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Reactivity of ammonium and iminium tetraphenylborates towards Pd(0)-complexes: selective allyl or proton transfer to Pd(0). Evidence of formation of the species $[HPd(dppe)_2][BPh_4]$

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Abstract

The reactivity of ammonium- and iminium-BPh_4 salts, $[CH_2{=}CHCH_2NH_3]BPh_4$, $[(CH_2{=}CHCH_2)HN{=}CMe_2]BPh_4$ and $[(PhCH_2)HN{=}CMe_2]BPh_4$, towards Pd(0)-complexes, [Pd(dppe)(dba)] and $[Pd(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane; dba = dibenzylideneacetone), has been investigated. Allyl-ammonium and -iminium tetraphenylborates $[CH_2{=}CHCH_2NH_3]BPh_4$ and $[(CH_2{=}CHCH_2)HN{=}CMe_2]BPh_4$ react with [Pd(dppe)(dba)] to afford, under mild conditions (293 K), $[(\eta^3\text{-}C_3H_5)Pd(dppe)][BPh_4]$, through selective oxidative transfer of allyl group from the ammonium or iminium cation to the Pd center. $[(PhCH_2)HN{=}CMe_2]BPh_4$ reacts with $[Pd(dppe)_2]$ to afford $[H{-}Pd(dppe)_2][BPh_4]$, that, under the reaction conditions, has poor stability as it undergoes hydride transfer to the iminium ion present in the reaction medium, affording $[Pd(dppe)_2][BPh_4]_2$.

Keywords: Pd–allyl complexes; Pd–hydrido complexes; Allyl transfer; Proton transfer; Alkylammonium tetraphenylborates; Iminium tetraphenylborates

1. Introduction

Recently [1], we have reported on the reactivity of anhydrous *N*-alkylammonium and *N*-alkyl-monosubstituted-iminium BPh_4 salts ($[RNH_3]BPh_4$ and $[RHN{=}CMe_2]BPh_4$, respectively; R = alkyl) [2,3], towards Ni(0)–phosphine complexes [4,5a] and shown that either C–N or H–N selective cleavage can take place. In fact, $[CH_2{=}CHCH_2NH_3]BPh_4$ (**1**) and $[(CH_2{=}CHCH_2)HN{=}CMe_2]BPh_4$ (**2**) oxidatively add to Ni(0)–phosphine complexes (Eqs. (1)–(3)) through selective activation of the N–C allyl bond to give new asymmetric cationic π-allyl complexes bearing both *P*- and *N*-ligands in the coordination sphere of Ni [4,5a].

$$[(Cy_3P)_2Ni(\eta^2\text{-}CO_2)] + [CH_2{=}CHCH_2NH_3]BPh_4 \xrightarrow{253\ K,\ THF,\ CO_2\ or\ N_2\ (0.1\ MPa)} [(\eta^3\text{-}C_3H_5)Ni(PCy_3)(NH_3)][BPh_4] + PCy_3 + CO_2 \quad (1)$$

$$[(Cy_3P)_2NiNNNi(PCy_3)_2] + 2[CH_2{=}CHCH_2NH_3]BPh_4 \xrightarrow{293\ K,\ THF,\ N_2} 2[(\eta^3\text{-}C_3H_5)Ni(PCy_3)(NH_3)][BPh_4] + 2PCy_3 + N_2 \quad (2)$$

$$[(Cy_3P)_2NiNNNi(PCy_3)_2] + 2[(CH_2{=}CHCH_2)HN{=}CMe_2]BPh_4 \xrightarrow{293\ K,\ toluene,\ N_2} 2[(\eta^3\text{-}C_3H_5)Ni(PCy_3)(\eta^1(N){-}HN{=}CMe_2)][BPh_4] + 2PCy_3 + N_2 \quad (3)$$

Conversely, *N*-benzylisopropylidene-iminium cation of $[(PhCH_2)HN{=}CMe_2]BPh_4$ (**3**) selectively reacts with $[(Cy_3P)_2NiNNNi(PCy_3)_2]$, via activation of the N–H bond, to afford a new terminal cationic Ni–hydride complex, $[trans\text{-}(H)Ni(PCy_3)_2(\eta^1(N){-}PhCH_2N{=}CMe_2)][BPh_4]$ (Eq. (4)), fully characterized both in solution and in the solid state [4].

$$[(Cy_3P)_2NiNNNi(PCy_3)_2] + 2[(PhCH_2)HN{=}CMe_2]BPh_4 \xrightarrow{293\ K,\ THF,\ N_2}$$

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$$2[trans\text{-}(H)Ni(PCy_3)_2(\eta^1(N)\text{–}PhCH_2N{=}CMe_2)][BPh_4] + N_2 \quad (4)$$

The examples reported above confirm the potential of alkyl-ammonium and -iminium tetraphenylborate salts as suitable reagents for the synthesis of new cationic transition metal complexes. Alkylammonium tetraphenylborates have been used as protolytic agents of M–C bonds in alkyl or aryl transition-metal complexes [6]. Allylammonium salts $[CH_2{=}CRCH_2NH_nEt_{3-n}]X$ (R = H, $n = 0,1$; R = Me, $n = 0$; X = ClO_4, BPh_4) have been shown to react with Pt(0) precursors to afford cationic π-allyl Pt(II) complexes [7]. As for the reactivity of iminium cations towards transition metal centers [8], it is known that *N*,*N*-dialkylsubstituted iminium ions can coordinate to low valent metal centers through either the C–N bond ($\eta^2(C,N)$) [8a,8b,8c,8f] or the electrophilic iminium carbon atom ($\eta^1(C)$) [8b,8f]. ($\eta^2(C,N)$ coordinated iminium cations are supposed to be intermediates in a few metal promoted reactions of tertiary amines [8g]. Low valent transition metal complexes can also promote the transformation of iminium groups into carbenes [8b] or induce oxidative [8e] or reductive [8f] coupling reactions.

As a continuation of previous work [4,5a] on the reaction of ammonium- and iminium-BPh_4 salts with metal centers in a low oxidation state, we have extended our investigation to Pd(0)-based systems. In this report we focus on the reactivity of alkyl-ammonium and -iminium BPh_4 salts **1**–**3** towards diphosphine-complexes of Pd(0). We describe the oxidative transfer of allyl group from a primary allylammonium or *N*-allyliminium cation to [Pd(dppe)(dba)] (**4**) and present spectroscopic evidence for the formation of the cationic Pd(II)–hydrido complex $[HPd(dppe)_2][BPh_4]$ (**5**). The reaction of salt **3** with [Pd(dppe)(dba)] has been reported elsewhere [5b,5c].

2. Results and discussion

2.1. Reactivity of $[CH_2{=}CHCH_2NH_3]BPh_4$ and $[(CH_2{=}CHCH_2)HN{=}CMe_2]BPh_4$ towards [Pd(dppe)(dba)]

Allyl-ammonium or -iminium tetraphenylborate salts **1** and **2** react with the coordinatively unsaturated species [Pd(dppe)(dba)] (**4**), in THF, at room temperature (293 K), to give the cationic π-allyl complex $[(\eta^3\text{-}C_3H_5)Pd(dppe)][BPh_4]$ (**6**) (Eqs. (5) and (6)). Complex **6** was isolated and fully characterized in solution by NMR

$$[Pd(dppe)(dba)] + [CH_2{=}CHCH_2NH_3]BPh_4 \xrightarrow{\text{THF, 293 K}} [(\eta^3\text{-}C_3H_5)Pd(dppe)][BPh_4] + dba + NH_3 \quad (5)$$

$$[Pd(dppe)(dba)] + [(CH_2{=}CHCH_2)HN{=}CMe_2]BPh_4 \xrightarrow{\text{THF, 293 K}} [(\eta^3\text{-}C_3H_5)Pd(dppe)][BPh_4] + dba + HN{=}CMe_2 \quad (6)$$

spectroscopy (see Section 4). $[(\eta^3\text{-}C_3H_5)Pd(dppe)]^+$ cation, albeit well known in the literature [9], was never isolated as having BPh_4^- as counterion. Table 1 shows a few selected NMR data for complex **6** which agree very well with those reported in the literature for $[(\eta^3\text{-}C_3H_5)Pd(dppe)][PF_6]$ [9a] and $[(\eta^3\text{-}C_3H_5)Pd(dppe)][BF_4]$ [9e] in the same solvent, $CDCl_3$.

The reactivity shown in Eqs. (5) and (6) resembles that observed with Ni(0) systems [4,5a]. Reaction (5) has character of novelty as allyl transfer from a *primary* allylammonium cation to Pd(0) complexes has never been documented before, as *quaternary* allylammonium cations ($RNEt_3^+$, R = allyl) were used so far [10]. Also, reaction (6) represents the first documented example of oxidative allyl transfer from an iminium ion to a metal center. Our data clearly demonstrate that (using primary allyl-ammonium or -iminium cations) the allyl group transfer, by far, remains the preferred process with respect to proton transfer. In fact, the ^{31}P-NMR (202 MHz, 293 K) spectrum of the reaction solution obtained by dissolving **4** (one equivalent) and **2** (one equivalent) in THF-d_8 showed only a singlet, at δ 57.87 ppm, assigned to **6**. Accordingly, no signals were evident in the hydride region of the ^{1}H-NMR (500 MHz, 293 K) spectrum of the reaction mixture. Under the working conditions, the signals due to the *syn* and *anti* protons of allyl group of **6** were very broad resonances approximately located at δ 4.8 and 3.2 ppm. As a result of *syn*-*anti* proton exchange, the resonance due to H_{meso} is a quintet at δ 5.63 ppm ($J = 10.66$ Hz). The other signals assigned to **6** were found at δ 2.51 (d, $J = 18.32$ Hz, CH_2CH_2), 6.68 (tr, $J = 7.20$ Hz, H_{para,BPh_4}), 6.82 (tr, $J = 7.35$ Hz, H_{meta,BPh_4}), 7.30 (m, H_{ortho,BPh_4}), 7.36–7.60 ppm (m, $H_{Ph,dppe}$).

Cationic π-allyl Pd(II) complexes are of interest in homogeneous catalysis and are, traditionally, prepared from neutral π-allyl Pd(II) complexes via halide abstraction [11]. A different synthetic approach implies the transfer of allyl group to Pd(0) precursors from allylesters [12] or salts of allyl derivatives [9d,9e,10,13]. Poorly stable allyloxophosphoniun salts [13], or *N*-allyl-2,4,6-triphenylpyridinium tetrafluoroborates [9d,9e] or allyltriethylammonium and *N*-allylpyridinium perchlorates [10] have been employed to this end. The use of allyl-ammonium or -iminium tetraphenylborates may have a synthetic relevance for the direct synthesis of cationic π-allyl Pd(II) complexes due to the fact that the ammonium salts are safe, stable and very reactive and can be obtained in a straightforward way [2–5].

Table 1
Selected ^{1}H- and ^{31}P-NMR data [a] (δ) for **6**, [(η^3-C_3H_5)Pd(dppe)][BF_4] and [(η^3-C_3H_5)Pd(dppe)][PF_6]

Compound	^{1}H-NMR δ_H (ppm)			^{31}P-NMR δ_P (ppm) [b]
	H_{syn}	H_{anti}	H_{meso}	
[(η^3-C_3H_5)Pd(dppe)][BPh_4] (**6**)	4.65 [c,d] m	3.09 [c,d] m	5.39 [c,d] m	51.88 [c,e]
[(η^3-C_3H_5)Pd(dppe)][BF_4]	$4.80 \div 4.85$ [f,g] m	$3.29 \div 3.40$ [f,g] m	$5.72 \div 5.83$ [f,g] m	51.7 [f,h]
[(η^3-C_3H_5)Pd(dppe)][PF_6]	4.84 [i,j] m, broad	3.32 [i,j] m, broad	5.82 [i,j] m	[k]

[a] Solvent is $CDCl_3$.
[b] Versus H_3PO_4.
[c] This work.
[d] Experimental conditions: 293 K, at 500 MHz. See also Section 4.
[e] Experimental conditions: 293 K, at 202 MHz.
[f] Data from Ref. [9e].
[g] At 250 MHz.
[h] At 162 MHz.
[i] Data from Ref. [9a].
[j] Experimental conditions: 307 K, at 60 MHz.
[k] δ_P (for the dppe ligand): 52.1 ppm, in $(CD_3)_2SO$ [9b].

2.2. Reactivity of [($PhCH_2$)HN=CMe_2]BPh_4 towards [Pd(dppe)$_2$]

At 293 K, in CH_2Cl_2, [($PhCH_2$)HN=CMe_2]BPh_4 (**3**) reacts with the coordinatively saturated species [Pd(dppe)$_2$] (**7**) to afford the cationic five-coordinated Pd–hydrido complex [HPd(dppe)$_2$][BPh_4] (**5**), as demonstrated by NMR (^{1}H, ^{31}P) spectroscopy. In fact, the ^{1}H-NMR (500 MHz, CD_2Cl_2, 293 K) spectrum of the reaction mixture [Pd(0) to BPh_4 molar ratio = 1:1.06], measured soon after (15 min) mixing the reactants, shows, in addition to the signals of **7** [δ 2.09 (m, CH_2–CH_2), 7.04 (tr, $J = 7.45$ Hz, $H_{meta,Pd(0)}$), 7.14 (tr, $J = 7.27$ Hz, $H_{para,Pd(0)}$), 7.36 ppm (m, $H_{ortho,Pd(0)}$)] and BPh_4^- anion [δ 6.85 (tr, $J = 7.12$ Hz, H_{para,BPh_4}), 7.00 (tr, $J = 7.46$ Hz, H_{meta,BPh_4}), 7.36 (m, H_{ortho,BPh_4})], new signals at δ −7.37 (quintet, $J = 53.7$ Hz), 2.30 (unresolved triplet), 7.20 (m) and 7.36 ppm (the latter masked by the signals of $H_{ortho,Pd(0)}$ and H_{ortho,BPh_4}) with relative intensity 1:8:32:8. The quintet at δ −7.37 ppm is indicative of the presence of a hydride proton coupled with four equivalent phosphorous nuclei and the whole set of these new signals is consistent with the formation of the cationic five-coordinate Pd–hydride species [HPd(dppe)$_2$]$^+$ according to reaction (7).

$$[(PhCH_2)HN{=}CMe_2]BPh_4 + [Pd(dppe)_2] \rightleftarrows [HPd(dppe)_2][BPh_4] + (PhCH_2)N{=}CMe_2 \qquad (7)$$

In the ^{1}H-NMR spectrum other signals are also evident at δ 4.27 (s), 1.94 (s) and 1.91 ppm (s), with relative intensity 2:3:3, which can be assigned, respectively, to the methylene and methyl protons of the species ($PhCH_2$)N=CMe_2 and [($PhCH_2$)HN=CMe_2]$^+$, that may undergo a rapid proton exchange.

The formation of the hydrido species **5** is also supported by ^{31}P-NMR (81 MHz, 293 K) experiments. In CD_2Cl_2 solution **7** shows, as expected, a single resonance at δ 30.86 ppm. Upon addition of one equivalent of the iminium salt **3**, a singlet immediately appears at δ 32.98 ppm in the ^{31}P{^{1}H} spectrum. The proton-coupled ^{31}P spectrum shows that the new signal has a doublet structure (term separation = 52.4 Hz) because of coupling of P nuclei with the hydride proton [14].

Reaction (7) is a rare example of proton transfer from a protonated imine to a transition metal center. As a matter of fact, when *C*-substituted *N*,*N′*-dialkyliminium cations have been used [8d], the transfer of an α proton to CpFe(CO)$_2^-$ to give CpFe(CO)$_2$H has been observed with formation of an enamine (Eq. (8)). In the present work, the intermediate formation of enamine ($PhCH_2$)HN–C(Me)=CH_2 has not been observed by NMR.

$$CpFe(CO)_2^- + [(R^1)(R_2HC)C{=}N(R^2)_2]^+ \rightarrow CpFe(CO)_2H + R_2C{=}C(R^1)N(R^2)_2 \qquad (8)$$

Complex **5** is an unprecedented example of five-coordinate cationic mononuclear Pd–hydrido complex [15] of the tipe [HM(L_2)$_2$]$^+$ (L_2 = diphosphine) that are well known in the literature for Ni(II) and Pt(II) [16]. For Pd(II), they have been described so far as extremely reactive and have neither been isolated, nor spectroscopically detected in solution [16]. Table 2 collects some selected spectral data for cation [HPd(dppe)$_2$]$^+$ (**5**$^+$) and a few related [HM(diphosphine)$_2$]$^+$ complexes of platinum and nickel. As data in Table 2 indicate, along the series [HNi(dppe)$_2$]$^+$, [HPd(dppe)$_2$]$^+$ and [HPt(dppe)$_2$]$^+$, the ^{31}P resonance due to the dppe ligands in [HM(dppe)$_2$]$^+$ cations is progressively upfield shifted ([HNi(dppe)$_2$]$^+$ (42.5 ppm), [HPd(dppe)$_2$]$^+$ (32.98 ppm), [HPt(dppe)$_2$]$^+$ (20.4 ppm)). However, in **5**$^+$, the hydride ligand is less shielded (−7.37 ppm) than

Table 2
Selected ^{1}H- and ^{31}P-NMR data for $[H-M(diphosphine)_2]^+$ complexes (M = Ni, Pd, Pt) [a]

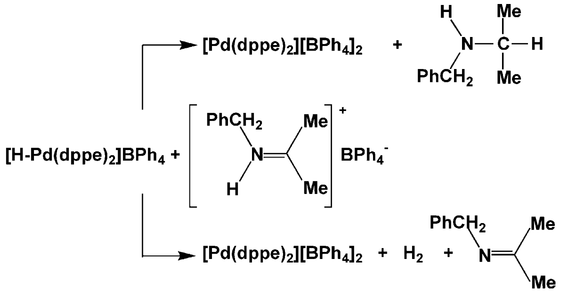
Complex	Solvent	^{1}H-NMR H–M		^{31}P{^{1}H}-NMR diphosphine	Reference
		δ_H (ppm)	$^2J_{H-M-P}$ (Hz)	δ_P (ppm) [b]	
$[HNi(dmpe)_2]PF_6$	CD_3CN	−14.02	8.5 (quintet)	24.6	[16a,16d]
$[HNi(depe)_2]PF_6$	CD_3NO_2	−14.16	(s)	46.2	[16a]
$[HNi(dppv)_2]BF_4$	CD_3CN	−11.87	10 (quintet)	56.71	[16e]
$[HNi(dppe)_2]PF_6$	**CD_2Cl_2**	**−12.87**	**2.4** [c]	**42.5**	[16a]
$[HPd(dppe)_2]BPh_4$	**CD_2Cl_2**	**−7.37**	**53.7 (quintet)**	**32.98**	This work
$[HPt(dppe)_2]PF_6$	**CD_3NO_2**	[d]	[d]	**20.4**	[16a]
$[HPt(dmpe)_2]PF_6$	CD_3CN	−11.55	30 (quintet)	−7.3	[16a,16d]
$[HPt(depe)_2]PF_6$	CD_3CN	−12.12	29 (quintet)	22.1	[16a,16d]

[a] dmpe = 1,2-bis(dimethylphosphino)ethane; depe = 1,2-bis(diethylphosphino)ethane; dppv = 1,2-bis(diphenylphosphino)ethylene.
[b] Versus H_3PO_4.
[c] Multiplicity not reported.
[d] Not reported.

in $[HPt(diphosphine)_2]^+$ (−11 ÷ −12 ppm) and $[HNi(diphosphine)_2]^+$ (−12 ÷ −14 ppm) complexes and, furthermore, the $^2J_{H-Pd-P}$ coupling constant (53.7 Hz) largely exceeds the $^2J_{H-M-P}$ values observed for related $[HPt(diphosphine)_2]^+$ (29–30 Hz) and $[HNi(diphosphine)_2]^+$ (0–10 Hz) cations.

Under the working conditions, the stability of **5** is quite modest. In the ^{31}P-NMR spectrum (81 MHz, CD_2Cl_2, 293 K) of the reaction mixture (Eq. (7)); Pd(0) to BPh_4 salt molar ratio = 1:1) a new resonance becomes clearly evident within 30 min at δ 57.07 ppm, suggesting the formation of cation $[Pd(dppe)_2]^{2+}$ [17]. The formation of this species is also supported by the appearance in the proton spectrum (500 MHz, CD_2Cl_2, 293 K; Pd(0) to BPh_4 salt molar ratio = 1:1.06) of an unresolved triplet at δ 2.03 ppm. In the ^{1}H spectrum, a weak signal also appears at δ 4.65 ppm due to formation of H_2, which has been further confirmed by GC analysis of the gas in equilibrium with the solution. Furthermore, new resonances, with relative intensity 2:1:6, are found at δ 3.61 (s), 2.81 (septet, $^3J_{HH} = 6.1$ Hz) and 1.05 ppm (d, $^3J_{HH} = 6.1$ Hz), respectively, which support the formation of the amine $PhCH_2NH(CHMe_2)$. The latter species has been unambiguously identified, together with the imine $PhCH_2N{=}CMe_2$, by a GC–MS analysis of the reaction mixture. An analogous reactivity was observed for a higher BPh_4 salt–Pd(0) molar ratio (2.09:1). These data show that **5** can interact with iminium cation $[(PhCH_2)HN{=}CMe_2]^+$ to give either molecular hydrogen and the imine $(PhCH_2)N{=}CMe_2$, or, by hydride transfer to the electrophilic iminium carbon, the amine $PhCH_2NH(CHMe_2)$ (Scheme 1).

Several attempts have been carried out to isolate complex **5** in a pure form from the reaction mixture, using both different Pd(0)–BPh_4 salt molar ratios (from 3:1 to 1:2) and a variety of experimental conditions, without success. Work-up of the reaction mixture allowed to isolate in a pure form only the new salt $[Pd(dppe)_2][BPh_4]_2$ **8** (as for the characterization, see Section 4) [18] together with variable amounts of the starting Pd(0)-complex **7**.



Scheme 1.

The reactivity of **3** towards **7** is affected by the nature of solvent. In CD_2Cl_2 (Eq. (7)); Pd(0) to BPh_4 salt molar ratio = 1:1.06), at 293 K, after a reaction time of 15 min, the **5** to **7** molar ratio, determined by integration of the signals at δ 7.20 (due to **5**) and 7.04 ppm (due to **7**), was equal to 1.12:1, from which a lower limit of the conversion α can be calculated ($\alpha = 53\%$) [19]. Differently from what observed in CD_2Cl_2, the ^{1}H-NMR (500 MHz, 293 K) spectrum of a THF-d_8 solution of **7** (1.5×10^{-2} mol l^{-1}) and **3** (3×10^{-2} mol l^{-1}) did not show any evidence of the typical hydride signal around δ −7 ppm. Nevertheless, the presence of **5** in the reaction solution, although in much lower concentration than in CD_2Cl_2, can be inferred by the immediate appearance of a new very weak signal at δ 2.3 ppm (unresolved triplet), assigned to the CH_2CH_2 protons of **5** [20]. However, also in THF, **5** further reacts with **3** according to what reported in Scheme 1.

The problem of the solution structure of cation $\mathbf{5}^+$ is quite puzzling. The NMR (^{1}H, ^{31}P) spectra, at room temperature (293 K), do not allow to distinguish among a square pyramidal structure and lower-symmetry coordination geometries (trigonal bipyramid or capped tetrahedron), which may undergo a fast fluxional process on the NMR time scale, at room temperature. VT-NMR [^1H(200 MHz), ^{31}P(81 MHz)] experiments in CD_2Cl_2 did not help to solve the problem as no complete decoalescence but only significant broadening of both quintuplet terms in the proton spectrum and the ^{31}P resonance of $\mathbf{5}^+$ (see Table 3) were observed upon temperature lowering (down to 178 K [21]), as already observed by other authors for the relevant Ni and Pt complexes [16d]. It is worth noting that line broadening is marked only for **5**, while it is very modest for **7** and **8**. This behavior suggests that $\mathbf{5}^+$ is fluxional, but does not provide any clear indication about the structure of the cation in solution.

3. Conclusions

The reactivity of ammonium- and iminium-BPh_4 salts towards low-valent Pd–diphosphine complexes has been investigated. The allyl salts $[CH_2{=}CHCH_2NH_3]BPh_4$ and $[(CH_2{=}CHCH_2)HN{=}CMe_2]BPh_4$ react with [Pd(dppe)(dba)] to afford the new salt $[(\eta^3\text{-}C_3H_5)Pd(dppe)][BPh_4]$, through selective oxidative transfer of allyl group from the *primary* ammonium or iminium cation to the metal center.

An unprecedented proton transfer from $[(PhCH_2)HN{=}CMe_2]BPh_4$ to $Pd(dppe)_2$ has been also decribed, which gives a rare five-coordinated cationic Pd–hydride, $[HPd(dppe)_2][BPh_4]$, spectroscopically detected (by NMR), for the first time, in solution. Under the working conditions, $[HPd(dppe)_2][BPh_4]$ is not stable as it acts as a hydride transfer agent towards the iminium cation $[(PhCH_2)HN{=}CMe_2]^+$ to afford the new salt $[Pd(dppe)_2][BPh_4]_2$.

4. Experimental

4.1. General

Unless otherwise stated, all reactions and manipulations were conducted under a dinitrogen atmosphere (as specified in the text), by using vacuum line techniques. All solvents were dried according to literature methods [22] and stored under N_2. Tetraphenylborate salts **1**–**3** were prepared as previously reported [2–4,5a]. [Pd(dppe)(dba)] was synthesized as described in the literature [23].

IR spectra were obtained with a Perkin–Elmer 883 spectrophotometer. NMR spectra were run on a Varian XL-200 or a Bruker AM 500 instrument, as specified in the text. ^1H and ^{13}C chemical shifts are in ppm versus Me_4Si and referenced to the solvent peak. ^{31}P resonances are reported in ppm versus H_3PO_4. GC–MS analyses were carried out with a Shimadzu GC-17A linked to a Shimadzu GCMS-QP5050 selective mass detector (capillary column: 60 m × 0.25 mm Supelco MDN-5S, 0.25 μm film thickness). Gas analyses were performed using a Carlo Erba Fractovap instrument.

4.2. Synthesis of $[Pd(dppe)_2]$

$[Pd(dppe)_2]$ was synthesized according to the literature procedure [17]. Below we report the NMR spectra of a pure sample of **7** in the solvents (CD_2Cl_2, THF-d_8) used in this work for studying reaction (7). ^1H-NMR (THF-d_8, 500 MHz, 293 K): δ 2.08 (m, 8H, CH_2CH_2), 6.99 (tr, 16H, $J = 7.52$ Hz, H_{meta}), 7.08 (tr, 8H, $J = 7.50$ Hz, H_{para}), 7.38 (m, 16H, H_{ortho}). ^1H-NMR (CD_2Cl_2, 500 MHz, 293 K): δ 2.09 (m, 8H, CH_2CH_2), 7.04 (tr, 16H, $J = 7.48$ Hz, H_{meta}), 7.15 (tr, 8H, $J = 7.50$ Hz, H_{para}), 7.38 (m, 16H, H_{ortho}). ^{31}P-NMR (CD_2Cl_2, 81 MHz, 293 K): δ 30.86 (vs. δ_P 30.6 ppm, in CH_2Cl_2 as solvent; see Ref. [17]).

4.3. Synthesis of $[(\eta^3\text{-}C_3H_5)Pd(dppe)][BPh_4]$ by reaction of $[CH_2{=}CHCH_2NH_3]BPh_4$ with [Pd(dppe)(dba)]

BPh_4 salt **1** (0.05475 g, 0.145 mmol) was added to a THF (4 ml) solution of [Pd(dppe)(dba)] (0.106 g, 0.144 mmol). The resulting solution, stirred at 293 K for 2 h, slowly turned from red to yellow–orange. The gas phase, periodically analyzed by GC throughout the reaction time, did not show detectable amounts of H_2.

The reaction mixture was concentrated in vacuo and 30 ml of Et_2O were layered. After cooling to 253 K overnight, the sticky oil separated was isolated by removing the mother solution with a syringe and washed

Table 3
Reaction of $[(PhCH_2)HN{=}CMe_2]BPh_4$ (**3**) with $[Pd(dppe)_2]$ (**7**). VT-$^{31}P\{^1H\}$-NMR (CD_2Cl_2, 81 MHz; **7** to **3** molar ratio = 1:1; see Section 4)

T (K)	$[HPd(dppe)_2][BPh_4]$		$[Pd(dppe)_2]$		$[Pd(dppe)_2][BPh_4]_2$	
	δ_P (ppm)	$w_{1/2}$ (Hz)	δ_P (ppm)	$w_{1/2}$ (Hz)	δ_P (ppm)	$w_{1/2}$ (Hz)
293	32.96	7	30.86	3	57.08	3
223	33.49	9	31.73	4	57.13	3
193	33.73	30	32.21	5	57.37	5
178	33.91	68	32.44	6	57.53	6

with Et_2O (3 × 10 ml). Upon drying in vacuo an orange solid was obtained and identified as **6**. Yield: 0.100 g, 80%. Anal. Found: C, 73.29; H, 5.69; P, 7.28; Pd, 12.25. Calc. for $C_{53}H_{49}BP_2Pd$: C, 73.58; H, 5.71; P, 7.17; Pd, 12.30%. As for the spectroscopic characterization, see below.

4.4. Synthesis of [(η^3-C_3H_5)Pd(dppe)][BPh_4] by reaction of [(CH_2=$CHCH_2$)HN=CMe_2]BPh_4 with [Pd(dppe)(dba)]

To a THF (4 ml) solution of **4** (0.108 g, 0.146 mmol) the BPh_4 salt **2** (0.064 g, 0.153 mmol), dissolved in THF (3 ml), was added and the resulting solution was stirred at 293 K for 2 h. The initially red solution turned to deep red, then to orange and finally to deep yellow. The GC analysis of the gas phase, periodically monitored throughout the reaction time, did not show any evidence of H_2 evolution.

To the reaction mixture, concentrated in vacuo, Et_2O (30 ml) was added. By cooling to 253 K, an orange oil separated, from which an orange solid was obtained (see above) and identified as **6**. Yield: 0.107 g, 85%. Anal. Found: C, 73.30; H, 5.82; P, 7.27; Pd, 12.38. Calc. for $C_{53}H_{49}BP_2Pd$: C, 73.58; H, 5.71; P, 7.17; Pd, 12.30%. IR (Nujol, KBr, cm^{-1}): 3050 (m-w), 3030 (m-w), 1575 (m-w), 1475 (m), 1430 (m), 1328 (w), 1300 (w), 1260 (w), 1175 (w), 1098 (m), 1060 (w), 1025 (w), 995 (m-w), 965 (w), 870 (w), 838 (w), 815 (m-w), 740 (m), 732 (m-s), 705 (s), 690 (m-s), 648 (w), 620 (w), 610 (m), 523 (m-s), 485 (m), 475 (m). ^{1}H-NMR (CD_2Cl_2, 500 MHz, 293 K): δ 2.52 (m, 4H, $\mathrm{C}H_2\mathrm{C}H_2$), 3.26 (m, 2H, H_{anti}), 4.84 (m, 2H, H_{syn}), 5.64 (septet, 1H, $J = 7$ Hz, H_{meso}), 6.83 (tr, 4H, $J = 7.20$ Hz, $\mathrm{H}_{para,\mathrm{BPh}_4}$), 6.98 (tr, 8H, $J = 7.42$ Hz, $\mathrm{H}_{meta,\mathrm{BPh}_4}$), 7.30 (m, 8H, $\mathrm{H}_{ortho,\mathrm{BPh}_4}$), 7.35–7.64 (m, 20H, $\mathrm{H}_{\mathrm{Ph,dppe}}$). The assignment of the allyl protons was supported by decoupling experiments from which the values of $^3J_{\mathrm{H}_{meso}-\mathrm{H}_{syn}}$ (7.33 Hz) and $^3J_{\mathrm{H}_{meso}-\mathrm{H}_{anti}}$ (13.6 Hz) were obtained. ^{13}C-NMR (CD_2Cl_2, 125 MHz, 293 K): δ 27.35 (virtual triplet, $J = 22.8$ Hz, $C\mathrm{H}_2C\mathrm{H}_2$), 71.36 (virtual triplet, $J = 15.4$ Hz, terminal allyl carbon atoms), 122.07 (s, $\mathrm{C}_{para,\mathrm{BPh}_4}$), 123.54 (tr, $J_{\mathrm{CP}} = 5.83$ Hz, C_{meso}), 125.95 (quartet, $^3J_{\mathrm{CB}} = 2.8$ Hz, $\mathrm{C}_{meta,\mathrm{BPh}_4}$), 130.09 (d, $^3J_{\mathrm{CP}} = 11.42$ Hz, $\mathrm{C}_{meta,\mathrm{dppe}}$), 132.64 (d, $^1J_{\mathrm{CP}} = 19.43$ Hz, $\mathrm{C}_{ipso,\mathrm{dppe}}$), 132.66 (s, $\mathrm{C}_{para,\mathrm{dppe}}$), 132.96 (d, $^2J_{\mathrm{CP}} = 7.15$ Hz, $\mathrm{C}_{ortho,\mathrm{dppe}}$), 136.30 (s, $\mathrm{C}_{ortho,\mathrm{BPh}_4}$), 164.40 (quartet, $^1J_{\mathrm{CB}} = 49.65$ Hz, $\mathrm{C}_{ipso,\mathrm{BPh}_4}$). ^{31}P-NMR ($CD_2Cl_2$, 202 MHz, 293 K): δ 53.65. ^{1}H-NMR ($CDCl_3$, 500 MHz, 293 K): δ 2.12 (m, 4H, $\mathrm{C}H_2\mathrm{C}H_2$), 3.09 (m, 2H, H_{anti}), 4.65 (m, 2H, H_{syn}), 5.39 (m, 1H, H_{meso}), 6.76 (tr, 4H, $J = 7.1$ Hz, $\mathrm{H}_{para,\mathrm{BPh}_4}$), 6.88 (tr, 8H, $J = 7.42$ Hz, $\mathrm{H}_{meta,\mathrm{BPh}_4}$), 7.20–7.54 (28H, $\mathrm{H}_{ortho,\mathrm{BPh}_4}$ and $\mathrm{H}_{\mathrm{Ph,dppe}}$). ^{31}P-NMR ($CDCl_3$, 202 MHz, 293 K): δ 51.88.

4.5. Reaction of [($PhCH_2$)HN=CMe_2]BPh_4 with [Pd(dppe)$_2$]: isolation and characterization of [Pd(dppe)$_2$][BPh_4]$_2$

To a CH_2Cl_2 (10 ml) solution of **7** (0.13000 g, 0.144 mmol) the BPh_4 salt **3** (0.13965 g, 0.299 mmol), previously dissolved in 10 ml of the same solvent, was added. The system was stirred at room temperature (293 K) for 6 h. Upon addition of n-C_5H_{12} (20 ml) and cooling to 253 K, a beige microcrystalline solid was obtained, isolated by filtration, washed with C_6H_6 (2 × 10 ml), dryed in vacuo and characterized as [Pd(dppe)$_2$][BPh_4]$_2$. Yield: 0.155 g, 70%. Anal. Found: C, 77.79; H, 5.97; P, 7.98; Pd, 6.88. Calc. for $C_{100}H_{88}B_2P_4Pd$: C, 77.90; H, 5.75; P, 8.04; Pd, 6.90%. IR (Nujol, KBr, cm^{-1}): 3055 (m-w), 3030 (m-w), 1575 (m-w), 1475 (m), 1430 (m), 1310 (w), 1300 (w), 1260 (w), 1100 (m), 1060 (w), 1025 (w), 995 (m-w), 870 (w), 838 (w), 810 (m-w), 740 (m), 730 (m-s), 703 (s), 685 (m-s), 650 (w), 620 (w), 610 (m), 530 (m-s), 510 (m), 475 (m). ^{1}H-NMR (Me_2SO-d_6, 500 MHz, 293 K): δ 2.97 (unresolved triplet, 8H, $\mathrm{C}H_2\mathrm{C}H_2$), 6.77 (tr, 8H, $J = 7.17$ Hz, $\mathrm{H}_{para,\mathrm{BPh}_4}$), 6.90 (tr, 16H, $J = 7.40$ Hz, $\mathrm{H}_{meta,\mathrm{BPh}_4}$), 7.17 (m, 16H, $\mathrm{H}_{ortho,\mathrm{BPh}_4}$), 7.25 (m, 16H, $\mathrm{H}_{ortho,\mathrm{dppe}}$), 7.34 (tr, 16H, $J = 7.56$ Hz, $\mathrm{H}_{meta,\mathrm{dppe}}$), 7.50 (tr, 8H, $J = 7.45$ Hz, $\mathrm{H}_{para,\mathrm{dppe}}$). ^{13}C-NMR ($Me_2SO$-$d_6$, 125 MHz, 293 K): δ 28.90 (m, broad, $C\mathrm{H}_2C\mathrm{H}_2$), 121.48 (s, $\mathrm{C}_{para,\mathrm{BPh}_4}$), 125.26 (quartet, $^3J_{\mathrm{CB}} = 2.6$ Hz, $\mathrm{C}_{meta,\mathrm{BPh}_4}$), 129.18, 132.74, 133.39 (all singlets, aromatic $\mathrm{C}_{\mathrm{dppe}}$), 135.51 (unresolved multiplet, $\mathrm{C}_{ortho,\mathrm{BPh}_4}$), 163.33 (quartet, $^1J_{\mathrm{CB}} = 49.3$ Hz, $\mathrm{C}_{ipso,\mathrm{BPh}_4}$).

4.6. Reactivity of [($PhCH_2$)HN=CMe_2]BPh_4 with [Pd(dppe)$_2$]: NMR experiments

*4.6.1. ^{1}H-NMR (CD_2Cl_2, 500 MHz, 293 K; **7** to **3** molar ratio = 1:1.06)*

Compounds **7** (0.01875 g, 0.0208 mmol) and **3** (0.01030 g, 0.0220 mmol) were dissolved in 0.5 ml of CD_2Cl_2, respectively. After mixing, the resulting solution was transferred into a NMR tube, and the spectrum was recorded after 15 min, 1 h and 3 h. The gas phase was analyzed by GC (H_2 was detected in the gas phase) and the reaction solution by GC–MS. The GC–MS analysis showed the presence of the imine ($PhCH_2$)N=CMe_2 (m/z 147 [M^+], 132, 117, 104, 91, 77, 69, 66, 56, 51, 42, 39) and confirmed (see Section 2) the formation of the amine $PhCH_2NH(CHMe_2)$ (m/z 149 [M^+], 134, 91, 77, 65, 41, 39).

*4.6.2. ^{1}H-NMR (CD_2Cl_2, 500 MHz, 293 K; **7** to **3** molar ratio = 1:2.09)*

Compounds **7** (0.02695 g, 0.0298 mmol) and **3** (0.02915 g, 0.0624 mmol) were dissolved, respectively, in 0.5 ml of CD_2Cl_2. After mixing, the resulting solution was analyzed as reported above. An analogous experiment was also carried out using THF-d_8 as solvent (see Section 2).

4.6.3. ^{31}P-NMR (CD_2Cl_2, 81 MHz, 293 K; 7 to **3** molar ratio = 1:1.01)

Compound **7** (0.03170 g, 0.0351 mmol) was dissolved in 3 g of CD_2Cl_2 and the $^{31}P\{^1H\}$ spectrum recorded (see Section 4.2). To this solution 0.01660 g of **3** (0.0355 mmol), dissolved in 1 g of CD_2Cl_2, were added under a N_2 stream and the resulting solution analyzed by ^{31}P-NMR (see Section 2).

4.6.4. VT-^{1}H-NMR (CD_2Cl_2, 200 MHz; 7 to **3** molar ratio = 1:1.19)

The reaction mixture was prepared by mixing 0.03715 g (0.0411 mmol) of **7**, dissolved in 0.5 ml of CD_2Cl_2, and 0.02280 g (0.0488 mmol) of **3** dissolved in the same solvent (0.5 ml). The spectrum of the reaction mixture was, then, recorded at the following temperatures: 293, 233, 193 and 178 K. The quintet due to complex **5** (see Section 2), originally located at δ −7.37 ppm at 293 K, markedly broadened upon lowering temperature and was found at −7.25 ppm at 233 K, −7.20 at 193 K and −7.16 at 178 K.

4.6.5. VT-^{31}P-NMR (CD_2Cl_2, 81 MHz; 7 to **3** molar ratio = 1:1)

The reaction solution was prepared by mixing 0.10605 g (0.117 mmol) of **7**, dissolved in 2.5 ml of CH_2Cl_2, and 0.05465 g (0.117 mmol) of **3** dissolved in 1 g of CD_2Cl_2. The spectrum of the reaction mixture was, then, measured in the temperature range 293–178 K. Decreasing temperature caused downfield shift of all signals and marked broadening of the signal assigned to **5** (see Table 3).

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[20] It is possible that in THF-d_8, at 293 K, equilibrium (7) lies, by far, at the left, most probably because of the ability of the solvent to stabilize the iminium ion through $N{-}H\cdots O$ hydrogen bonds.

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