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Synthesis, Characterization, and Reactivity of Cationic Hydride $[HPd(diphosphine)_2]^+CF_3SO_3^-$, the Missing Member of the Family $[HM(dppe)_2]^+X^-$ (M = Ni, Pd, Pt). DFT QM/MM Structural Predictions for the $[HPd(dppe)_2]^+$ Moiety

Michele Aresta,*,[†] Angela Dibenedetto,[†] Eliana Amodio,[†] Imre Pápai,[‡] and Gábor Schubert[‡]

Department of Chemistry and METEA Research Center, University of Bari, Via Celso Ulpiani 27,
70126 Bari, Italy, and Chemical Research Centre, Hungarian Academy of Sciences,
H-1525 Budapest, P.O.B. 17, Hungary

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The synthesis, characterization, and properties of the cationic hydride $[HPd(dppe)_2]^+CF_3SO_3^-\cdot 1/8THF$, the missing member of the family $[HM(dppe)_2]^+X^-$ (M = Ni, Pd, Pt), are described. The Pd hydride is not stable in solution and may react as either a proton or a hydride donor. DFT QM/MM calculations of the $[HPd(dppe)_2]^+$ moiety have allowed us to predict its structure and reactivity.

In this paper, we describe the synthesis, characterization, and properties of the cationic hydride $[HPd(dppe)_2]^+CF_3SO_3^-\cdot 1/8THF$ (**1**), the missing member of the family $[HM(dppe)_2]^+X^-$ (M = Ni, Pd, Pt). While the Ni[1] and Pt[2] analogues of $[HPd(dppe)_2]^+CF_3SO_3^-\cdot 1/8THF$ are known for some time, **1** could not be isolated[2] by using the same procedures as for Ni and Pt. Recently, using an independent synthetic methodology, we were able to observe in solution a nonisolable species that contained cation $[HPd(dppe)_2]^+$ with BPh_4^- as a noncoordinating counterion.[3] Now we report the correct conditions for the isolation of **1** as a yellow solid that has made possible the study of its reactivity. We also describe DFT QM/MM calculations carried out for the cationic $[HPd(dppe)_2]^+$ moiety.

When strictly anhydrous CF_3SO_3H is added in stoichiometric amount to a solution of $Pd(dppe)_2$[4] in anhydrous tetrahydrofuran (THF) at 273 K, a yellow solid precipitates that analyzes for $[HPd(dppe)_2]^+CF_3SO_3^-\cdot 1/8THF$ (**1**),[5] stable for days under dinitrogen at 253 K (eq 1) in the solid state.

$$Pd(dppe)_2 + CF_3SO_3H = \underset{\mathbf{1}}{[HPd(dppe)_2]^+CF_3SO_3^-} \qquad (1)$$

The infrared spectrum of solid **1** (CsI disks, Nujol) shows a band at 1916 cm^{-1} (νPd−H) that is at lower energy than that found for the corresponding Ni (1964 and 1943 cm^{-1}) and Pt (2070 cm^{-1}) hydrido complexes.[2] Other bands are at 1268 (ν_{as} SO_3), 1223 (ν_s CF_3), 1143 (ν_{as} CF_3), 1030 (ν_s SO_3), 637, 571, and 518 (SO_3 deformations) cm^{-1}. The IR absorptions suggest that the $CF_3SO_3^-$ anion is not coordinated to palladium.[6] The 900−800 cm^{-1} region of the IR spectrum shows the presence of bands of medium intensity at 873, 864, 821, and 812 cm^{-1} and a weak band at 845 cm^{-1}, due to CH_2 rocking vibrations of the diphosphine ligands. We have previously shown[7] that a square planar geometry of two dppe ligands around a metal center generates two bands of medium intensity and a weak band in the 900−800 cm^{-1} region, while a regular or distorted tetrahedral arrangement gives rise to four medium intensity bands and a weak band in the same region. Therefore, the IR data suggest that the $[HPd(dppe)_2]^+$ moiety of the solid Pd-hydride does not have a square pyramidal geometry (Figure 1a), with four P atoms in a square planar arrangement, and support a capped tetrahedron (Figure 1b) or a distorted trigonal bipyramid (Figure 1c) as the most probable structure in the solid state.

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* To whom correspondence should be addressed. E-mail: aresta@metea.uniba.it.

[†] University of Bari.

[‡] Hungarian Academy of Sciences.

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(5) To a yellow solution of $Pd(dppe)_2$ (0.219 g, 0.242 mmol) in anhydrous THF (25 mL), prepared under dinitrogen at 293 K, was added strictly anhydrous CF_3SO_3H (21.4 μL, 0.242 mmol), and the resulting mixture was stirred at 273 K for 3 h, during which a yellow solid was formed. The solution was concentrated and the obtained yellow solid filtered under dinitrogen, washed with anhydrous THF (3 × 2 mL), dried in vacuo, and characterized as $[HPd(dppe)_2]^+CF_3SO_3^-\cdot 1/8THF$ (**1**). Yield: 0.180 g, 0.170 mmol, 70.0%. Anal. Calcd for $C_{53}H_{49}F_3O_3P_4SPd\cdot 1/8THF$, **1**: C, 60.49; H, 4.74; P, 11.66; Pd, 10.02; S, 3.02%. Found: C, 60.87; H, 5.07; P, 11.49; Pd, 10.07; S, 2.84%.

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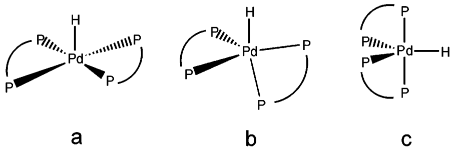

Figure 1. Possible structures of the cationic $[HPd(dppe)_2]^+$ moiety.

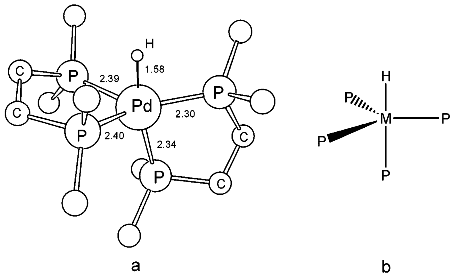

Figure 2. (a) IMOMM-optimized structure of the $[HPd(dppe)_2]^+$ cation with selected bond distances (in Å). The phenyl groups of the dppe ligands are represented by open spheres; the hydrogens of the ethane groups have been omitted for clarity. (b) Schematic structure of the $[HM(PR_3)_4]^+$ species.

To gain more insight into the structure of the cationic hydride species, we performed hybrid QM/MM calculations for the $[HPd(dppe)_2]^+$ moiety using the IMOMM methodology.[8]

The optimized structure of the gas phase $[HPd(dppe)_2]^+$ moiety indeed displays a distorted tetrahedral arrangement of the two diphosphine ligands around the metal center with the hydride atom positioned above a P_3 face of the distorted P_4 tetrahedron. The calculated Pd−P distances fall between 2.3 and 2.40 Å (Figure 2a), indicating that the coordinated dppe ligands are not equivalent.

This is not surprising given that one of the diphosphines is coplanar with the Pd−H bond ($dppe^{||}$), whereas the other lies nearly perpendicular to the hydride bond ($dppe^{\perp}$). This structure can be paralleled with those of $[HM(PR_3)_4]^+$ type monodentate phosphine hydride complexes,[9] which adopt a C_{3v} trigonal bipyramidal geometry with the hydride ligand in the axial position (see Figure 2b). However, the relatively narrow bite angle (∼86°) of the chelating dppe imposes a constraint on $dppe^{\perp}$ that coordinates with longer Pd−P bonds than $dppe^{||}$. Our structural predictions for $[HPd(dppe)_2]^+$ are consistent with the X-ray structure of an analogue complex, $HCo(dppe)_2$, recently reported by DuBois et al.[10]

The ^1H NMR spectrum of **1** in CD_2Cl_2 at 293 K shows, in addition to the resonances due to the aromatic and aliphatic protons,[11a] a quintet of multiplets at −7.58 ppm (1 H, $^2J_{P-H} = 54.4$ Hz) due to the hydride. The $^{31}P\{^1H\}$ NMR shows a broad singlet at 34.48 ppm.[11b] Such features match quite well the data reported for the Ni and Pt relevant complexes.[2,10] When reaction 1 is carried out in CH_3CN/THF, the resulting palladium hydride complex is not stable, so that a white solid is obtained that corresponds to the dicationic Pd complex $[Pd(dppe)_2]^{2+}2(CF_3SO_3^-)$. When **1** is added to CH_3CN at 298 K, it promptly reacts to afford a yellow solid that analyses for $Pd(dppe)_2$, and molecular hydrogen. From the yellowish mother solution, a white precipitate is obtained, characterized as $[Pd(dppe)_2]^{2+}2(CF_3SO_3^-)$ (see eq 2). This reaction demonstrates that **1** can transfer a hydride or a proton. The mechanism of formation of H_2 and the role of the solvent are still under investigation.

$$2[HPd(dppe)_2]^+CF_3SO_3^- = Pd(dppe)_2 + [Pd(dppe)_2]^{2+}2(CF_3SO_3^-) + H_2 \quad (2)$$

Reaction 2 is a new unprecedented reduction of a Pd(II)−H complex to Pd(0) through a proton transfer. A second molecule undergoes H^- abstraction, affording a Pd^{2+} moiety and H_2. The nature of the products has been confirmed by comparison with authentic samples and by ^1H and ^{31}P NMR spectra of the isolated species. We have monitored the reaction of **1** with CH_3CN in CD_2Cl_2 by ^1H and ^{31}P NMR. The intensity of the hydride signal at −7.58 ppm decreases with time, while a new signal appears at ca. −4.97 ppm (doublet, $^2J_{P-H} = 220.4$ Hz), which then vanishes with time. Simultaneously, H_2 is formed that gives a signal at 4.58 ppm. The $^{31}P\{^1H\}$ spectrum shows the slow disappearance of the signal at 34.54 ppm, while three new signals appear at 32.23, 33.38, and 58.35 ppm. The signal at 33.38 disappears with time, leaving only signals at 32.23 ($Pd(dppe)_2$) and 58.35 ($[Pd(dppe)_2]^{2+}$) ppm. Such features agree with the formation of a short-living intermediate hydride that converts into the final products reported in eq 2. When **1** is recrystallized from CH_2Cl_2/THF, a new hydride is isolated that shows a broad IR Pd−H stretching at 1900 cm^{-1}. The rest of the IR spectrum is substantially similar to that of **1**, with the exception of the region 900−800 cm^{-1} where changes are evident. Attempts to run the ^1H and ^{31}P NMR spectra afforded the conversion of the hydride into the products described in reaction 2. Such features show that hydride **1** is not stable in solution and can be isolated in reaction 1 because of its low solubility in THF at 273 K.

Solid **1** reacts with CO_2 (6 MPa) to afford a white complex that shows in its IR spectrum in Nujol two bands at 1630 and 1655 cm^{-1}, due to a formate moiety. Conversely, **1** does not react with carbonyl complexes such as $Ni(CO)_2(PPh_3)_2$ in CD_2Cl_2.

Compound **1** reacts very easily with a variety of H^+-donor or -acceptor species. In particular, it behaves as a hydride donor toward acids over a wide range of pK_a values ($-16 < pK_a < 10$).[12] In fact, an excess of CF_3SO_3H may convert **1** into the dicationic Pd complex $[Pd(dppe)_2]^{2+}2(CF_3SO_3^-)$, with release of H_2.[13] Much more intriguing is the reaction of **1** with the iminium tetraphenylborate salt $[(PhCH_2)HN{=}CMe_2]BPh_4$, which affords the Pd(II) dicationic complex and

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(8) See Supporting Information.

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(11) (a) ^1H NMR (CD_2Cl_2, 500 MHz, 293 K): δ 2.28 (s broad, 8 H, $Ph_2PCH_2CH_2PPh_2$), 7.24 (m, 32 H, *o*- and *m*-dppe), 7.40 (t, 8 H, *p*-dppe). (b) ^{31}P NMR experiments were run in CD_2Cl_2 at 202.48 MHz and 293 K.

(12) CF_3SO_3H, $pK_a = -16$ (in H_2O); $[(PhCH_2)HN{=}CMe_2]BPh_4$, $pK_a = 5.64$ (in H_2O/EtOH 10%).

(13) The addition of CF_3SO_3H to a solution of **1** in CD_2Cl_2 causes the appearance of a signal at 4.55 ppm in the ^1H NMR spectrum because of H_2, while the ^{31}P signal shifts from 34.48 to 58.35 ppm. Such resonance is characteristic of $[Pd(dppe)_2]^{2+}2(CF_3SO_3^-)$ that can be isolated from the reaction mixture.

the amine that is the result of an attack by the hydride onto the electrophilic carbon of the imine moiety (eq 3). The latter reaction is much slower than the former. Reaction 3 affords the same products observed when Pd(dppe)$_2$ is reacted with the iminium tetraphenylborate salt.[3c]

$$[\mathrm{HPd(dppe)_2}]^+\mathrm{CF_3SO_3}^- + [\mathrm{(PhCH_2)HN{=}CMe_2}]\mathrm{BPh_4} = [\mathrm{Pd(dppe)_2}]^{2+}(\mathrm{CF_3SO_3}^-)(\mathrm{BPh_4}^-) + \mathrm{(PhCH_2)HN{-}CHMe_2} \quad (3)$$

We have compared the reactivity of the [HPd(dppe)$_2$]$^+$ species with those of corresponding Ni and Pt analogues by calculating the energy of the gas phase [HM(dppe)$_2$]$^+$ + BH$^+$ = [M(dppe)$_2$]$^{2+}$ + H$_2$ + B reaction with various base (B) molecules and obtained the following trend for the hydride donor abilities: Pd > Pt > Ni.[8] We have also estimated the deprotonation energies of the [HM(dppe)$_2$]$^+$ complexes and found that the most acidic species corresponds to M = Pd.[8] Our results thus suggest that the [HPd(dppe)$_2$]$^+$ complex is more reactive and less stable than its first and third row analogues which is in line with experimental evidence available for the hydride of the Co and Ni triads.[14] They also provide a reasonable rationale for previous difficulties in synthesizing the Pd hydride.[2]

The reaction of the 18e$^-$ species Pd(dppe)$_2$ with a proton donor is of general interest as it can be considered a paradigm of the class of reactions of covalent tetrahedral species of general formula EX$_4$ with either a nucleophile (eq 4, where E is the carbon atom involved in a S$_N$2 process) or an electrophile (eq 5, where E is a metal center involved in protonation or alkylation processes).

$$\mathrm{EX_4 + Y^- \rightleftarrows EX_4Y^- \rightleftarrows EX_3Y + X^-} \quad (4)$$

$$\mathrm{EX_4 + A^+ = EX_4(A)^+} \quad (5)$$

The nature of the pentacoordinated adduct that is a common feature of the two processes and its geometry are still matter of investigation by theoretical groups for detailing the energy of the reaction and the barriers of interconverting limit structures.[15]

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Supporting Information Available: Computational details, Cartesian coordinates of the IMOMM-optimized structure of the [HPd(dppe)$_2$]$^+$ moiety, deprotonation energies calculated for the HM(dppe)$_2$$^+$ + B = M(dppe)$_2$ + BH$^+$ reactions (M = Ni, Pd, Pt; B = NH$_3$, NEt$_3$ and CF$_3$SO$_3$$^-$), energies of the gas phase [HM(dppe)$_2$]$^+$ + BH$^+$ = [M(dppe)$_2$]$^{2+}$ + H$_2$ + B reactions (M = Ni, Pd, Pt; B = NH$_3$, NEt$_3$, CF$_3$SO$_3$$^-$). This material is available free of charge via the Internet at http://pubs.acs.org.

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