Journal of Organometallic Chemistry 696 (2011) 871–878

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Chemoselectivity control in the reaction of a dinuclear chloro-bridged cyclopalladated complex with potassium diphenylphosphide

Valeria A. Stepanova [a], Valery V. Dunina [b], Irina P. Smoliakova [a,*]

[a] Chemistry Department, University of North Dakota, 151 Cornell St., Stop 9024, Grand Forks, ND 58202-9024, USA
[b] Chemistry Department, M. V. Lomonosov Moscow State University, 1 Leninskie Gory, Moscow 119991, Russian Federation

ARTICLE INFO

Article history:
Received 20 July 2010
Received in revised form
3 September 2010
Accepted 7 October 2010
Available online 14 October 2010

Keywords:
Cyclopalladated complexes
$KPPh_2$
Aminophosphines
Palladium(II) phosphido complexes

ABSTRACT

Reactions of $KPPh_2$ with the dimeric cyclopalladated complex $\{Pd(N\cap C)(\mu\text{-}Cl)\}_2$ **1** derived from *N,N*-dimethylbenzylamine were studied using different reagent ratios, temperature, reaction time, concentrations and solvents. Complex **3**, the μ-Cl-μ-PPh_2 analog of **1**, was obtained in 76% yield in the one-hour reaction using the 1:1 ratio of dimer **1** and $KPPh_2$ in THF at rt. *ortho*-(Diphenylphosphino)benzylamine **4** was synthesized in 58% yield by reacting complex **1** with 4.5 equiv. of $KPPh_2$ in THF at rt. A possible mechanism of the aminophosphine formation is proposed on the basis of the experimental data including $^{31}P\{^1H\}$ NMR spectra of reaction mixtures.

1. Introduction

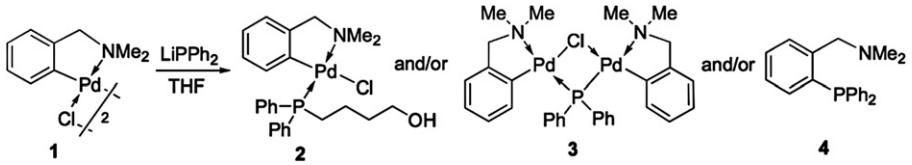
One of the most promising applications of cyclopalladated complexes (CPCs) is ligand transformation using reactions of the Pd–C bond [1,2]. The most studied reagents in these reactions are alkynes, allenes, alkenes, and carbon monoxide, although isocyanides, acyl halides, halogens and a few other types of compounds have been used as well [1,2]. Our group has been interested in reactions of CPCs with alkali metal phosphides because of possible transformations of cyclopalladated complexes into aminophosphines, diphosphines and related compounds containing a PR_2 group and another functionality. Previously, brief studies by Sokolov et al. [3,4], Bolm et al. [5] and Dunina et al. [6] revealed that PPh_3 adducts of *C,N*-cyclopalladated complexes react with $LiPPh_2$ or $KPPh_2$ to yield either the corresponding aminophosphines or their Pd(0) complexes. Recently, we reported a detailed investigation of the $LiPPh_2$ reactions with the dinuclear chloro-bridged CPC **1** and showed that three products are formed in these transformations: (1) the corresponding mononuclear derivative **2** with $Ph_2P(CH_2)_4OH$ as an auxiliary ligand, (2) complex **3**, which is the μ-Cl-μ-PPh_2 analog of dimer **1**, and (3) *ortho*-(diphenylphosphino)benzylamine **4** (Scheme 1) [7].

Compounds **2**–**4** were formed selectively by varying the structure of the $LiPPh_2$ reagent, which was affected by (i) the preparation method, (ii) the presence of byproducts, such as LiCl and PhLi, (iii) solvent polarity, (iv) concentration and (v) age of the phosphide reagent. Transformations of complex **1** upon the action of the $LiPPh_2$ reagents were also sensitive to the addition order and reaction time. In spite of preparing aminophosphine **4** in excellent yields, the reactions were difficult to control because even minor changes provided different results. It is noteworthy that the use of three $LiPPh_2$ solutions in THF purchased from Sigma–Aldrich Co. provided varied and often irreproducible data.

One can expect that, due to different coordination properties of lithium and potassium cations, replacing the former for the latter in the phosphide reagent should significantly decrease the problem of controlling the reagent's structure and, therefore, its reactivity [8]. Monomeric, dimeric, trimeric and polymeric structures have been reported for $LiPR_2$ reagents in solid state and solution [9–16]; however, $KPPh_2$ in solution is most likely to have a monomeric form, though other structures cannot be completely ruled out. While organolithium reagents, in general, can readily form mixed aggregates, related species are less feasible for $KPPh_2$. Coordination of $KPPh_2$ to THF and other ethereal solvents is expected to be significantly weaker [17–19]; therefore, in common solvents including THF and toluene, this reagent is likely to have the same structure. By replacing lithium for potassium, possible catalysis by LiCl, reported for some reactions with organolithium reagents, would be impossible [20]. In addition, due to the high sensitivity of the $LiPPh_2$ reactions with CPCs to minor changes, we were unable

* Corresponding author. Tel.: +1 701 777 3942; fax: +1 701 777 2331.
E-mail address: ismoliakova@chem.und.edu (I.P. Smoliakova).

0022-328X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2010.10.020



Scheme 1.

to obtain reproducible data while monitoring the transformations using ^{31}P NMR spectroscopy. With the goal of investigating the possibility and practical convenience of using $KPPh_2$ in reactions with dinuclear chloro-bridged CPCs, we undertook the study of the reactions of this reagent with complex **1**, and herein we report our findings.

2. Results and discussion

2.1. The $KPPh_2$ reagent

In this study, two 0.5 M solutions of $KPPh_2$ in THF were used: one purchased from Sigma–Aldrich Co. and the other prepared in our lab from K metal and $ClPPh_2$ using a known procedure [21]. The $^{31}P\{^1H\}$ NMR spectra of both reagents in d_8-THF were identical and exhibited a broadened peak at δ −20.5 ppm. The structure of the $KPPh_2$ reagents remained unchanged over a period of a year as determined by the identical broadness and chemical shift of the ^{31}P signal. In reactions with CPC **1**, the purchased and synthesized $KPPh_2$ solutions provided essentially the same results (*vide infra*) and were used interchangeably.

2.2. Factors affecting reactions of complex **1** with $KPPh_2$

First, reactions of the dimeric CPC **1** with $KPPh_2$ were studied using different ratios of the reagents (for details, see Supplementary Material). The standard conditions included the use of THF as a solvent, addition of $KPPh_2$ to the CPC solution, a complex concentration of 10 mg/mL (C_o) and stirring for 18 h at rt. The reaction with the 1:1 ratio of dimer **1** and $KPPh_2$ (the 2:1 ratio of Pd:PPh_2) resulted in for formation of the μ-Cl-μ-PPh_2 complex **3**, with no traces of aminophosphine **4**. An increase in the reagent ratio to 1:2 led to the same product, although in a reduced yield. The further increase in the reagent ratio resulted in a change of chemoselectivity and formation of aminophosphine **4** with no traces of complex **3**. The highest yield of 58% was obtained using the 1:4.5 ratio. It is noteworthy that in the reactions furnishing compound **4**, tetraphenyldiphosphine monoxide was isolated as well. Its formation is a result of oxidation of Ph_2PPPh_2, a byproduct of aminophosphine **4** (see below).

The effects of reaction time and temperature were also evaluated (for details, see Supplementary Material). The best yield of complex **3**, 76%, was obtained after stirring the 1:1 reaction mixture for 1 h at rt. The highest yield of aminophosphine **4** was obtained at rt after 18 h, while at −43 °C this compound was isolated in less than 5% yield.

2.3. Reactions of complex **3** with $KPPh_2$

To determine whether complex **3** is an intermediate of the aminophosphine synthesis, reactions of the former with 3.5 equiv. of $KPPh_2$ were performed at rt for 18 h in THF and toluene. The reaction in THF yielded 25% of the aminophosphine, while in toluene 52% of the desired compound was isolated along with 22% of the unreacted complex **3**. In the latter reaction, traces of THF were present because $KPPh_2$ was impossible to dissolve in toluene. For comparison, in our previous study, it was determined that the reaction of complex **3** with $LiPPh_2$ in THF leads to the aminophosphine; the same reaction in toluene provided a complex mixture of unidentified products [7]. These results suggest that the μ-PR_2-μ-Cl complexes can be intermediates in the formation of aminophosphines from the corresponding μ-Cl dimeric CPCs and metal phosphides in a coordinating solvent.

2.4. $^{31}P\{^1H\}$ NMR spectra

To shed more light on a possible mechanism of the described transformations, reactions of CPC **1** with $KPPh_2$ were monitored using $^{31}P\{^1H\}$ NMR spectroscopy. Particularly, two reaction mixtures containing the 1:4.5 ratio of CPC **1** and $KPPh_2$ in d_8-THF were monitored: one sample at −42 °C over 5 h (Fig. 1) and the other during a slow warm-up from −40 °C to rt. In the first experiment, the spectra of the reaction mixture taken after mixing the reagents and in 5 h were very similar and contained signals of aminophosphine **4** (δ −26.0 ppm) and Ph_2PPPh_2 (δ −26.4 ppm). In addition, there were three more significant signals: a broadened singlet at δ −50.6 ppm (**B**) and two doublets at δ −12.8 and −13.5 ppm with J_{PP} = 80 Hz (**C**, Fig. 1). No signal of complex **3** (δ 30.2 ppm) was detected in the spectra of this reaction mixture. Relative intensities of the major signals, **C**: aminophosphine **4**: Ph_2PPPh_2: **B**, in the spectra taken ca. 30 min after mixing the reagents and in 5 h were similar: 1.00:0.73:0.20:1.36 and 1.00:0.77:0.20:1.14, respectively. These data suggest that at −42 °C, the composition of the 1:4.5 reaction mixture was practically the same after 30 min and 5 h after mixing the reagents.

In the second experiment (see Supplementary Material for the spectra), the initial spectrum resembled the ones obtained at −42 °C. When the sample was warmed up to −20 °C, two new doublets showed up at δ −16.4 and −16.0 ppm and J_{PP} = 80 Hz. When the temperature reached −10 °C, the intensity of signal **B** at δ −50.6 ppm decreased, and later, at 0 °C, it disappeared. Signal **B** must belong to an intermediate of this reaction containing either one P atom or two of them with a very small coupling constant. Two doublets at δ −13.4 and −12.8 ppm appeared first and the other two doublets at δ −16.4 and −16.0 ppm showed up later; therefore, these signals belong to two different compounds, with two P atoms in each structure. The J value of the two sets of two doublets suggests that two P atoms are likely to be separated by two bonds and cis to each other. The two sets of two doublets disappeared after warming the reaction mixture to rt. Therefore, the signals are most likely to belong to intermediates, not impurities or byproducts. It is also notable that no signal of complex **3** (δ 30.2 ppm) was detected in the spectra of the reaction mixture. The signals of Ph_2PPPh_2 (ca. −25.7 ppm) and aminophosphine **4** (ca. −25.5 ppm) were observed in the spectrum taken at −20 °C. However, the Ph_2PPPh_2 signal was gradually vanishing during the warm-up: its signal was overlapped with the singlet of aminophosphine **3** in the spectrum taken at 0 °C and became invisible at 20 °C [22]. Two low-intensity singlets at ca. 131 and 14 ppm in the spectrum recorded at −20 °C became more prominent at 0 and 20 °C. We suggest that these singlets may belong to the $(Ph_2P)_2Pd(II)$ species formed as a result of oxidative addition of Ph_2PPPh_2 to Pd(0) (see below).

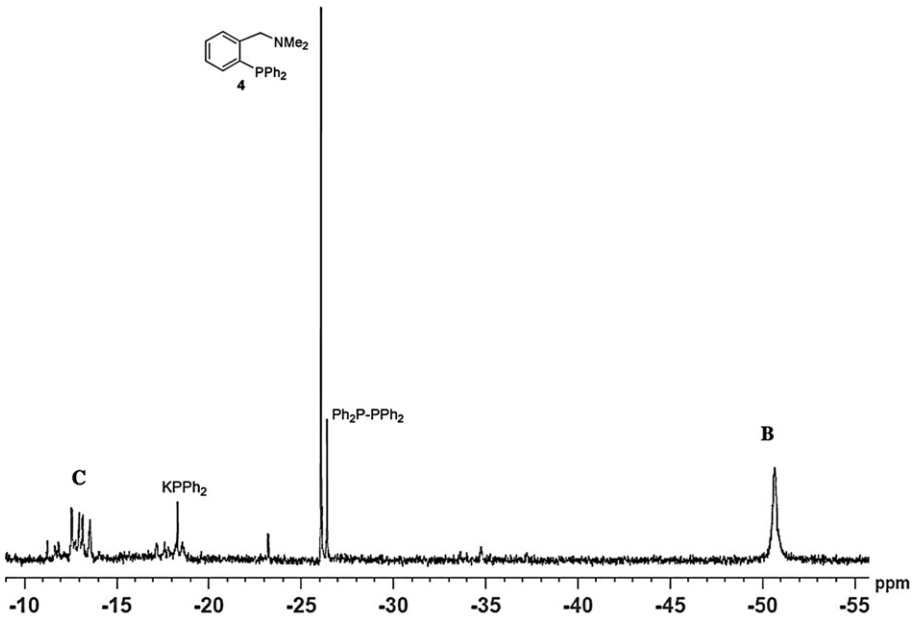


Fig. 1. The $^{31}P\{^{1}H\}$ NMR spectrum of the 1:4.5 (dimer 1: $KPPh_2$) reaction mixture in d_8-THF at −42 °C taken in ca. 30 min after mixing the reagents.

The $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture with the 1:1 ratio of dimer **1** and $KPPh_2$, taken at rt in ca. 30 min after mixing the reagents, contained an intense singlet at δ 30 ppm assigned to complex **3**, another significant singlet at δ −78 ppm, two peculiar doublets with the coupling constant, *J*, of 41.5 Hz at δ 107 and 6 ppm and several low-intensity singlets (Fig. 2).

Previously, we suggested [7] that reactions of dimeric μ-Cl CPCs with $LiPPh_2$ leading to aminophosphines take place through the formation of either intermediate **A** (in toluene without traces of coordinating THF) or **D** (in THF; see structures of **A** and **D** in Scheme 2). Formation of intermediate **D** would require 2 equiv. of $KPPh_2$ per one dimeric complex **1** (a 1:1 ratio of Pd:PPh_2), while 4 equiv. of the phosphide are necessary to obtain intermediate **D** (a 1:2 ratio of Pd:PPh_2). In an attempt to observe intermediate **A**, the ^{31}P NMR spectrum of the 1:2 (dimer **1**:$KPPh_2$) reaction mixture was taken (Fig. 3a). The spectrum contained a number of signals, including the one at δ 30 ppm assigned to complex **3**. The most intense signals were singlets at δ 85 and −82 ppm. Other notable signals were two doublets with $J = 40$ Hz at δ 5 and 100 ppm. No signal of aminophosphine **4** was detected in this experiment. Another spectrum of the same 1:2 reaction mixture was taken in 3 h and showed no notable changes. When excess $KPPh_2$ (more than 2 equiv.) was added to the same reaction mixture (overall more than 4 equiv. of the phosphide per 1 equiv. of dimer **1**), the spectrum changed significantly (Fig. 3b). The singlet of aminophosphine **4** at δ −29 ppm appeared and became the most prominent signal. Also, the singlets at 85 and −82 ppm and two

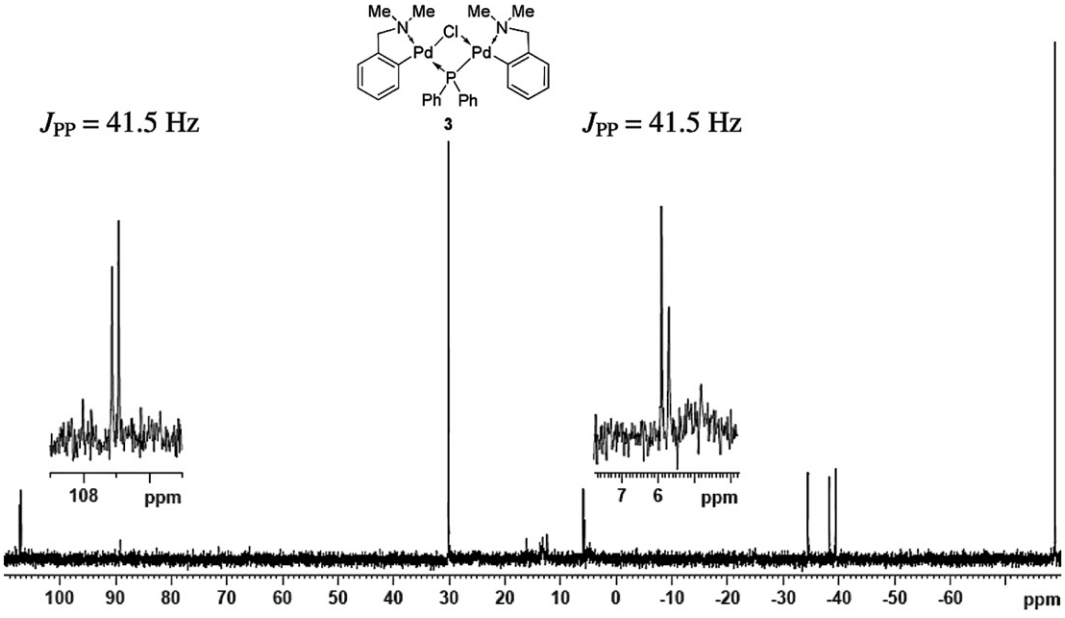
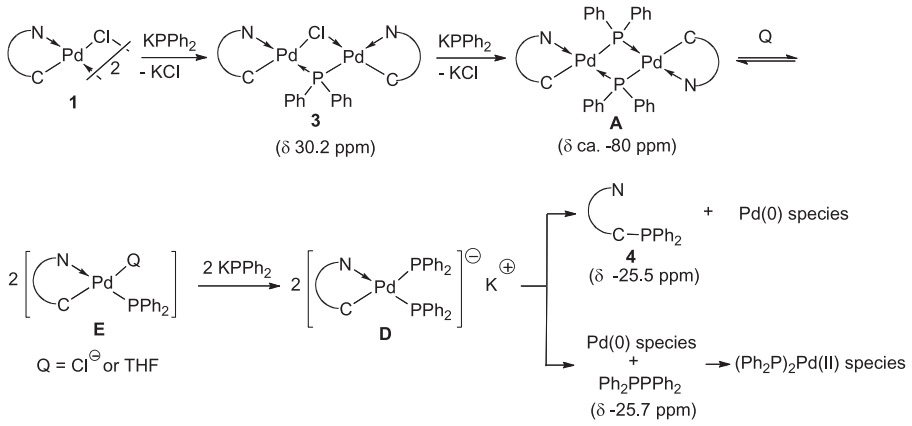


Fig. 2. The $^{31}P\{^{1}H\}$ NMR spectrum of a 1:1 reaction mixture (dimer 1:$KPPh_2$) in d_8-THF at rt taken in ca. 30 min after mixing the reagents.



Scheme 2.

doublets at 5 and 100 ppm disappeared. In addition, two sets of two low-intensity doublets, around δ 12–20 ppm showed up (Fig. 3b). Either one of the sets or both of them were also observed in the spectra of the 1:4.5 mixtures (see Fig. 1 and Supplementary Material).

2.5. Possible mechanism of the aminophosphine formation

On the basis of the NMR data and the results of the experiments described above, we suggest a mechanism for the formation of aminophosphine **4**, which is depicted in Scheme 2. We propose that the reaction between CPC **1** and $KPPh_2$ begins with the formation of μ-Cl-μ-PPh_2 complex **3**. Reaction of this complex with a second equiv. of $KPPh_2$ furnishes the di-μ-phosphido intermediate **A**. Related Pd(II) and Pt(II) complexes with two bridging diphenylphosphido groups are known and the ^{31}P NMR data for representative compounds of this kind (**I**–**IV**) are presented in Chart 1 [23–26]. Among a variety of reported diphosphido-bridged complexes, only one of them, $\{LPt(\mu\text{-}PPh_2)\}_2$, contains a cyclometallated ligand (HL = benzo[*h*]quinoline) [27]. According to the X-ray analysis, this complex has the anti geometry in the solid state. Unfortunately, no other data are known for this compound because it is insoluble in common solvents [27]. Intermediate **A** may have either anti or syn geometry; the former complex is expected to be more thermodynamically favorable considering a significant difference in ligands' trans influence for both isomers [28]. The anti isomer is expected to give an upper-field singlet in the ^{31}P NMR

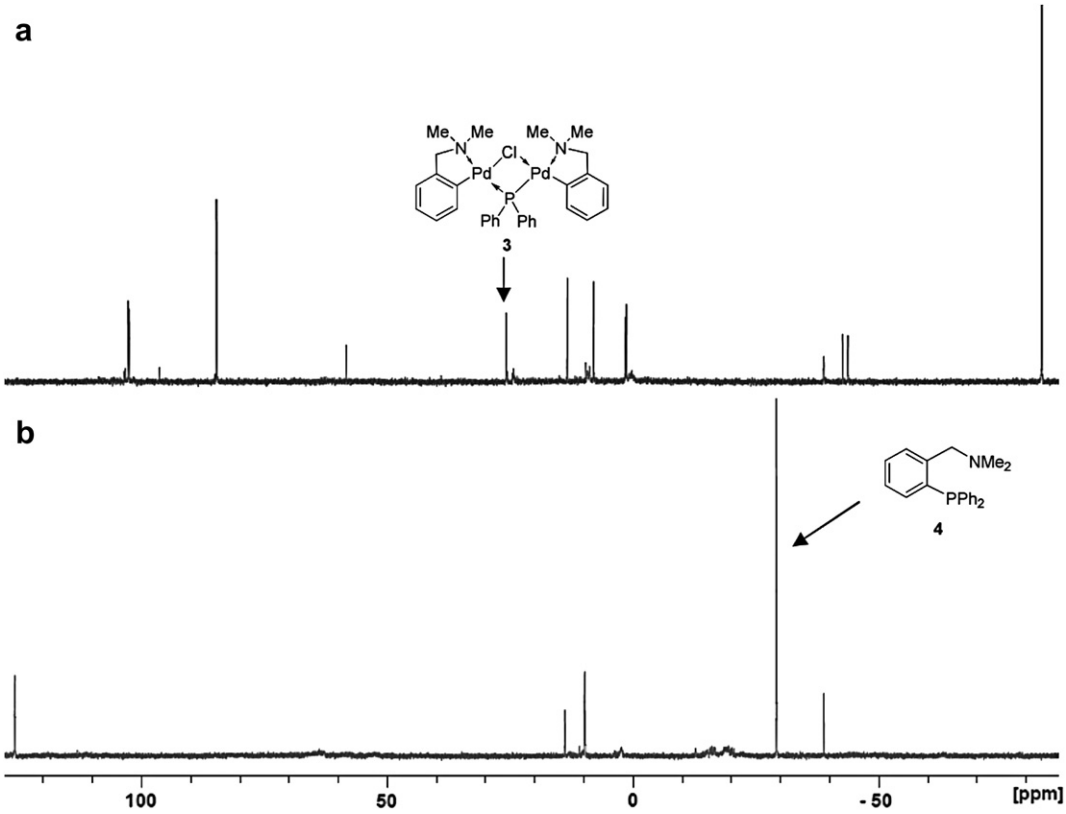
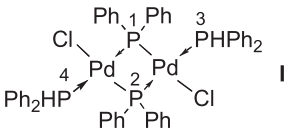
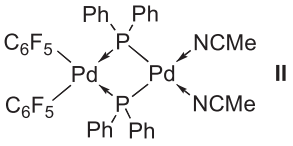


Fig. 3. a) The $^{31}P\{^1H\}$ NMR spectrum of the 1:2 reaction mixture of dimer 1 and $KPPh_2$ in d_8-THF in 30 min after mixing at rt; and b) the spectrum after addition of excess $KPPh_2$ to the same 1:2 mixture at rt.



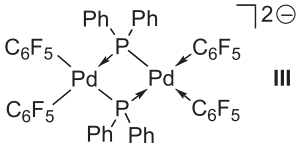
I

$PHPh_2$: –2.8 (m);
μ-PPh_2: -132.7 (m); $^2J_{1,2} = 262$, $^2J_{2,3} = 423.8$, $^2J_{1,3} = 26.0$, $^4J_{3,4} = -3$ ($CDCl_3$) [23,24]



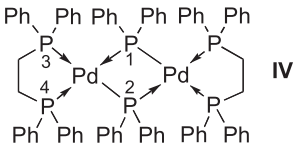
II

μ-PPh_2: –106.0 [$(CD_3)_2CO$] [25]



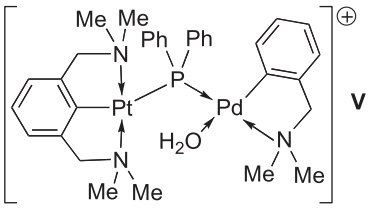
III

μ-PPh_2: –105.6 [$(CD_3)_2CO$] [26]



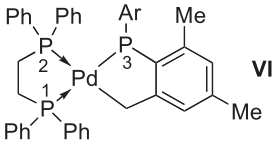
IV

μ-PPh_2: –321.4; P(3,4): –92.4; $^2J_{1,2} = 349.4$, $^2J_{1,3} = 28.2$, $^2J_{2,3} = 311.0$ (CH_2Cl_2) [24]



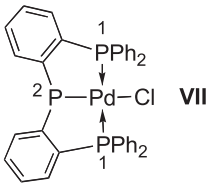
V

μ-PPh_2: 42.6 [$(CD_3)_2CO$] [29]



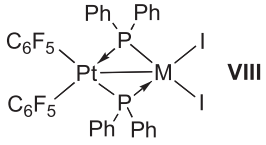
VI

P(1): 36.4; P(2): 34.4; P(3): 24.7; $^2J_{1,2} = 21$; $^2J_{1,3} = 124$; $^2J_{2,3} = 8$ (d_8-PhMe) [30]



VII

P(1): 62.2 (d);
P(2): 123.18 (t); $^2J = 24$ (C_6D_6) [31]



VIII

M = Pt, μ-PPh_2: 280.5
M = Pd, μ-PPh_2: 321.5 (CD_2Cl_2) [25]

Chart 1. Known representative Pd complexes containing the PPh_2 group and their ^{31}P NMR spectroscopy data [23–26,29–31]. (Coupling constants, *J*, are given in Hz; chemical shift values, δ, are reported in ppm relative to 85% H_3PO_4).

spectrum (cf. Chart 1), while the syn dimer, if formed at all, is to give two doublets with significantly different chemical shift values. We suggest that the singlet at δ –82 ppm in the spectrum of the 1:2 mixture (Fig. 3a, *cf.* the singlet at δ –78 ppm in Fig. 2) may belong to the anti isomer of intermediate **A**. The chemical shift of this intermediate is close to those reported for the μ-PPh_2 group in a number of Pd(II) and Pt(II) diphosphido-bridged complexes, such as **I**–**IV** (Chart 1) [23–26].

The ^{31}P NMR signal of compound **A** (δ ca. –80 ppm) was prominent in the spectra of both 1:1 and 1:2 reaction mixtures at rt (dimer **1**:$KPPh_2$; Figs. 2 and 3a) [32]. However, the signal of **A** disappeared upon addition of excess $KPPh_2$ in THF at rt (Fig. 3b). It is reasonable to suggest that when a 1:4.5 ratio of dimer **1** and $KPPh_2$ is used in THF, intermediate $\{(N\cap C)Pd(\kappa^1\text{-}PPh_2)_2\}K$ (**D**) is formed. For comparison, a number of Pt(II) and Pd(II) complexes with a terminal PR_2 ligand have been reported or proposed as reaction intermediates [29,33–38]. Complexes $\{(C_6F_5)_2M(\kappa^1\text{-}PPh_2)_2\}^{2-}$ (M = Pt or Pd) were obtained in situ by reacting *cis*-$\{(C_6F_5)_2M(PHPh_2)_2\}$ with 2 equiv. of *n*-BuLi in THF, although no spectral data were reported for the compounds [26]. Previously, we reported that 2 equiv. of $LiPPh_2$ was necessary in the reaction of dimer **1** in order to obtain aminophosphine **4** in PhMe, while the same reaction in the coordinating solvent THF took place with 4.5 equiv. of $LiPPh_2$. Transformation of the neutral intermediate **A**, $\{(N\cap C)Pd(\mu\text{-}PPh_2)\}_2$, into the anionic intermediate **D**, $\{(N\cap C)Pd(\kappa^1\text{-}PPh_2)_2\}^-$, in THF containing byproduct KCl is likely to occur through the mononuclear complex **E**, $\{(N\cap C)Pd(\kappa^1\text{-}PPh_2)Q\}$, where Q is Cl^- or THF. Due to the absence of the literature data for closely related complexes, it is impossible to reliably assign the proposed intermediates **D** and **E** to particular signals in the ^{31}P NMR spectra of the 1:4.5 reaction mixture of dimer **1** and $KPPh_2$ in THF (Fig. 1). For example, reported chemical shifts for Pd(II) complexes with a terminal PAr_2 group vary (Chart 1, structures **VI** and **XII**) [30,31]; in addition, structures of these complexes are significantly different from the proposed intermediates **D** and **E**. Nevertheless, the peculiar singlet at δ –50.7 ppm (signal **B** in Fig. 2) may belong to intermediate **E.** During the ^{31}P NMR monitoring of the 1:4.5 reaction mixture at –42 to rt in d_8-THF, this signal appeared in the very first scan and was the most intense at the lower temperature, which suggests high reactivity of the intermediate giving rise to this broadened singlet. One of the two sets of two doublets between –11 and –17 ppm (J_{PP} = 80 Hz) observed in the $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures (signal

C in Fig. 1) may belong to intermediate **D**. It is noteworthy that neither signal **B** nor **C** was observed in ^{31}P NMR spectra of the 1:4.5 reaction mixtures in C_6D_6-PhMe at rt.

The reductive elimination is to be the last step of the transformation, which provides aminophosphine **4**, Ph_2PPPh_2 and Pd(0)-containing species (Scheme 2). Signals of the free aminophosphine **4** and Ph_2PPPh_2 were observed in the spectra of the 1:4.5 reaction mixtures (Fig. 1).

As was noted above, the amount of Ph_2PPPh_2 formed in the studied transformations was steadily decreasing during the warm-up of the 1:4.5 reaction mixture. Yet, some amount of $Ph_2P(O)PPh_2$ was practically always isolated during chromatographic separations of the 1:4.5 reaction mixtures. The analysis of the 1:4.5 reaction mixture after 18 h at rt using analytical two-dimensional TLC [39] indicated that aminophosphine **3** was present in the reaction mixture not as a complex with Pd(0) or Pd(II) but as a free ligand (its spot was on the diagonal), while Ph_2PPPh_2, at least partly, was forming during the chromatography (the spot of the diphosphine was off the diagonal). We suggest that Ph_2PPPh_2 reacts with the Pd(0)L_n species formed in the final step of the reaction sequence to furnish Ph_2P–Pd(II)L_2–PPh_2, Ph_2P–Pd(II)L_3 and/or related complexes. Then, during the chromatographic separation on silica gel, these complexes are converted back to Pd(0) and Ph_2PPPh_2. (Pd(0) black was clearly seen on preparative TLC, but was not visible in the reaction mixtures before chromatographic separations.) Previously, Kawaguchi et al. reported that both Pd(II) and Pd(0) are capable of catalyzing hydrophosphination reactions of Ph_2PPPh_2 [40,41]. In these reactions, the formation of $PdL_2(PPh_2)_2$ species was proposed. It was also reported that $Pd(PhCN)_2Cl_2$ reacted with Ph_2PPPh_2 to yield a complex of the formula $Pd(P_2Ph_4)Cl_2$ [42]. The composition of this complex was supported by elemental analysis [42]. The ^{31}P NMR spectrum of this complex in $CDCl_3$ contained a singlet at 76.4 ppm [42]. On the other hand, in the Pd(0)-catalyzed allylic phosphination reactions of $HPPh_2$, Ph_2PPPh_2 was isolated in 1–40% yield depending on the reaction conditions [43]. Similar observations were reported for hydrophosphination of styrenes by $Pd(PhCN)_2Cl_2$ [44]. High lability of the P–P bond in R_2PPR_2 was observed in the metathesis reactions of diphosphines in CH_2Cl_2: $Ph_2PPPh_2 + Me_2PPMe_2 \rightleftarrows 2Me_2PPPh_2$ [45]. The hypothesis that Pd(0)L_n complexes formed in the studied transformations are capable of reacting with Ph_2PPPh_2 to yield Ph_2P–Pd(II)L_m and/or related Pd(II) species can be supported by the fact that, in our trial experiment, the Pd(II)-catalyzed reaction of *N*,*N*-dimethylbenzylamine with $KPPh_2$ furnished aminophosphine **4** in 25% yield. This result suggests that Pd(II) is likely to be converted to Pd(0) and then back to Pd(II) to begin a new catalytic cycle.

It is noteworthy that for aminophosphine **4** (L), its Pd(0) complex PdL_3 has been reported [46]. The air-sensitive complex was instable at rt in solutions. The ^{31}P NMR spectrum of this compound exhibited two signals, at δ 17.3 and −16.7 ppm (d_8-PhMe, −40 °C, 85% H_3PO_4). The latter singlet was due to the presence of the free aminophosphine in the sample. It was also determined that in this complex, the aminophosphine was coordinated to the metal primarily or exclusively through the P atom. For comparison, Pd(II) complexes $LPdMe_2$, LPdMeX (X = I, Br, Cl or OTf) and $LPdCl_2$ of aminophosphine **4** exhibited bidentate P,N chelate coordination [46–49]. Compounds LPdMeCl and LPdMe(OTf) both provided a ^{31}P NMR signal at δ 37.7 ppm ($CDCl_3$, rt) [48], while the spectrum of $LPdCl_2$ had a singlet at 22.9 ppm ($CDCl_3$, rt, 85% H_3PO_4) [49]. In our study, the $^{31}P\{^1H\}$ NMR spectra of 1:4.5 reaction mixtures of dimer **1** and $KPPh_2$ exhibited a few low-intensity singlets in the 5–15 ppm region but no signals between 15 and 50 ppm (see, for example, Fig. 3b, d_8-THF, $P(OEt)_3$ as standard). These singlets may belong to Pd(0) or Pd(II) complexes with a dative P–Pd bond; however, their structures are impossible to determine.

Recently, evidence of Pd(III) intermediates in the $Pd(OAc)_2$-catalyzed C–H arylation and acetoxylation was reported [50,51]. These reactions presumably proceed through the formation of μ-AcO-CPCs. In our case, formation of Pd(III) intermediates is unlikely. The Pd(III)–Pd(III) P-containing intermediates are expected to give ^{31}P NMR signals in a very low field (cf. data for compounds **VIII**, Chart 1) [25]. No signals above 130 ppm were observed in the ^{31}P NMR spectra of the studied reactions. Also, the "open-book" geometry of dimeric μ-AcO-CPCs with a short distance between two Pd atoms is quite different from μ-di-PPh_2 and μ-Cl-μ-PPh_2 complexes with a relatively planar geometry of the {PdP_2Pd} [27] and {PdClPPd} [6] core. For the Pd-catalyzed acetoxylation and a few related reactions proceeding through the formation of cyclopalladated complexes, the involvement of the Pd(IV) intermediates were also proposed [52–54]. Unfortunately, we could not find relevant ^{31}P NMR data for Pd(IV) complexes to compare them with our spectra. However, formation of some Pd(0) black in all reactions during chromatographic separations on silica gel makes the hypothesis of the Pd(IV) intermediates in the reactions of CPCs with metal phosphides unlikely.

3. Conclusions

Both the purchased and lab synthesized $KPPh_2$ reagents provided practically identical and reproducible results in the reactions with complex **1** making $KPPh_2$ a more reliable reagent for reactions with CPCs than $LiPPh_2$. By controlling the reagent ratio and temperature, it was possible to selectively obtain either the μ-Cl-μ-PPh_2 complex **3** or aminophosphine **4**. Longer reaction times benefit the formation of aminophosphine **4**, while the best yield of complex **3** was obtained in a one-hour reaction. A drawback of using $KPPh_2$ in reactions with CPC **1** is that overall product yields are lower than those obtained by us in the best experiments with $LiPPh_2$ [7]. The proposed mechanism for obtaining **4** from CPC **1** in THF is supported by $^{31}P\{^1H\}$ NMR data and includes the consecutive formation of the corresponding complexes with one and two bridging PPh_2 groups.

Currently, we are studying stoichiometric and catalytic reactions of mono- and dinuclear μ-Cl and μ-OAc CPCs with different metal phosphides in order to obtain a set of structurally different P^*- and C^*,P^*-chiral aminophosphines, potent catalysts in asymmetric transformations.

4. Experimental

4.1. General methods and materials

All reactions with $KPPh_2$ were carried out under a positive pressure of argon using Schlenk techniques. Purifications by column chromatography were carried out using Natland silica gel 60 (230 mesh). Preparative thin-layer chromatography (TLC) was carried out using 200 × 250 mm glass plates with an unfixed layer of Natland or Merck silica gel 60 (230 mesh). Analytical TLC was performed on Whatman silica gel 60 (F_{254}) 250 μm precoated plates. Compounds were visualized on TLC plates using UV light (254 nm) and/or iodine stain. Routine ^1H (500 MHz), $^{13}C\{^1H\}$ (126 MHz) and $^{31}P\{^1H\}$ (202 MHz) as well as DEPT, COSY and HMQC spectra were recorded on a Bruker AVANCE 500 NMR spectrometer. Chemical shifts are reported in ppm with $SiMe_4$ as an internal standard (^1H and ^{13}C) or $P(OEt)_3$ as an external standard (^{31}P). Spin–spin coupling constants, *J*, are given in Hz. Spectra of the products obtained in reactions of the $KPPh_2$ reagents with CPCs were recorded in $CDCl_3$ unless otherwise stated. Toluene was dried by refluxing over K/benzophenone, distilled under Ar, and stored over potassium. THF was distilled over K/benzophenone under Ar immediately before use. Acetone was purified by distillation over $KMnO_4$. Other solvents were distilled over CaH_2. Potassium metal was obtained from Acros. The 0.5 M

$KPPh_2$ solutions in THF were either purchased from Sigma–Aldrich Co. or synthesized in our lab by using a known general method[21] as described below. Chlorodiphenylphosphine was distilled under vacuum prior to use. Complex di-(μ-chloro)bis-{[2-(*N*,*N*-dimethylamino)methyl]phenyl-*C*,*N*}dipalladium(II) (**1**) was obtained from the corresponding benzylamine in 95% yield using a reported procedure [55]. Other chemicals were used as purchased without further purification.

4.2. Preparation of $KPPh_2$

Pieces of K (150 mg, 3.8 mmol) and THF (7.0 mL) were placed into a 10-mL Ar-filled Schlenk flask. Then $ClPPh_2$ (0.65 mL, 3.5 mmol) was added drop wise in 6 min. The reaction mixture immediately turned bright orange. The reaction mixture was stirred at 35 °C overnight prior to further uses. Complete conversion of $ClPPh_2$ was confirmed by ^{31}P NMR data. $^{31}P\{^1H\}$ NMR (δ, ppm, d_8-THF): −20.5 (broad).

4.3. Preparation of the $KPPh_2$ samples for $^{31}P\{^1H\}$ NMR spectra

0.25 mL of a 0.5 M solution of $KPPh_2$ in THF were mixed with 0.01 mL of d_8-THF at rt, so the estimated concentration of the reagents in the NMR samples was 0.48 M. The $^{31}P\{^1H\}$ NMR spectra were taken at rt unless otherwise noted.

4.4. Synthesis of μ-chloro-μ-diphenylphosphido-{[2-(N,N-dimethylamino)methyl]phenyl-C,N}dipalladium(II) (3)

CPC **1** was placed into an Ar-filled 10-mL Schlenk flask and THF or toluene (1 mL per 10 mg of complex **1**) was added. Then a 0.5 M solution of $KPPh_2$ in THF was added drop wise in ca. 5 min. The yellow mixture turned red. The reaction mixture was stirred in an Ar atmosphere at rt for 1 h, unless otherwise noted. After solvent removal, the crude product was dissolved in CH_2Cl_2 and the solution was filtered through a layer of Celite. The filtrate was concentrated and the crude product was purified using preparative TLC (silica gel, 6:1 benzene-acetone) affording complex **3** as a yellow solid in 76% yield. $^{31}P\{^1H\}$ NMR (δ, ppm): 30.2 (d_8-THF), 25.1 ($CDCl_3$). Other spectroscopic data were in accord with those of an authentic sample prepared earlier in our lab [7].

4.5. Synthesis of ortho-(diphenylphosphino)-N,N-dimethylbenzylamine (4)

CPC **1** was placed into an Ar-filled 10-mL Schlenk flask and THF or toluene (1 mL per 10 mg of complex **1**) was added. Then a 0.5 M solution of $KPPh_2$ in THF was added drop wise in ca. 5 min, during which the yellow mixture turned red. The reaction mixture was stirred in an Ar atmosphere at rt for 18 h, unless noted otherwise. After solvent removal, the solid residue was dissolved in CH_2Cl_2 and purified using preparative TLC (silica gel, 8:1 benzene-acetone) affording pure aminophosphine **4**. For yields, see Supplementary Material, Tables 1–4. Spectroscopic data of aminophosphine **4** were in accord with those of an authentic sample obtained in our lab previously [7].

For low temperature $^{31}P\{^1H\}$ NMR monitoring of reaction mixtures, 0.1 mL of THF were substituted for 0.1 mL of d_8-THF and 0.35 mL of a reaction mixture was transferred in a J. Young NMR tube as soon as reagents were combined.

Acknowledgment

Financial support has been received from ND EPSCoR through NSF grant No. EPS-0447679.

Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2010.10.020.

References

[1] J.M. Vila, M.Y. Pereira, The Pd-C Building Block of Palladacycles: A Cornerstone for Stoichiometric C-C and C-X Bond Assemblage. in: J. Dupont, M. Pfeffer (Eds.), Palladacycles. Synthesis, characterization and applications Wiley-VCH Verlag GmbH, Weinheim, 2008, pp. 87–108.
[2] J. Dupont, C.S. Consorti, J. Spencer, Chem. Rev. 105 (2005) 2527–2571.
[3] V.I. Sokolov, L.L. Troitskaya, O.A. Reutov, J. Organomet. Chem. 202 (1980) C58–C60.
[4] L.L. Troitskaya, Z.A. Starikova, T.V. Demeshchik, V.I. Sokolov, Russ. Chem. Bull. 48 (1999) 1738–1743.
[5] C. Bolm, K. Wenz, G. Raabe, J. Organomet. Chem. 662 (2002) 23–33.
[6] (a) V.V. Dunina, L.G. Kuz'mina, J.A.K. Howard, N.A. Kataeva, M.Y. Rubina, A.G. Parfyonov, Y.A. Veits, Y.K. Grishin, Direct Route from Chiral Palladacycles to Enantioselective Aminophosphine Palladium(0) Catalysts, in: 10th IUPAC Symposium on Organo-Metallic Chemistry Directed toward Organic Synthesis (OMCOS-10), Versailles, France, 1999; P-124.
(b) Y.K. Grishin, M.Y. Rubina, N.A. Kataeva, A.V. Churakov, L.G. Kuz'mina, J.A.K. Howard, V.V. Dunina, CCDC, XOZPIL, 2002, private communication.
[7] V.A. Stepanova, V.V. Dunina, I.P. Smoliakova, Organometallics 28 (2009) 6546–6558.
[8] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, sixth ed. John Wiley & Sons, Inc., New York, 1999, p. 107.
[9] H.J. Reich, R.R. Dykstra, Organometallics 13 (1994) 4578–4585.
[10] A. Zschunke, E. Bauer, H. Schmidt, K. Issleib, Z. Anorg. Chem. 495 (1982) 115–119.
[11] I.J. Colquhoun, H.C.E. McFarlane, W. McFarlane, Phosphorus and Sulfur 18 (1983) 61–64.
[12] I.J. Colquhoun, H.C.E. McFarlane, W. McFarlane, J. Chem. Soc. Chem. Commun. (1982) 220–221.
[13] K. Issleib, A. Tzschach, Chem. Ber 92 (1959) 1118–1126.
[14] R.A. Jones, A.L. Stuart, T.C. Wright, J. Am. Chem. Soc. 105 (1983) 7459–7460.
[15] P.B. Hitchcock, M.F. Lappert, P.P. Power, S.J. Smith, J. Chem. Soc. Chem. Commun. (1984) 1669–1700.
[16] R.A. Bartlett, M.M. Olmstead, P.P. Power, Inorg. Chem. 25 (1986) 1243–1247.
[17] A. Loupy, B. Tchoubar, Salt Effects in Organic and Organometallic Chemistry. VCH, Federal Republic of Germany, Weinheim, 1992, 277.
[18] G. Merle, J. Gole, Bull. Soc. Chim. Fr. (1976) 1082–1088.
[19] D.H. O'Brien, C.R. Russell, A.J. Hart, J. Am. Chem. Soc. 98 (1976) 7427.
[20] L. Gupta, A.C. Hoepkert, K.J. Singh, D.B. Collum, J. Org. Chem. 74 (2009) 2231–2233 (and references cited therein).
[21] M. Reisser, A. Maier, G. Maas, Eur. J. Org. Chem. (2003) 2071–2079.
[22] For the spectra, see Supplementary Material. The halfwidths' values of the aminophosphine signals in the spectra of the reaction mixture at −20 and +20 °C were the same, $\nu_{1/2} = 4.6$ Hz, while for the corresponding signal at 0 °C displayed a shoulder and had a significantly higher ν1/2 value of 12.0 Hz. For comparison, the Ph2PPPh2 signal in the spectrum at −20 °C has $\nu_{1/2} = 7.7$ Hz.
[23] R. Giannandrea, P. Mastrorilli, C.F. Nobile, Inorg. Chim. Acta 284 (1999) 116–118.
[24] J.B. Brandon, K.R. Dixon, Can. J. Chem. 59 (1981) 1188–1200.
[25] I. Ara, N. Chaouche, J. Forniés, C. Fortuño, A. Kribii, A.C. Tsipis, Organometallics 25 (2006) 1084–1091.
[26] J. Forniés, C. Fortuño, R. Navarro, F. Martínez, A.J. Welch, J. Organomet. Chem. 394 (1990) 643–658.
[27] A. Díez, J. Forniés, A. García, E. Lalinde, M.T. Moreno, Inorg. Chem. 14 (2005) 2443–2453.
[28] For the concept of transphobia, see: (a) J. Vicente, A. Arcas, D. Bautista, P.G. Jones, Organometallics 16 (1997) 2127–2138;
(b) V.V. Dunina, O.N. Gorunova, Russ. Chem. Rev. 74 (2005) 871–913;
(c) J. Vicente, A. Arcas, M.-D. Gálvez-López, F. Juliá-Hernández, D. Bautista, P.G. Jones, Organometallics 27 (2008) 1582–1590 (and references cited therein).
[29] F. Maassarani, M.F. Davidson, I.C.M. Wehman-Ooyevaar, D.M. Grove, M.A. van Koten, W.J.J. Smeets, A.L. Spek, G. van Koten, Inorg. Chim. Acta 235 (1995) 327–338.
[30] M.A. Zhuravel, D.S. Glueck, L.N. Zakharov, A.L. Rheingold, Organometallics 21 (2002) 3208–3214.
[31] M. Mazzeo, M. Lamberti, A. Massa, A. Scettri, C. Pellecchia, J.C. Peters, Organometallics 27 (2008) 5741–5743.
[32] Complex $\{(N\cap C)Pd(\mu\text{-}PPh_2)\}_2$ can be formed in the 1:1 reaction mixture as a result of decomposition of the corresponding μ-Cl-μ-PPh_2 complex 3 in THF, see for example data Supplementary Material, Table 2, entries 1–3.
[33] S.E. Tunney, J.K. Stille, J. Org. Chem. 52 (1987) 748–753.
[34] F. Maassarani, Eur. J. Inorg. Chem. (2008) 4835–4850.
[35] A. Handler, P. Peringer, E. Muller, J. Chem. Soc. Dalton Trans. (1990) 3725–3727.
[36] C. Scriban, D.K. Wicht, D.S. Glueck, L.N. Zakharov, J.A. Golen, A.L. Rheingold, Organometallics 25 (2006) 3370–3378.

[37] C. Scriban, D.S. Glueck, A.G. DiPasquale, A.L. Rheingold, Organometallics 25 (2006) 5435–5448.
[38] F. Cecconi, C.A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini, G. Scapacci, Inorg. Chim. Acta 189 (1991) 105–110.
[39] A.I. Vogel revised by B.S. Furniss, A, J. Hannaford, P.W.G. Smith, A.R. Tatchel, in: Vogel's Textbook of Practical Organic Chemistry, fifth ed. Longman Group UK Limited, Singapore, 1989 p. 206.
[40] S. Kawaguchi, S. Nagata, A. Nomoto, M. Sonoda, A. Ogawa, J. Org. Chem. 73 (2008) 7928–7933.
[41] S. Nagata, S. Kawaguchi, M. Matsumoto, I. Kamiya, A. Nomoto, M. Sonoda, A. Ogawa, Tetrahedron Lett. 48 (2007) 6637–6640.
[42] R. Giannandrea, P. Mastrorilli, C.F. Nobile, M. Dilonardo, Inorg. Chim. Acta 249 (1996) 237–238.
[43] P. Butti, R. Rochat, A.D. Sadow, A. Togni, Angew. Chem. Int. Ed. 47 (2008) 4878–4881.
[44] M.O. Shulyupin, M.A. Kazankova, I.P. Beletskaya, Org. Lett. 4 (2002) 761–763.
[45] (a) H.C.E. McFarlane, W. McFarlane, J. Chem. Soc. Chem. Commun. (1972) 1189–1190;
(b) R.K. Harris, E.M. Norval, M. Fild, J. Chem. Soc. Dalton Trans. (1979) 826–831;
(c) D.J. Dodds, M.F. Haddow, A.G. Orpen, P.G. Pringle, G. Woodward, Organometallics 25 (2006) 5937–5945.
[46] W. de Graaf, S. Harder, J. Boersma, G. van Koten, J. Organomet. Chem. 358 (1988) 545–562.
[47] W. de Graaf, J. Boersma, W.J.J. Smeets, A.L. Spek, G. van Koten, Organometallics 8 (1989) 2907–2917.
[48] P.H.P. Brinkmann, G.A. Luinstra, J. Organomet. Chem. 572 (1999) 193–205.
[49] J.G. Fierro-Arias, R. Redón, J.J. García, S. Hernández-Ortega, R.R.A. Toscano, D. Morales-Morales, J. Mol. Catal. A 233 (2005) 17–25.
[50] (a) D.C. Powers, M.A.L. Geibel, J.E.M.N. Klein, T. Ritter, J. Am. Chem. Soc. 131 (2009) 17050–17051;
(b) D.C. Powers, T. Ritter, Nat. Chem. 1 (2009) 302–309.
[51] N.R. Deprez, M.S. Sanford, J. Am. Chem. Soc. 131 (2009) 11234–11241.
[52] S.R. Whitfield, M.S. Sanford, J. Am. Chem. Soc. 129 (2007) 15142–15143.
[53] A.R. Dick, M.S. Sanford, Tetrahedron 62 (2006) 2439–2463.
[54] N.R. Deprez, M.S. Sanford, Inorg. Chem. 46 (2007) 1924–1935.
[55] O.A. Zalevskaya, V.V. Dunina, V.M. Potapov, L.G. Kuz'mina, Y.T. Struchkov, Zh. Obshch. Khim. 55 (1985) 1332–1341.