Synthesis and spectroscopy of binuclear phosphine bridged palladium hydrides: $Pd_2HX_3[dppm]_2$ (X = Br, I; dppm = bis[diphenylphosphino]methane)

Rein U. Kirss *, David A. Forsyth, Marc A. Plante

Department of Chemistry, Northeastern University, Boston, MA 02115, USA

Abstract

Reactions of orange–red dichloromethane solutions of $Pd_2X_2dppm_2$ (X = Br, I; dppm = bis{diphenylphosphino}methane) with aqueous, concentrated HBr or HI at ambient temperature yields dark green solids which analyze for $Pd_2HX_3dppm_2$ (**1a** X = Br and **1b** X = I). No reaction is observed between $Pd_2X_2dppm_2$ and aqueous, concentrated HCl. Line shape analysis of dynamic ^{31}P-NMR spectra for **1a** and **1b** over a 100 °C range indicates that in each case a system involving two sets of chemically equivalent ^{31}P nuclei, mutually coupled, is exchanging ^{31}P environments via initial exchange with a less populated intermediate system in which all four ^{31}P nuclei are equivalent. From lineshape analysis of the ^{31}P spectra, activation parameters for the rates going to the symmetrical intermediates are as follows: **1a**: $\Delta G^\dagger(-78°) = 7.8 \pm 0.2$ kcal mol^{-1}, $\Delta H^\dagger = 7.5$ kcal mol^{-1}, $\Delta S^\dagger = -1.3$ e.u. and for **1b**: $\Delta G^\dagger(-78°) = 9.7 \pm 0.3$ kcal mol^{-1}, $\Delta H^\dagger = 8.9$ kcal mol^{-1}, $\Delta S^\dagger = -3.9$ e.u. Similar analysis of dynamic ^1H spectra for **1b** over a 80 °C range reveals two exchanging Pd–H sites with activation parameters for the exchange: $\Delta G^\dagger(-78°) = 9.5 \pm 0.3$ kcal mol^{-1}, $\Delta H^\dagger = 8.2$ kcal mol^{-1}, $\Delta S^\dagger = -6.9$ e.u. Compounds **1a** and **1b** decompose to a 1:2 mixture of $Pd_2X_2dppm_2$ and PdX_2dppm in solution with the evolution of hydrogen. Compound **1b** reacts with PPh_3 yielding $[HPPh_3^+][I^-]$ and $Pd_2I_2dppm_2$ while reaction of **1b** with KOH also yields $Pd_2I_2dppm_2$. Decomposition of **1b** is unchanged in the presence of styrene with no evidence for the formation of iodoethylbenzene or ethylbenzene.
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Keywords: Dinuclear palladium hydrides; Oxidative addition; Dynamic NMR spectroscopy

1. Introduction

The oxidative addition of small molecules (e.g. H_2, HX, or X_2 where X = halides and R = alkyl or aryl) to transition metal compounds is characteristic of coordinatively unsaturated, sixteen valence electron, d^8 metal complexes and is often implicated in catalytic processes involving these compounds [1]. The palladium(I) dimers, $Pd_2X_2dppm_2$ (X = Cl, Br, I, dppm = bis(diphenylphosphino) methane) react with X_2 to form thermally unstable palladium(II) dimers, $[Pd_2X_4dppm_2]$ [2]. Reaction of $Pd_2Cl_2dppm_2$ with H_2S yields $Pd_2Cl_2(\mu$-S)dppm_2 and is accompanied by the evolution of hydrogen [3] while $Pd_2X_2dppm_2$ acts as a hydrogenation catalyst [4].

In neither case are Pd-H intermediates from oxidative addition to Pd(I) detected. The oxidative addition of HX (X = Cl, Br) to $Pd_2Cl_2dppm_2$ forming $Pd_2HX_3dppm_2$ has been inferred from spectroscopic studies [5]. These dinuclear palladium hydrides were not isolated but react further with additional HX to form $Pd_2X_4dppm_2$ and H_2. Nevertheless, a series of hydride-bridged dipalladium dppm complexes $[Pd_2R_2(\mu$-H)dppm_2]PF_6$ [6] can be prepared by reduction of $[Pd_2R_2(\mu$-Cl)dppm_2]PF_6$ compounds, suggesting that additional examples of stable dinuclear palladium hydride complexes might be isolated [7]. Encouraged by the latter work we have re-investigated the reactions between $Pd_2X_2dppm_2$ and HX (X = Br, I). In the present paper we describe the synthesis and characterization of two binuclear palladium hydrides, $Pd_2HBr_3dppm_2$ and $Pd_2HI_3dppm_2$, from reactions between $Pd_2X_2dppm_2$ (X = Cl, Br, I) and concentrated

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* Corresponding author. Fax: +1-617-373-8795.
E-mail address: rkirss@neu.edu (R.U. Kirss).

aqueous hydrobromic or hydroiodic acid suggesting oxidative addition of HX and retention of the dppm bridged structure.

2. Experimental

2.1. General procedures

All compounds described in this work were handled using Schlenck techniques, in a M. I. Braun glove box under a purified argon or nitrogen atmosphere or on a vacuum line equipped with oil diffusion and mechanical pumps (10^{-3} Torr) [8]. Solvents were purified by refluxing over Na/benzophenone (benzene, toluene, tetrahydrofuran), Na (hexane) or P_2O_5 (dichloromethane) and distilled prior to use. Deuterated dichloromethane (CD_2Cl_2) was purchased from Cambridge Isotope Laboratories and dried as described above. $PdCl_2$, $PdBr_2$, triphenylphosphine, and bis(diphenylphosphino)methane (dppm), were purchased from Strem Chemicals and used as received. $Pd_2X_2dppm_2$ (X = Cl, Br, I) were prepared by literature methods [9].

NMR spectra were recorded at 300 MHz for ^1H and 121.4 MHz for $^{31}P\{^1H\}$ on a Varian XL300 spectrometer in 5 mm tubes equipped with a Teflon valve (Wilmad Glass, Inc.). Proton chemical shifts are referenced to TMS at 0 ppm with the residual protons in the solvent ($CDHCl_2$ at δ 5.24 ppm) as a calibrant. Phosphorus chemical shifts are reported relative to external 85% H_3PO_4 (0.0 ppm) with $Pd_2X_2dppm_2$ as a calibrant for low temperature spectra. Low temperature spectra were obtained from samples in 5-mm tubes in a 10 mm probe pre-calibrated for temperature determination. UV–vis spectra were recorded on a Perkin Elmer Lambda 4B UV–vis spectrometer. Conductivity measurements were performed in CH_2Cl_2 solution using a Beckman Instruments Model RC 16B2 Conductivity Bridge. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

2.2. Preparation of Pd₂HBr₃dppm₂ (1a)

Addition of 10 ml, (180 mmol) degassed, 48% aqueous HBr to a solution containing 390 mg (0.34 mmol) $Pd_2 Br_2dppm_2$ dissolved in 25 ml of CH_2Cl_2 caused the orange organic layer to turn dark green within 30 s. After stirring for 15 min, the CH_2Cl_2 layer was transferred by cannula to a clean vessel and the solvent was removed under vacuum. A dark green solid (105 mg, 25% yield), **1a**, was isolated. IR (KBr): 1572 cm^{-1}, 1483, 1434, 1188, 1097, 1026, 999, 775, 737, 688, 516, 485. ^1H (CD_2Cl_2, 20 °C): δ −8.46 (br s, 1H, Pd–H), 4.36 (br m, 4H, PCH₂P), 7.1–7.9 (four m, 40H, Ph₂PCH₂PPh₂); $^{31}P\{^1H\}$ (CD_2Cl_2, 20 °C): δ 3.15 s UV/vis (CH_2Cl_2): λ_{max} 607 nm. Anal. Calc. for

$C_{50}H_{45}Br_3P_4Pd_2$: C, 49.13; H; 3.71; Br, 19.61. Found: C, 49.48; H, 3.78; Br, 18.42%.

The yield of **1a** is improved by reducing the reaction time. For example, reaction of 130 mg (0.12 mmol) $Pd_2Cl_2dppm_2$ with excess aqueous HBr for 5 min yielded 87 mg (58% yield) of **1a**. The fine powdery product sticks to the walls of the reaction vessel rendering isolation of the product difficult and lowers the percent yield. The aqueous layer was evaporated to dryness. No phosphorous signals were observed in the ^{31}P-NMR spectrum of the residue.

Reaction of 170 mg (0.16 mmol) $Pd_2Cl_2dppm_2$ in 10 ml CH_2Cl_2 with 4 ml (72 mmol) of 48% aqueous DBr in D_2O yielded 150 mg of $Pd_2DBr_3dppm_2$ (75% yield). IR (KBr): 1540 cm^{-1}, 1487, 1433, 1262, 1097, 1035, 999, 781, 737, 688, 516, 482. ^1H (CD_2Cl_2): δ 4.36 (br m, 4H, PCH₂P), 7.1–7.9 (four m, 40H, Ph₂PCH₂PPh₂).

2.3. Preparation of Pd₂HI₃dppm₂ (1b)

As described for **1a**, addition of 10 ml, (55 mmol) degassed, 48% aqueous HI to a solution containing 131 mg (0.11 mmol) $Pd_2I_2dppm_2$ dissolved in 30 ml of CH_2Cl_2 caused the orange organic layer to turn dark green within 30 s. After stirring for 15 min, the CH_2Cl_2 layer was transferred by cannula to a clean vessel and the solvent was removed under vacuum. A dark green solid (79 mg, 55% yield), **1b**, was isolated. After verifying the molar conductivity of $[Pd_2(CH_3)_2(\mu-I)dppm_2][I]$ in our apparatus as a control experiment, Λ_M of **1b** was measured as 1 cm² mol^{-1} Ω^{-1}. UV–vis (CH_2Cl_2): λ_{max} = 663 nm. IR (KBr): 1721 cm^{-1}, 1572, 1482, 1433, 1263, 1095, 1026, 998, 777, 736, 689, 541, 515, 509, 485. ^1H (CD_2Cl_2, 20 °C): δ −6.14 (br s, 1H, Pd–H), 4.94 (br m, 4H, PCH₂P), 7.2–7.8 (four m, 40H, Ph₂PCH₂PPh₂); $^{31}P\{^1H\}$ (CD_2Cl_2, 20 °C): δ −2.77 s. Anal. Calc. for $C_{50}H_{45}I_3P_4Pd_2$: C, 44.05; H, 3.33; I, 27.92. Found: C, 43.90; H, 3.34; I, 27.59%.

Compound **1b** can also be prepared from reactions of $Pd_2Cl_2dppm_2$ and excess aqueous HI in comparable yields.

2.4. Attempted metathesis of 1b with NaPF₆ and NH₄PF₆

A solution of **1b** was prepared by addition of 10 ml (55 mmol) of 48% aqueous HI to 137 mg (0.13 mmol) $Pd_2Cl_2dppm_2$ in 50 ml CH_2Cl_2 at 0 °C. After 5 min, the green organic layer was decanted onto excess NH_4PF_6 and stirred for 15 min. The green solution was washed with 2 × 10 ml water, dried over $Na_2 SO_4$ and evaporated to dryness yielding 40 mg of a green solid. ^{31}P-NMR (CD_2Cl_2) reveals a mixture of **1b**, $Pd_2I_2dppm_2$ and PdI_2dppm. Substitution of $NaPF_6$ for NH_4PF_6 leads to the same result. Longer reaction times lead to

complete decomposition to a 2:1 mixture of PdI_2dppm to $Pd_2I_2dppm_2$.

2.5. Thermal decomposition of 1a and 1b

Compound **1b** (110 mg, 0.086 mmol) was heated to 100 °C under vacuum (100 mTorr) for 8 h. Analysis of the green solid by ^{1}H-NMR revealed that 50% of the starting material had decomposed to a 1:1 ratio of $Pd_2I_2dppm_2$ to PdI_2dppm.

Compound **1a** (400 mg, 0.33 mmol) was dissolved in 10 ml of DMF in a 50-ml Schlenck tube. The solution was frozen at −196 °C and evacuated to a base pressure of 10^{-2} Torr. After thawing the solution was stirred at ambient temperature until the green color of **1a** was replaced by the red color of $Pd_2Br_2dppm_2$. The evolution of hydrogen gas was followed by gas chromatography using the method described for H_2 evolution in reactions of $Pd_2Cl_2dppm_2$ and H_2S [3].

A solution of 25 mg (0.019 mmole) **1b** in CD_2Cl_2 was monitored by ^{31}P-NMR over 3 days. The green solution turns brown and finally red. The intensity of the broad resonance at −2.77 ppm decreases accompanied by the appearance of signals for $Pd_2I_2dppm_2$ at −9.84 ppm and PdI_2dppm at −62.0 ppm. Integration of the latter resonances indicates a 1:2 ratio of dinuclear to mononuclear products.

2.6. Reaction of 1b with triphenylphosphine

A 5-mm NMR tube equipped with a Teflon valve (Wilmad Glass Co.), was charged with 25 mg (0.019 mmole) of **1b** and 5 mg (0.019 mmole) PPh_3 in the glove box. CD_2Cl_2 was transferred under vacuum to the tube cooled in liquid nitrogen (−196 °C). After sealing, the tube was thawed immediately prior to recording the ^{1}H- and ^{31}P-NMR spectra. A rapid color change from green to red was observed within 10 min of thawing. ^{1}H-NMR indicated formation of a 4:1 ratio of $Pd_2I_2dppm_2$ to PdI_2dppm by integration of the $Ph_2PCH_2PPh_2$ resonances (quintet at 4.18 and triplet at 4.44 ppm, respectively). ^{31}P-NMR spectra confirm the formation of $Pd_2I_2dppm_2$, PdI_2dppm and $[PPh_3H^+][I^-]$ (^{31}P resonance at −10.3 ppm by comparison with the spectra of authentic samples.

2.7. Reaction of 1b with potassium hydroxide

A 5.8 mM solution (10 ml, 58 mmol) of **1b** was added to excess, pulverized KOH by syringe and stirred for 1 h. The green color of **1b** is replaced by a dark red color. The solution was filtered to remove KOH. Solvent was evaporated from the filtrate yielding a dark red solid. An 8:1 ratio of $Pd_2I_2dppm_2$ to PdI_2dppm was determined by integration of the CH_2 resonances of the dppm ligands in the ^{1}H-NMR spectrum of the product.
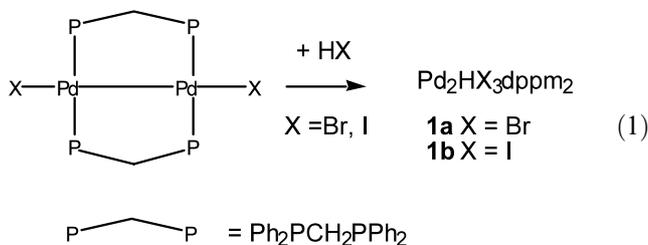
2.8. Reaction of 1b with styrene

Compound **1b** (100 mg, 0.075 mmol) and 16 µl (0.14 mmol) of styrene were dissolved in 2 ml CD_2Cl_2. ^{1}H-NMR indicates that **1b** is the sole palladium species present. The green color is replaced by a red color upon refluxing for 2 h. ^{1}H-NMR reveals a 2:1 mixture of PdI_2dppm to $Pd_2I_2dppm_2$. The ratio of styrene to palladium compounds remains constant. There is no evidence for formation of (iodoethyl)benzene.

The same results were observed when a solution of 31 mg (0.023 mmol) **1b** and 10 µl (0.088 mmol) styrene were heated under 1 atm. of H_2 in CD_2Cl_2.

3. Results

Addition of aqueous, concentrated HBr or HI to a dichloromethane solution of $Pd_2X_2dppm_2$ (X = Cl, Br, I) at ambient temperature leads to a rapid color change from orange red to dark green for the upper organic layer. No reaction is observed with aqueous, concentrated HCl. Separation of the layers and evaporation of the dichloromethane yields dark green solids of formula $Pd_2HX_3dppm_2$ (Eq. (1), **1a** X = Br and **1b** X = I).

$$
\begin{array}{c}
\text{structure} \quad \xrightarrow{+\ HX} \quad Pd_2HX_3dppm_2 \\
X = Br,\ I \quad \begin{array}{l} \mathbf{1a}\ X = Br \\ \mathbf{1b}\ X = I \end{array}
\end{array} \tag{1}
$$

$$ P\text{—}P = Ph_2PCH_2PPh_2 $$

Compounds **1a** and **1b** can also be prepared from $Pd_2Cl_2dppm_2$ and excess concentrated aqueous HX. The use of concentrated acid is critical as reactions between $Pd_2Cl_2dppm_2$ and less concentrated of HBr or gaseous HBr fails to produce the green color characteristic of $Pd_2HBr_3dppm_2$ leading instead to halide exchange and isolation of a 2:1 mixture of $Pd_2Br_2dppm_2$ and $PdBr_2dppm$.

The green solids are stable for weeks at −20 °C but heating **1b** at 100 °C under vacuum for 8 h leads to ≈ 50% decomposition to a 1:1 ratio of $Pd_2I_2dppm_2$ to PdI_2dppm. Dichloromethane solutions of both **1a** and **1b** decompose to a 1:2 mixture of $Pd_2X_2dppm_2$ and PdX_2dppm between 24 h (**1a**) and 72 h (**1b**) at ambient temperature. Formation of H_2 was measured by gas chromatography. The decomposition of **1a,b** in solution has thwarted attempts to grow crystals suitable for X-ray diffraction. The elemental analyses for **1a,b** are consistent with addition of HX to $Pd_2X_2dppm_2$ with no evidence for addition or retention of water. The measured bromine content of **1a** is lower than the calculated value, however, it is consistent with the loss

of HBr from the thermally unstable compound **1a**. The halide analysis for the more stable **1b** is well within acceptable limits. The similar spectral properties of **1a** and **1b**, (vide infra) support the assigned composition for **1a**.

Reaction of **1b** with triphenylphosphine yields triphenylphosphonium iodide, [PPh$_3$H][I], and a 4:1 mixture of Pd$_2$I$_2$dppm$_2$ to PdI$_2$dppm. Addition of a CH$_2$Cl$_2$ solution of **1b** to pulverized KOH leads to recovery of nearly 90% Pd$_2$I$_2$dppm$_2$ with the remaining 10% as PdI$_2$dppm. Exposure of solutions of **1b** to neutral alumina leads to an immediate discharge of the green color and isolation of Pd$_2$I$_2$dppm$_2$–PdI$_2$dppm mixtures making it difficult to apply strategies used in the preparation of [Pd$_2$R$_2$(μ-H)dppm$_2^+$][PF$_6^-$] [6] in the synthesis of cationic derivatives of **1a,b**.

The nature of **1a,b** was investigated by variable temperature ^{1}H- and ^{31}P-NMR spectroscopy. ^{1}H-NMR spectra for **1b** at 20 °C reveal a broad singlet at -6.14 (width at half height ≈ 42 Hz) assigned to a Pd–H resonance. Additional resonances in the ^{1}H spectrum at 4.94 (br m), and 7.2–7.8 ppm (four br m) are assigned to the methylene and aryl protons, respectively, of the green complex, Pd$_2$HI$_3$dppm$_2$. The ratio of the resonances at -6.14 and 4.94 ppm is found to be 1:4, consistent with a single Pd–H bond per molecule of **1b**. Similar spectra are observed for **1a** with a broad Pd–H resonance observed at -8.46 ppm. Substitution of DBr for HBr in equation 1 yields a dark green product spectroscopically identical to **1a** with the exception of the missing Pd–H resonance at -8.46 ppm. The chemical shifts for the Pd–H resonances are well within the range reported for palladium hydride complexes [6] [10] [11].

Dynamic NMR studies were carried out for **1a** and **1b** in CD$_2$Cl$_2$ solution. Cooling a sample of the latter compound from 20 to -58 °C leads to a steady upfield shift of the Pd–H resonance accompanied by a doubling in line width (Fig. 1) in the ^{1}H spectra at 300 MHz. At -78 °C the Pd–H resonance splits into two broad singlets at -6.54 and -7.5 ppm in a 4:1 ratio, respectively. The chemical shift values for the two Pd–H resonances are shifted further upfield at -98 °C but there is no further change in their relative intensities. The line shape changes are entirely reproducible and reversible. The absence of better resolved Pd–H resonances does not allow a bridging hydride to be distinguished from a terminal hydride based on phosphorus–proton coupling. Limited solubility of **1b** in CDFCl$_2$ and other low melting solvents prevents further investigations at even lower temperatures.

Proton decoupled ^{31}P spectra at 121.4 MHz show line shape changes over a temperature range of more than 100 °C. At -90 °C and below, the ^{31}P spectra for **1b** consist of two mutually coupled triplets and a singlet that occurs at a slightly lower frequency than the highest frequency triplet (Fig. 2, Table 1). The relative intensities of the triplet resonances to the singlet are 4:1, identical to the ratio of Pd–H resonances in the low temperature ^{1}H spectra. At higher temperatures, the two triplets and singlet broaden and eventually merge to a singlet. As can be seen in Fig. 2, the singlet appears to merge into the high frequency triplet as the temperature is raised, creating a larger, distorted triplet. The two triplets merge as the temperature is raised further. Again, the line shape changes are entirely reproducible and reversible. Similarly, two triplets are seen in Fig. 3 at the lowest temperature of -118 °C (155 K, Table 1) in the ^{31}P{^{1}H} spectrum of **1a**. The higher frequency triplet in this case is larger and distorted on the high frequency side, indicating the melding in of a higher frequency signal which is not resolved at this temperature due to exchange broadening.

Complete line shape analysis of the dynamic NMR spectra for **1a** and **1b** indicates that in each case a system involving two sets of two chemically equivalent ^{31}P nuclei, mutually coupled, is exchanging ^{31}P environments via initial exchange with a less populated intermediate system in which all four ^{31}P nuclei are equivalent. The complete line shape analysis was accomplished with the gNMR program [12]. Plots of theoretical spectra for different exchange rates are shown beside the experimental spectra in Figs. 2 and 3. Eyring plots of log k/T versus $1/T$ constructed from the kinetic data were satisfactorily linear and gave activation parameters for the rates going to the symmetrical intermediates as follows: **1a** $\Delta G^\dagger(-78°) = 7.8 \pm 0.2$ kcal mol^{-1}, $\Delta H^\dagger = 7.5$ kcal mol^{-1}, $\Delta S^\dagger = -1.3$ e.u.; for **1b** $\Delta G^\dagger(-78°) = 9.7 \pm 0.3$ kcal mol^{-1}, $\Delta H^\dagger = 8.9$ kcal mol^{-1}, $\Delta S^\dagger = -3.9$ e.u. The exchange process can not involve any substantial amount of direct exchange of the nuclei giving rise to the two triplets. Direct exchange would give rise to line shape changes that would not match the observed spectra. Fig. 4 is an example that shows the line shape simulation for the occurrence of only a direct exchange process for **1b** at a rate of 66 s^{-1}. The singlet assigned to the intermediate is not broadened in Fig. 4. If direct exchange were competitive with exchange through the intermediate, the singlet would broaden and blend with the other signals and, depending on the relative rates, spectra would show various line shapes between the limiting case in Fig. 4 and the limiting case in Fig. 2.

The variable temperature ^{1}H-NMR data for **1b** agree with the results from the ^{31}P spectra. Two Pd–H environments exchange rapidly above -90 °C. Activation parameters calculated from Eyring plots as above are within experimental error of the ^{31}P data: $\Delta G^\dagger(-78°) = 9.5$ kcal mol^{-1}, $\Delta H^\dagger = 8.2$ kcal mol^{-1}, $\Delta S^\dagger = -6.9$ e.u.

The IR spectra of **1a,b** offer little insight into the nature of the Pd–H bond. A definitive assignment for
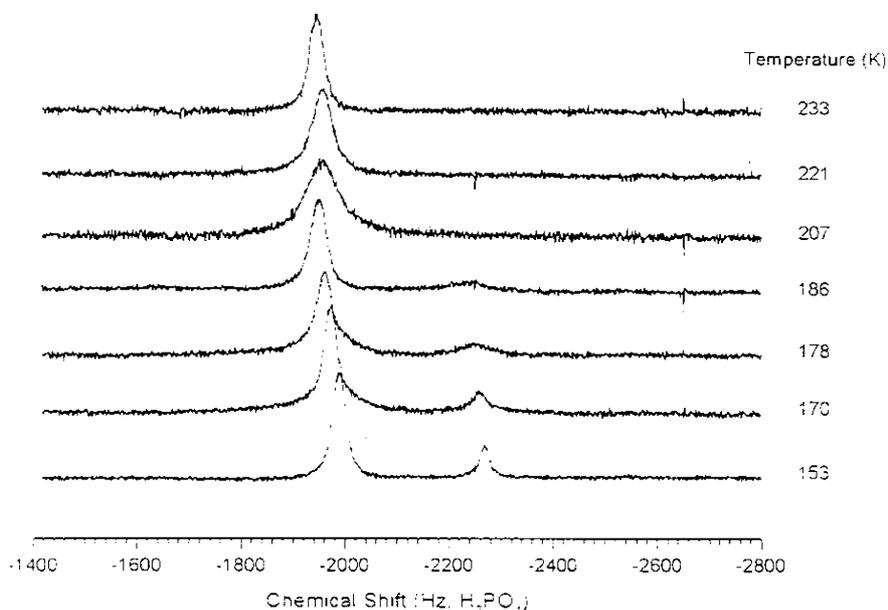
Fig. 1. Dynamic ^{1}H-NMR spectra at 300 MHz **1b** in CD_2Cl_2. Scale in ppm is arbitrarily referenced to tetramethylsilane with residual protons in the solvent ($CDHCl_2$) as a calibrant.
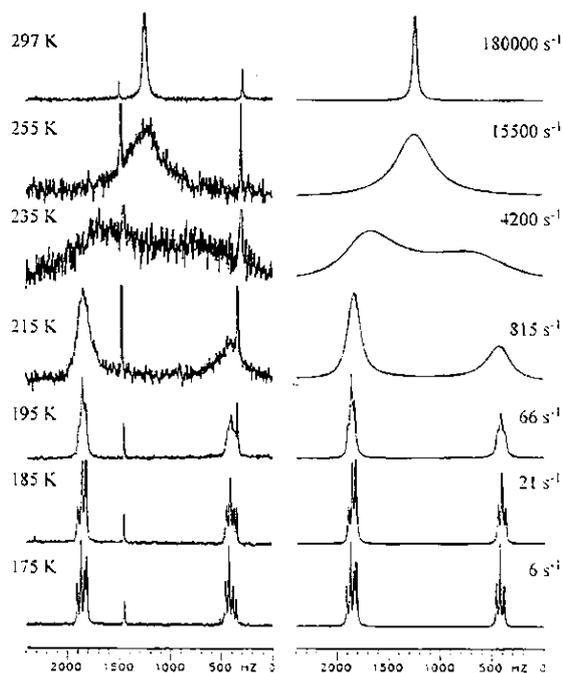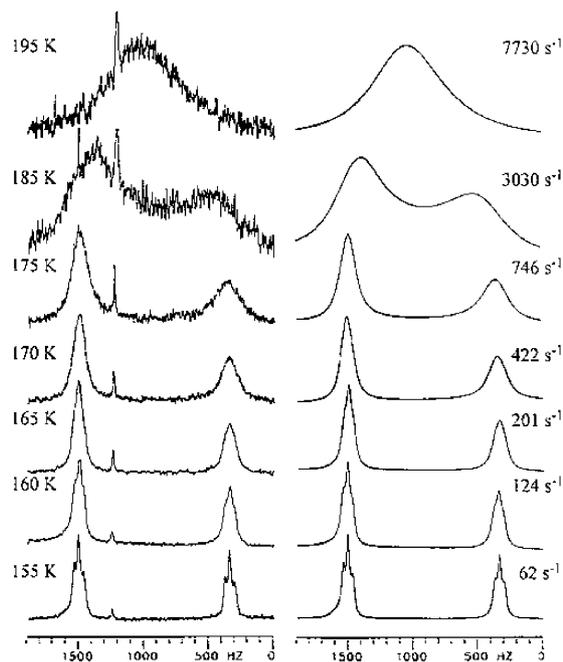

Fig. 2. Dynamic ^{31}P-NMR spectra at 121.4 MHz **1b** in CH_2Cl_2. Scale in Hz is arbitrarily referenced; see Table 1 for correct chemical shifts in ppm at the lowest temperature measured. The small non-exchanging singlets at 1440 and 350 Hz correspond to minor side-products $Pd_2I_4dppm_2$ and $Pd_2I_2dppm_2$, respectively.

Fig. 3. Dynamic ^{31}P-NMR spectra at 121.4 MHz **1a** in CH_2Cl_2. Scale in Hz is arbitrarily referenced; see Table 1 for correct chemical shifts in ppm at the lowest temperature measured. The small non-exchanging singlet at 1250 Hz corresponds to a minor side-products $Pd_2Br_4dppm_2$.

Pd–H absorptions can not be made. IR spectra of terminal, mononuclear palladium hydrides, $[Pd(PCy_3)_2H(L)][BF_4]$ (L = H_2O, CH_3CN) [13], are characterized by two absorptions at ≈ 720 cm^{-1} (δ Pd–H) and ≈ 2080–2115 cm^{-1} (ν Pd–H) neither of which are observed in the IR spectra of **1a,b**. Reduction

of mononuclear palladium(II) compounds with monodentate and chelating bidentate phosphine ligands gives rise to dinuclear hydride complexes such as $Pd_2(PPh_3)_4(\mu\text{-H})(\mu\text{-CO}][CF_3CO_2]$, $Pd_2dppp_2(\mu\text{-CO})(\mu\text{-H})^+$, and $Pd_2dippp(\mu\text{-H})_2$ but IR spectra for the bridging hydride complexes are not reported [14]. Similarly no assignment of IR absorptions for bridging

Table 1
Summary of ^{31}P-NMR chemical shift data For **1a** and **1b**

| Compound	T (K)	Chemical shift (ppm)			
		unsymm. int.	sym. int.	$Pd_2X_4dppm_2$	$Pd_2X_2dppm_2$
1a	155	6.93 [a], − 2.62 [a]	7.78 [b]	4.90	
	rel. conc.	1.00		0.15	
1b	165 K	2.84 [c], − 8.95 [c]	2.30	− 0.67	− 9.61
	rel. conc.	1.00		0.24	

[a] Mutually coupled with $J = 38$ Hz.
[b] From line shape analysis.
[c] Mutually coupled with $J = 36$ Hz.

hydride ligands in $[Pd_2R_2(\mu\text{-H})dppm_2][PF_6]$ [6] nor bridging hydride moieties in dinuclear platinum hydride complexes are reported [15].

After verifying the molar conductivity of $Pd_2I_2(CH_3)_2dppm_2$ [16] in our apparatus, the molar conductivity of **1b** ($\Lambda_M = 1$ cm^2 mol^{-1} Ω^{-1}) suggests that the latter is a non-electrolyte in CH_2Cl_2. The molar conductivity of **1b** is similar to that of $Pd_2I_2dppm_2$ and $Pd_2I_4dppm_2$ and much smaller than for $Pd_2I_2(CH_3)_2dppm_2$ (Table 2).

aqueous HX solutions. The products in Eq. (1) (**1a,b**) are extracted into the lower density, dichloromethane phase driving the reaction to completion and allowing for the facile separation of **1a,b** from excess acid before further reactions can occur. The failure of gaseous HX or lower concentrations of aqueous HX to produce $Pd_2HX_3dppm_2$ suggests that the formation constants for **1a,b** are small and that high concentrations of HX are required to drive the reaction to products. Even so, **1a** and **1b** are thermally unstable, decomposing to mixtures of $Pd_2X_2dppm_2$ and PdX_2dppm (Eq. (2)).

$$(2)$$
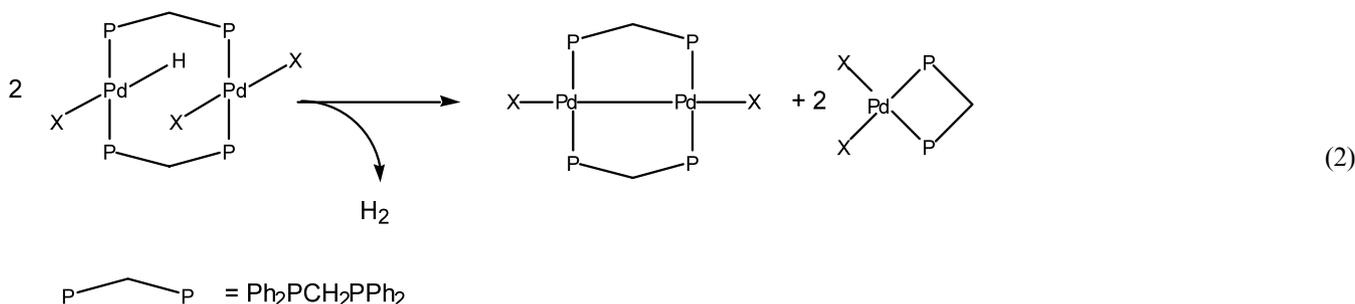
4. Discussion

4.1. Synthesis and Reactivity of *1a,b*

Reactions between concentrated HI or HBr and bis(diphenylphosphino) bridged palladium(I) dimers yield new dinuclear palladium hydrides, $Pd_2HX_3dppm_2$ (X = Br, I) as determined by elemental analysis and NMR spectrosocopy. These results confirm the brief reports of such compounds in the literature where apparently transient complexes with formula $Pd_2HX_3dppm_2$ (X = Br, I) were proposed in reactions between $Pd_2X_2dppm_2$ and HX [5]. Our ability to isolate and characterize **1a,b** lies in the use of concentrated,

Addition of base (PPh$_3$ or KOH) to **1a,b** allows for the removal of HX but this pathway competes with the loss of hydrogen and formation of a mixture of $Pd_2X_2dppm_2$ and PdX_2dppm. The facile deprotonation of mononuclear palladium hydrides such as $[(Cy_3P)_2Pd(H)(H_2O)^+]$ by excess phosphine or hydroxide has been reported [17].

The reaction between **1b** and styrene suggests that reductive elimination of HI is preferred over insertion into the Pd–H bond, a reaction typical of some palladium hydrides [18]. The preferential loss of HI is consistent with the reported reaction between dimethylacetylene dicarboxylate and the mononuclear palladium hydride $[(Cy_3P)_2Pd(H)NO_3]$ [19]. The isolation of

$Pd(PCy_3)_2(MeO_2CC=CCO_2Me)$ reflects a preference for reductive elimination of HX.

A precedent for reversible oxidative addition/reductive elimination of HX from dinuclear, platinum group metal complexes has been reported. The dinuclear platinum(I) compound, $Pt_2Cl_2dppm_2$, is protonated by HCl in chloroform yielding $[Pt_2Cl_2(\mu\text{-H})dppm_2][Cl]$ [20]. The protonation reaction is reversible; stirring $[Pt_2Cl_2(\mu\text{-}H)dppm_2][Cl]$ in CH_2Cl_2 regenerates $Pt_2Cl_2dppm_2$ with the loss of HCl. Reductive elimination of HX from mononuclear bis(phosphine)palladium(II) hydrido chlorides is often implicated in catalytic cycles [21].

The mechanism of hydrogen elimination from **1a,b** remains unclear. It has been proposed that **1a,b** react with HX to form H_2 and $Pd_2X_4dppm_2$ which in turn, decomposes to two equivalents of PdX_2dppm [5]. The demonstrated loss of HX from **1a,b** forming $Pd_2X_2dppm_2$ provides a source of HX for reaction with additional **1a,b** as shown in Eq. (3). Eq. (3) predicts a 2:1 ratio of PdX_2dppm to $Pd_2X_2dppm_2$, as observed in the thermal decomposition experiments involving **1a,b** (Eq. (2)). The reaction of $Pd_2X_2dppm_2$ with HX also resembles the reactions of $Pd_2X_2dppm_2$ with H_2E (E = S, Se) and X_2. [22] Hydrogen sulfide and hydrogen selenide react with $Pd_2Cl_2dppm_2$ by oxidative addition followed by dehydrogenation to the stable, isolable A-frame complexes $Pd_2Cl_2(\mu\text{-E})dppm_2$ (E = S, Se) (Eq. (4)). The formation of H_2 is proposed to involve deprotonation of the terminal EH ligand followed by reaction between H^+ and the Pd–H bond.

4.2. Solution structures of *1a,b*

Palladium hydride resonances in di- and polynuclear palladium phosphine hydride complexes have been observed over a wide range of chemical shift values ranging from 5.01 ppm (septuplet) for the bridging hydride in $[Pd_4dppm_4H_2]Cl_2$ [10] to -12.42 ppm (triplet) for the terminal palladium hydride $[Pd_2(\mu\text{-}Cl)H(CH_3)dppm_2][BPh_4]$ [11]. The bridging hydride ligands in cationic $[Pd_2R_2(\mu\text{-H})dppm_2]^+[PF_6^-]$ [6], are distinguished by quintets for the Pd–H resonances between -7.8 to -9 ppm. Details of variable temperature ^1H- or ^{31}P-NMR experiments for these dppm bridged compounds are not reported. The room temperature singlet in the ^{31}P-NMR spectrum of $Pd_2(dippp)_2(\mu\text{-H})(\mu\text{-CO})[Cl]$ [14c,d] broadens at $-80\,^{\circ}C$ but a limiting spectrum was not achieved.

The dynamic NMR spectra for **1a** and **1b** are consistent with two sets of two mutually coupled, chemically equivalent ^{31}P nuclei exchanging ^{31}P environments with a less populated intermediate system in which all four ^{31}P nuclei are equivalent. Thus the solution structure of **1a** and **1b** involves rapid equilibration of a symmetrical and an unsymmetrical structure. The bulk of the literature on dppm bridged palladium dimers suggests an equilibrium between a symmetrical hydride bridged dimer A (Fig. 5) and an unsymmetrical halide bridged dimer B where both A and B are ionic palladium(II) derivatives or tight ion pairs. For example, protonation of the $Pd_2I_2(\mu\text{-CH}_2)dppm_2$ with HBF_4 yields the ionic Pd(II) dimer $[Pd_2I(\mu\text{-I})(CH_3)\text{-}$

(3)

$P{\diagup\diagdown}P = Ph_2PCH_2PPh_2$

(4)

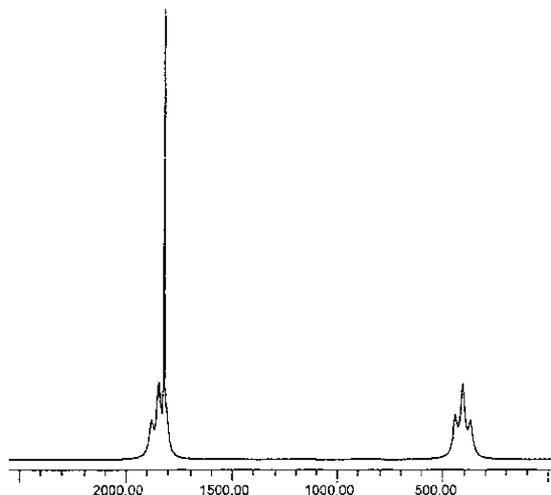$P{\diagup\diagdown}P = Ph_2PCH_2PPh_2$
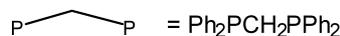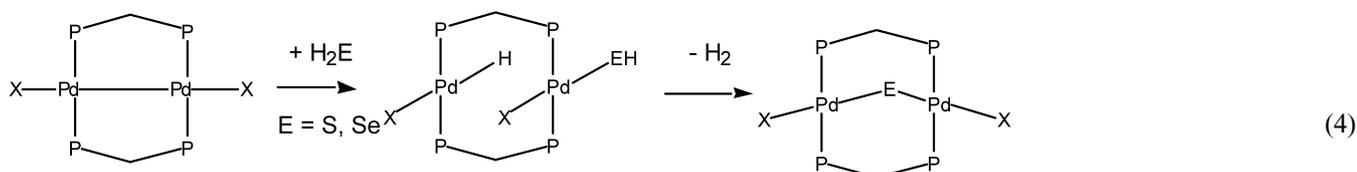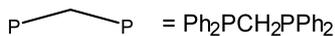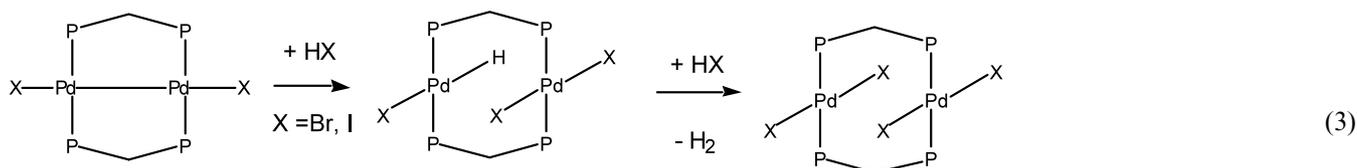
Fig. 4. Calculated ^{31}P-NMR spectra at 121.4 MHz **1b** for direct exchange of phosphorus nuclei at a rate of 66 s^{-1}

Table 2
Molar Conductivities of dppm bridged palladium dimers in CH_2Cl_2

Compound	Λ_M (cm^2 mol^{-1} Ω^{-1})
1b	1
Pd$_2$I$_2$dppm$_2$	0.2
Pd$_2$I$_4$dppm$_2$ [a]	0.2
Pd$_2$I$_2$Me$_2$dppm$_2$ [b]	53

[a] At −40 °C Λ_M at ambient temperature was 0.6 but some decomposition is expected.
[b] From Ref. [17] and verified in this work.

dppm$_{2+}$][BF$_4^-$] [16]. The ambient temperature ^{31}P{^{1}H}-NMR spectrum of [Pd$_2$I(μ-I)(CH$_3$)dppm$_{2+}$][BF$_4$] closely resembles that of **1a,b** below −90 °C. The singlet in the ^{31}P-NMR spectrum of Pd$_2$I$_2$(μ-CH$_2$)dppm$_2$ is replaced by two triplets at 13.1 and 3.1 ppm in [Pd$_2$(μ-I)(CH$_3$)(I)dppm$_{2+}$][BF$_4^-$]. The presence of a bridging
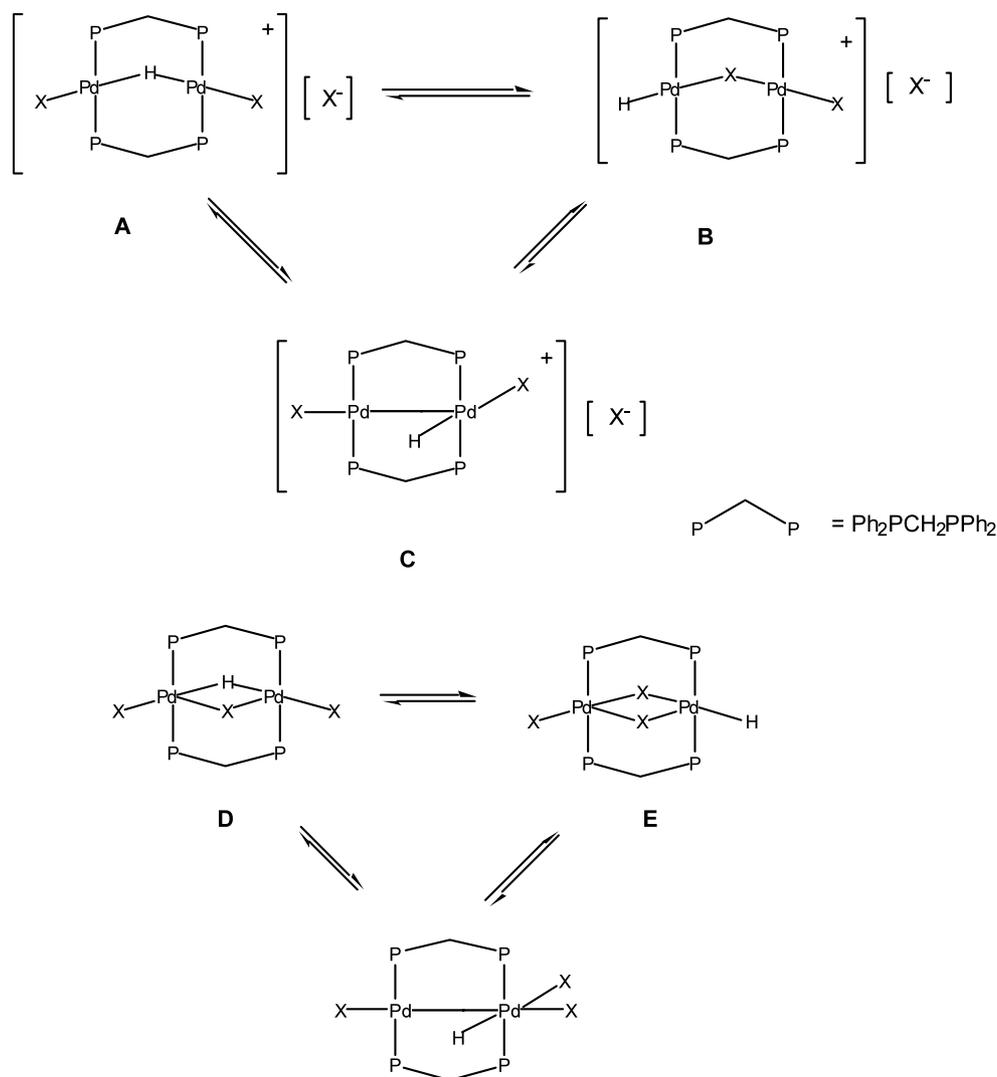
Fig. 5. Possible Solution Structures For **1a,b**.

iodide ligand $[Pd_2(\mu\text{-}I)(CH_3)(I)dppm_{2+}][BF_4^-]$ was verified by single crystal X-ray analysis. The room temperature ^{31}P-NMR spectra of the symmetrical dipalladium(II) cations $[Pd_2R_2 (\mu\text{-}Cl)dppm_2^+][PF_6^-]$ (R = CH$_3$, Ph) and $[Pd_2R_2(\mu\text{-}H)dppm_2^+][PF_6^-]$ (R = CH$_3$, Ph) are also singlets while the ^{31}P spectra of unsymmetrical compounds $[Pt_2(CH_3)Ph (\mu\text{-}Cl)dppm_2^-]$-$[PF_6^-]$ and $[PtPd(CH_3)_2(\mu\text{-}Cl)dppm_2^+][PF_6^-]$, consist of two triplets [6]. Equilibration of A and B can be achieved through an unbridged intermediate C similar to that proposed for the fluxionality observed in $[Pt_2H_2Cl\ dppm_2^+]$ [20] and $[PtPd(CH_3)_2(\mu\text{-}Cl)dppm_2^+]$ $[PF_6^-]$ [23].

The difficulty with structures **A** and **B** is the low molar conductivity for **1b** and our inability to exchange one of the halide ligands for PF_6^-. The molar conductivity of **1b** in CH$_2$Cl$_2$ ($\Lambda_M = 1$ cm^2 mol^{-1} Ω^{-1}) is significantly lower than that reported for $[Pd_2(\mu\text{-}I)(CH_3)(I)dppm_{2+}][BF_4^-]$ ($\Lambda_M = 59$ cm^2 mol^{-1} Ω^{-1}) or Pd$_2$I$_2$(CH$_3$)$_2$dppm$_2$ ($\Lambda_M = 53$ cm^2 mol^{-1} Ω^{-1}) in the same solvent [16]. The molar conductivity of **1b** is similar to that of Pd$_2$I$_2$dppm$_2$ ($\Lambda_M = 0.2$ cm^2 mol^{-1} Ω^{-1}) and Pd$_2$I$_4$dppm$_2$ ($\Lambda_M = 0.2$ cm^2 mol^{-1} Ω^{-1} at -40 °C, 0.6 cm^2 mol^{-1} Ω^{-1} at ambient temperature. Under the same conditions used in the preparation of $[Pd_2R_2(\mu\text{-}Cl)dppm_2^+][PF_6^-]$, attempts at exchanging PF_6^- for I$^-$ in **1b** led invariably to decomposition to PdI$_2$dppm and Pd$_2$I$_2$dppm$_2$. These observations suggest the candidates for the symmetrical and unsymmetrical structures for **1a,b** must include **D** and **E** (Fig. 5). The μ-iodo, μ-hydrido complex, $[Pd_2(\mu\text{-}H)(\mu\text{-}I)I_2dppm_2]$ (structure **D**) is consistent with the molar conductivity data but is unprecedented in the literature of dinuclear, dppm bridged palladium complexes. Nevertheless, dinuclear palladium complexes with two bridging hydrides, e.g. Pd$_2$dippp$_2$(μ-H)$_2$ [24], or halide ligands Pd$_2$(CH$_3$)$_2$(μ-Cl)$_2$(AsPh$_3$)$_2$, Pd$_2$Cl$_2$(μ-Cl)$_2$(AsPh$_3$)$_2$ and $[Pd_2dppm_2(\mu\text{-}Cl)_2^{+2}][BF_4^-]_2$ are known [6,25,26]. The unsymmetrical dimer **D** follows from the proposed face to face structure of Pd$_2$X$_4$dppm$_2$ [2,5]. Our inability to observe P–H coupling further hampers our efforts at distinguishing between **A** and **E**.

5. Conclusions

Two new dinuclear palladium hydride complexes **1a,b** have been prepared by oxidative addition of hydrogen halides to formally palladium(I) centers in phosphine bridged palladium dimers Pd$_2$X$_2$dppm$_2$ similar to the oxidative addition of H$_2$S or halogens to Pd$_2$Cl$_2$dppm$_2$. The resulting hydride complexes exhibit dynamic behavior

The solution structures of **1a,b** are consistent with covalent bonding between palladium, hydride and all three halide ligands or the existence of an extremely tight ion pair. This is quite different from palladium (alkyl)hydride complexes $[Pd_2R_2(\mu\text{-}H)dppm_{2+}][PF_6^-]$, palladium (alkyl) halide complexes Pd$_2$I$_2$(CH$_3$)$_2$dppm$_2$ and platinum hydride complexes $[Pt_2Cl_2(\mu\text{-}H)dppm_{2+}][X^-]$ (X = Cl, PF$_6$) all of which behave as electrolytes. Further studies on the origin of the intense green color and structure of **1a,b** are in progress.

References

[1] (a) J.P. Collman, L.S. Hegedus, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1980;
(b) C.M. Lukehart, Fundamental Transition Metal Organometallic Chemistry, Brooks/Cole Publishing Co, Monterey, CA, 1985.

[2] C.T. Hunt, A.L. Balch, Inorg. Chem. 20 (1981) 2267.

[3] T.Y.H. Wong, A.F. Barnabbas, D. Sallin, B.R. James, Inorg. Chem. 34 (1995) 2278.

[4] T.E. Eisenschmid, R.U. Kirss, P.P. Deutsch, S.I. Hommeltoft, R. Eisenberg, J. Bargon, R.G. Lawler, A.L. Balch, J. Am. Chem. Soc. 109 (1987) 8089.

[5] B.R. James, Pure Appl. Chem. 69 (1997) 2213.

[6] (a) C. Xu, G.K. Anderson, Organometallics 13 (1994) 3981;
(b) R.A. Stockland, Jr, G.K. Anderson, N.P. Rath, Inorg. Chim. Acta 259 (1997) 173.

[7] K.A. Fallis, C. Xu, G.K. Anderson, Organometallics 12 (1993) 2243.

[8] D.F. Shriver, Manipulation of Air Sensitive Compounds, McGraw Hill, New York, 1969.

[9] P.G. Pringle, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1983) 889.

[10] R.U. Kirss, R. Eisenberg, Inorg. Chem. 28 (1989) 3372.

[11] S.J. Young, B. Kellenberger, J.H. Reibenspies, S.E. Himmel, M. Manning, O.P. Anderson, J.K. Stille, J. Am. Chem. Soc. 110 (1988) 5744.

[12] Spectra were analyzed using the g NMR program, Chewell Scientific Publishing Ltd., Oxford, UK.

[13] P. Leoni, M. Sommovigo, M. Pasquali, S. Midollini, D. Braga, P. Sabatino, Organometallics 10 (1991) 1038.

[14] (a) V.N. Zudin, V.D. Chinakov, V.M. Nekipelov, V.A. Likholobov, Yu.I. Yermakov, J. Organometal. Chem. 289 (1985) 425;
(b) M. Portnoy, F. Frolow, D. Milstein, Organometallics 10 (1991) 3960;
(c) M. Portnoy, D. Milstein, Organometallics 13 (1994) 600;
(d) I. Toth, C.J. Elsevier, Organometallics 13 (1994) 2118;
(e) A.R. Siedle, R.A. Newmark, W.B. Gleason, Inorg. Chem. 30 (1991) 2005.

[15] M.P. Brown, R.J. Puddephatt, M. Rashidi, K.R. Seddon, Inorg. Chim. Acta 23 (1977) L27.

[16] A.L. Balch, C.T. Hunt, C.-L. Lee, M.M. Olmstead, J.P. Farr, J. Am. Chem. Soc. 103 (1981) 3764.

[17] P. Leoni, M. Sommovigo, M. Pasquali, S. Midollini, D. Braga, P. Sabatino, Organometallics 10 (1991) 1038.

[18] V.V. Grushin, Chem. Rev. 96 (1996) 2011.

[19] H.C. Clark, C.R. Milne, J. Organometal. Chem. 161 (1978) 51.

[20] M.P. Brown, R.J. Puddephatt, M. Rashidi, J. Chem. Soc. Dalton Trans. (1978) 516.

[21] J. Tsuji, Palladium Reagents and Catalysts, Wiley, New York, 1995.

[22] (a) G. Besenyi, C.-L. Lee, J. Gulinski, S.J. Rettig, B.R. James, D.A. Nelson, M.A. Lilga, Inorg. Chem. 26 (1987) 3622;
(b) G. Besenyi, L. Parkyanyi, L.I. Simandi, B.R. James, Inorg. Chem. 34 (1995) 6118.

[23] C. Xu, G.K. Anderson, Organometallics 15 (1996) 1760.

[24] (a) M.D. Fryzuk, B.R. Lloyd, G.K.H. Clentsmith, S.J. Rettig, J. Amer. Chem. Soc. 113 (1991) 4332;
(b) M.D. Fryzuk, B.R. Lloyd, G.K.H. Clentsmith, S.J. Rettig, J. Amer. Chem. Soc. 114 (1994) 3804.

[25] F. Neue, M. Ghedini, A. Tiripicchio, F. Ugozzoli, Organometallics 11 (1992) 795.

[26] In both $Pd_2dippp_2(\mu\text{-}H)_2$ and $[Pd_2dppm_2(\mu\text{-}Cl)_2][BF_4]_2$ the diphosphine ligand does not bridge the two palladium but chelates a single metal center.