulate the formation of the phosphenate "$(PhO)PO_2$" as a side product. In contrast to the reported photo-Arbuzov rearrangement of uncoordinated cyclic phosphites [21], we never observed any decomposition or rearrangement of **L1** if **L1** was irradiated with light on its own or as a ligand of the respective bisphosphite complex $[CpCo(\mathbf{L1})_2]$. For this Arbuzov-like rearrangement to take place it seems to be essential to have a vacant coordination site at the cobalt center.



Scheme 4. Photolysis of **3** and the formation of **6**.



Scheme 5. Postulated possible degradation pathway.

Our computations show that the degradation of complex **3**, following an intramolecular isomerization reaction with the formation of an alkyl complex, which — in this case — subsequently dissociates into the corresponding butadiene complex **6** and phosphenate "$(PhO)PO_2$" as a side product, is endergonic by 8.68 kcal/mol, and therefore, thermodynamically not favorable. Since phosphenates like $(PhO)PO_2$ have been reported to be highly instable and generally short lived species [22] and favor the formation of larger molecules by oligomerization [23], we have computed the trimerization by the formation of a six-membered ring structure. This trimerization reaction is highly exergonic by 51.87 kcal/mol (17.29 kcal/mol per $(PhO)PO_2$). Owing to the formation of the phosphenate clusters to be the driving force of the reaction, this leaves the overall reaction to be exergonic by 8.61 kcal/mol. These energetic data reasonably explain the observed formation of complex **6** instead of **5** and support our proposed degradation mechanism involving an Arbuzov rearrangement as the essential step.

Conclusions

We reported on the light-induced photolysis of a CpCo(I)-coordinated cyclic phosphite—olefin ligand leading to the complex $[CpCo(\eta^4\text{-butadiene})]$ (**6**) in moderate yield but high purity and proposed an Arbuzov-like rearrangement leading to a C—O bond cleavage and the removal of all traces of phosphorus from the solution by the formation of easily polymerized phosphenates. This observation contrasts the coordination behavior on irradiation of a structurally related phosphite—olefin ligand containing an open-chain, terminal olefin moiety, which leads to the coordination of the olefin by replacing another neutral ligand.

Experimental section

Compound **2** and **4** [11] as well as the phosphite—olefin ligand **L2** [24] were synthesized according to published procedures. For the photochemistry two halogen lamps (460 W each, $\lambda_{max} = 363$, 406, 419, 436, 548, 588, 591 nm) have been used for irradiation of the thermostated Schlenk-type reaction vessel.

Synthesis of ***L1***

L1 was synthesized after a modified procedure from Ingenuin et al. [25] Sodium (138 mg, 5 mmol) was washed with *n*-hexane (3×) before 3-buten-1-ol (3.3 mL, 38 mmol) was added and gas evolution was observed. Then triphenylphosphite (10 mL, 58 mmol) was added to the solution which turned red–brown and a solid precipitated. This suspension was heated at 100 °C for 2 h before the mixture was allowed to cool to room temperature. The red–brown oil was removed from the white precipitate via syringe and the last residues of phenol were removed by bulb-to-bulb distillation (100 °C, 0.5 mbar). After 6 h at this temperature no more phenol was recovered and the desired phosphite–olefin could be distilled at 180 °C and 0.5 mbar. ^{1}H NMR (C_6D_6) $\delta = 2.37$ (m, 2H), 3.93 (q, $J = 6.8$ Hz, 1H), 4.13 (q, $J = 6.8$ Hz, 1H), 4.98–5.10 (m, 2H), 5.67–5.83 (m, 1H), 6.96–7.11 (m, 6H), 7.17–7.29 (m, 4H) ppm; ^{31}P NMR (C_6D_6) $\delta = 129.2$ (s) ppm; ^{13}C NMR (C_6D_6) $\delta = 35.2$ (s), 61.6 (s), 115.3 (s), 117.3 (s), 120.2 (s), 120.4 (s), 120.8 (s), 123.8 (s), 124.3 (s), 129.6 (s), 129.7 (s), 134.3 (s) ppm.

Synthesis of ***3***

Compound **1** (0.14 mL, 1 mmol) and the ligand **L1** (0.19 mL, 1 mmol) are stirred at room temperature for 24 h. The solution is filtered over a small amount of neutral Al_2O_3 (Brockman Type I), which is washed with THF (10 mL). After removal of the solvent the deep red liquid is dried under vacuum. A solution in pentane at 4 °C affords the desired compound as a red solid. (Yield: 306 mg, 85%) ^{1}H NMR (C_6D_6) $\delta = 4.35$ (m, CH_2, 1H), 4.40 (m, CH_2, 1H), 4.46 (m, CH_2, 1H), 4.51 (m, CH_2, 1H), 4.57 (s, Cp, 5H), 5.19 (t, $J = 2.0$ Hz, CH, 2H), 6.90 (m, Ph, 1H), 7.07 (t, $J = 7.9$ Hz, Ph, 2H), 7.22 (m, Ph, 2H) ppm; ^{31}P NMR (C_6D_6) $\delta = 177.68$ (bs) ppm; ^{13}C NMR (C_6D_6) $\delta = 62.5$ (d, $J = 5.1$ Hz), 82.6 (d, $J = 2.0$ Hz), 122.3 (d, $J = 5.4$ Hz), 124.4 (d, $J = 2.0$ Hz), 128.6 (s), 129.6 (s), 152.7 (s) ppm. CI (isobutane) *m*/*z* 362 [M^+], 334 [$M - (CO)^+$]; EA calc.: C, 53.06%; H, 4.45%; found: C, 52.91%; H, 4.45%.

Synthesis of ***6***

Compound **3** (177 mg, 0.49 mmol) is dissolved in THF (6 mL) and irradiated at 25 °C for 6 h. A short filtration over neutral aluminum oxide with THF results in a red solution, which is carefully reduced under vacuum at lower temperatures (the resulting red solid is volatile). (Yield: 36 mg, 41%) ^{1}H NMR (C_6D_6) $\delta = -0.31$ (ddt, $J = 8.2$, 1.6 Hz, 0.7 Hz, 2H), 1.75 (dd, $J = 7.6$, 1.5 Hz, 2H), 4.59 (s, 5H), 4.92 (m, 2H) ppm; ^{13}C NMR (C_6D_6) $\delta = 31.3$ (s), 78.5 (s), 79.7 (s) ppm. CI (isobutane) *m*/*z* 178.

Computational details

All geometries were fully optimized at the BP86 [26] level of density functional theory in combination with the SVP basis set [27] for H, C, N, O, Si and P as well as the LANL2DZ basis set [28] for Co. The optimized structures were characterized at the same level as energy minimums by frequency calculations. Furthermore, single-point energy calculations at the BP86 level with the TZVP basis set [29] for H, C, N, O, Si and P as well as LANL2DZ basis set for Co. The thermal corrections to enthalpy and Gibbs free energy at 298 K from the frequency analysis are added to the total electronic energy. Therefore we have used the corrected Gibbs free energy (ΔG) at 298 K for our discussion and comparisons. All calculations have been done with Gaussian 09 program [30].

Acknowledgments

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Appendix A. Supplementary material

CCDC 988726 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.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.04.013.

References

[1] (a) K.P.C. Vollhardt, Angew. Chem. Int. Ed. Engl. 23 (1984) 539–556;
(b) J.A. Varela, C. Saá, Chem. Rev. 103 (2003) 3787–3802;
(c) P.R. Chopade, J. Louie, Adv. Synth. Catal. 348 (2006) 2307–2327;
(d) C.J. Scheuermann, B.D. Ward, New J. Chem. 32 (2008) 1850–1880;
(e) N. Weding, M. Hapke, Chem. Soc. Rev. 40 (2011) 4525–4538;
(f) V. Gandon, in: K. Tanaka (Ed.), Transition-Metal-mediated Aromatic Ring Construction, John Wiley & Sons, Inc., 2013, pp. 1–35.
[2] (a) H. Wadepohl, T. Borchert, K. Büchner, H. Pritzkow, Chem. Ber. 126 (1993) 1615–1618;
(b) H. Wadepohl, Angew. Chem. Int. Ed. Engl. 31 (1992) 247–262;
(c) H. Wadepohl, H. Pritzkow, Polyhedron 8 (1989) 1939–1941;
(d) H. Wadepohl, T. Borchert, K. Buechner, M. Herrmann, F.-J. Paffen, H. Pritzkow, Organometallics 14 (1995) 3817–3826;
(e) N. Weding, A. Spannenberg, R. Jackstell, M. Hapke, Organometallics 31 (2012) 5660–5663;
(f) E.N. Jacobsen, R.G. Bergman, J. Am. Chem. Soc. 107 (1985) 2023–2032;
(g) A. Goswami, C.-J. Maier, H. Pritzkow, W. Siebert, J. Organomet. Chem. 690 (2005) 3251–3259.
[3] (a) C. Schaefer, R. Gleiter, F. Rominger, Dalton Trans. (2004) 4146–4151;
(b) C. Schaefer, R. Gleiter, F. Rominger, Organometallics 23 (2004) 2225–2227.
[4] (a) H. Wadepohl, T. Borchert, H. Pritzkow, J. Chem. Commun. Chem. Soc. (1995) 1447–1448;
(b) H. Wadepohl, T. Borchert, H. Pritzkow, Chem. Ber. 130 (1997) 593–603;
(c) H. Wadepohl, A. Metz, in: Metal Clusters in Chemistry, Wiley-VCH Verlag, 2008, pp. 269–289.
[5] (a) C.E. Barnes, W.D. King, J.A. Orvis, J. Am. Chem. Soc. 117 (1995) 1855–1856;
(b) F. Jiang, T.P. Fehlner, A.L. Rheingold, J. Am. Chem. Soc. 109 (1987) 1860–1861.
[6] R. Lal De, K. Maiti, Indian J. Chem. 40A (2001) 1097–1100.
[7] J. Foerstner, F. Olbrich, H. Butenschön, Angew. Chem. Int. Ed. Engl. 35 (1996) 1234–1237.
[8] Example: A. Christiansen, D. Selent, A. Spannenberg, M. Köckerling, H. Reinke, W. Baumann, H. Jiao, R. Franke, A. Börner Chem. Eur. J. 17 (2011) 2120–2129.
[9] P.W.N.M. van Leeuwen, Appl. Catal. A Gen. 212 (2001) 61–81.
[10] T.B. Brill, S.J. Landon, Chem. Rev. 84 (1984) 577–585.
[11] I. Thiel, A. Spannenberg, M. Hapke, ChemCatChem 5 (2013) 2865–2868.
[12] R.L. Pruett, W.R. Myers, US Patent 3 159 659, to Union Carbide Corporation, USA, 1964.
[13] W.H. Hersh, F.J. Hollander, R.G. Bergman, J. Am. Chem. Soc. 105 (1983) 5834–5846.
[14] B. Eaton, J.A. King, K.P.C. Vollhardt, J. Am. Chem. Soc. 108 (1986) 1359–1360.
[15] Theoretical study: K.K. Baldridge, J.M. O'Connor, M.-C. Chen, J.S. Siegel J. Phys. Chem. A 103 (1999) 10126–10131.
[16] T.L. Cottrell, The Strengths of Chemical Bonds, second ed., Butterworths Scientific Publications, London, 1958.
[17] J.K. McDonald, J.A. Merritt, A.E. Stanley, US Patent 4 529 489, to United States Dept. of the Navy, USA, 1985.
[18] (a) H. Neukomm, H. Werner, J. Organomet. Chem. 108 (1976) C26–C28;
(b) H. Werner, R. Feser, Z. Anorg. Allg. Chem. 458 (1979) 301–308.
[19] J. Clemens, H. Neukomm, H. Werner, Helv. Chim. Acta 57 (1974) 2000–2010.
[20] H.L. Ji, J.H. Nelson, A. De Cian, J. Fischer, Organometallics 11 (1992) 1618–1626.
[21] M.S. Landis, N.J. Turro, W. Bhanthumnavin, W.G. Bentrude, J. Organomet. Chem. 646 (2002) 239–246.
[22] D.E.C. Corbridge, in: Phosphorous: Chemistry, Biochemistry and Technology, sixth ed., CRC Press, Taylor & Francis Group, 2013, pp. 1296–1298.
[23] F. Cramer, H. Hettler, Chem. Ber. 91 (1958) 1181–1188.

[24] (a) R.A. Kadyrov, I.K. Shakirov, R.P. Arshinova, S.G. Gnevashev, R.R. Shagidullin, B.A. Arbuzov, Rus. Chem. Bull. 38 (1989) 964–971;
(b) B.A. Arbuzov, A.V. Aganov, V.V. Klochkov, Izv. Akad. Nauk. SSSR Ser. Khim. 5 (1982) 1195;
(c) S.G.A. Van Assema, A.W. Ehlers, F.J.J. de Kanter, M. Schakel, A.L. Spek, M. Lutz, K. Lammertsma, Chem. Eur. J. 12 (2006) 4333–4340;
(d) I. Morita, K. Kunimoto, M. Tsuda, S.-I. Tada, M. Kise, K. Kimura, Chem. Pharm. Bull. 35 (1987) 4144–4154.

[25] H. Ingenuin, P.C. William, F.C. Lanoue, US Patent 2 834 798, to SHEA CHEMICAL CORP, Columbia, 1958.

[26] J.P. Perdew, Phys. Rev. B 33 (1986) 8822–8824.

[27] A. Schaefer, H. Horn, R. Ahlrichs, J. Chem. Phys. 97 (1992) 2571–2577.

[28] (a) P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299–310;
(b) T.H.J. Dunning, P.J. Hay, Modern Theoretical Chemistry, third ed., 1976. New York;
(c) S. Huzinaga, J. Anzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, H. Tatewaki, Gaussian Basis Sets for Molecular Calculations, Elsevier, Amsterdam, 1984.

[29] A. Schaefer, C. Huber, R. Ahlrichs, J. Chem. Phys. 100 (1994) 5829–5835.

[30] G.W.T.M.J. Frisch, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian, Inc., Wallingford CT, 2010.