Hydrido Complexes of Palladium

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Contents

Vladimir Grushin was born in Moscow, Russia. Having received his Ph.D. degree in chemistry at the State University of Moscow in 1984, he moved to the Institute of Organo-Element Compounds, USSR Academy of Sciences, then to the University of Ottawa, and finally joined the faculty at Wilfrid Laurier University, Waterloo, Ontario, Canada. His research interests are in the areas of organometallic chemistry and catalysis with metal complexes, transition metal hydrides, and halonium ions.

I. Introduction

Hydrido complexes of transition metals represent a unique class of compounds which play an exceedingly important role in various fields of chemistry. In addition to their remarkable relevance to theoretical and coordination chemistry, transition metal hydrides are of considerable significance in catalysis, organic synthesis, and hydrogen storage. The first transition metal hydride was synthesized and intuitively, but correctly, formulated as $[H_2Fe(CO)_4]$ in the early 1930s.[1] More than 20 years had passed since that discovery before the synthesis and reliable characterization of $[\eta^5-C_5H_5)_2ReH]$,[2a] $[(Et_3P)_2Pt(H)-Cl]$,[2b] and $[ReH_9]^{2-}$ anion[2c] established unambiguously the fact of existence of the transition metal−hydrogen bond, its covalent character and considerable strength. The extensive and highly successful research in the field of transition metal hydrides for the last 40 years, has left an impressive legacy. Three books[3−5] and a number of reviews[6−27] have been published on various general aspects of hydrido transition metal chemistry, including molecular hydrogen complexes.[20−27]

Palladium hydrides are of special interest due to their exceptional relevance to catalysis. Perhaps, no other metal can compete with palladium in the ability to catalyze efficiently many useful processes, such as various oxidation, reduction, isomerization, carbonylation, and coupling reactions, aromatic nucleophilic substitution, cyclizations, cycloadditions, and others. In fact, various hydrido complexes of palladium have been proposed as key intermediates in diverse Pd-catalyzed reactions described in hundreds of experimental papers and several specialized monographs.[28−30] Obviously, the synthesis of palladium hydrides and investigation of their chemical properties represent a special challenge in organometallic chemistry and catalysis. However, the number of palladium hydrido complexes synthesized and reliably characterized to date is rather small, and the reactivity of Pd hydrido complexes still remains insufficiently explored. Despite the well-known, exceptionally high affinity of Pd metal for hydrogen,[31]

soluble molecular hydrides of palladium are rather unstable, and in many cases they cannot be isolated, but only generated and characterized in solution at low temperature. The stability of similar hydrides decreases dramatically when going from platinum to palladium. For instance, $[(Ph_3P)_2Pt(H)Cl]$ is air- and moisture-stable in the solid state and in solution, even in the presence of alkali or strong acids, whereas $[(Ph_3P)_2Pd(H)Cl]$ decomposes immediately upon exposure to air and is only moderately stable under neutral conditions in an inert atmosphere. Many Pt polyhydrides, including one recently reported η^2-H_2 complex[32] and a number of mononuclear dihydrides have been prepared and fully characterized. At the same time, nonclassical Pd hydrides have not been prepared thus far (except for the matrix-isolated PdH_2; see section VI). The only mononuclear Pd dihydride, $[(Cy_3P)_2Pd(H)_2]$, described in the literature[33,34] has not been unambiguously characterized due to its poor solubility (see section II.A.f). In the excellent, exhaustive review of Ni, Pd, and Pt hydrides by Roundhill,[35] which was published 20 years ago, one can find data on 220 platinum hydrides, 45 nickel hydrides, and only 21 hydrido complexes of Pd.[36] Although many new hydrido complexes of palladium have been synthesized since then, the situation, in general, has not changed. Among the nickel triad metals, palladium remains the least generous contributor to the overall number of reliably characterized molecular hydrides.

The early data on hydrido complexes of palladium can be found in Hartley's book[39] and the previously mentioned review by Roundhill.[35] A brief survey, covering the literature up to 1979, was later published by Maitlis, Espinet, and Russell.[40] For the last 15 years the chemistry of Pd hydrides has developed quite significantly, opening new horizons in this very difficult but challenging field. Among the recent accomplishments are (i) the first examples of the hydrido ligand location in a number of X-ray studies of Pd complexes, (ii) the development of new, efficient methods for generation of Pd hydrido species, (iii) the synthesis and first full characterization of binuclear Pd complexes with bridging hydrido ligands, (iv) the discovery of novel complexes of Lewis acids with binuclear Pd hydrides, (v) the discovery of complexes with a novel Pd−H−P bonding mode, (vi) preparation and structural characterization of stoichiometric solid state ternary palladium hydrides, and (vii) remarkable theoretical studies on hydrido complexes of palladium. The goal of this review is to present, classify, analyze, and generalize data on the synthesis, structural characterization, stability, and reactivity of molecular palladium hydrides. Some catalytic aspects will also be considered and discussed, but only to limited extent (see section V). We do not think that all numerous articles where Pd hydrides were proposed, without firm proof, as intermediates in various catalytic and stoichiometric transformations, should be cited here. Neither is it justified, in our opinion, to survey in the present article all pieces of work describing indirect evidence for *in situ* generation and subsequent reactions of hydridopalladium species.[41] Most attention will rather be paid

to those hydrido complexes which have been isolated and fully, reliably characterized.

II. Synthesis of Mononuclear Palladium Hydrides

The first palladium hydride to be isolated[53−55] and structurally characterized[56] was $[(Et_3P)_2Pd(H)Cl]$. Since the mid-1960s, a number of neutral and cationic hydrido complexes of palladium have been prepared and characterized by various techniques. In fact, all known general methods for the synthesis of transition metal hydrides can be applied to the preparation of (hydrido)palladium complexes. These include the reduction methods, oxidative addition of acids and some element−hydrogen bonds to low-valent Pd species, hydrogenolysis of the Pd−C bond, β-elimination reactions, and ligand exchange processes in which the Pd−H bond of the starting hydride remains intact. As most Pd hydrides are considerably labile, the reaction conditions for their synthesis should be carefully chosen and meticulously optimized. In addition, it is worth emphasizing the well-established fact that many procedures for the preparation of Ni and Pt hydrides cannot be extended to similar Pd complexes.
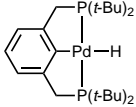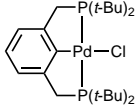
A. Neutral Hydrides

a. Reduction of Palladium Compounds

In 1958, Chatt, Duncanson, and Shaw[2b,57] reported their attempt to apply the reduction techniques, which proved efficient in the synthesis of (hydrido)-platinum complexes (e.g., N_2H_4, $LiAlH_4$), to the synthesis of Pd hydrides. An IR frequency (2035 cm^{-1}), ascribable to ν(Pd−H) of $[(Et_3P)_2Pd(H)Cl]$, was observed. However, neither in this case, nor in the reduction of $[(Et_3P)_2PdCl_2]$ with Ph_3GeH[54] were palladium hydrides isolated in pure form. The hydrido complex, $[(Et_3P)_2Pd(H)Cl]$, was obtained in pure form only when Brooks and Glockling[53−55] used Me_3GeH instead of Ph_3GeH, as the reducing agent. The more stable bromopalladium hydride, $[(Et_3P)_2Pd(H)Br]$, was obtained similarly, the reduction being catalyzed by palladium black (eq 1). Both hydrides were characterized by elemental analysis, IR, and ^1H NMR spectroscopy.[55] Although successful with the triethylphosphine complexes, this method failed to produce pure $[(Pr_3P)_2Pd(H)Cl]$. Furthermore, the reduction of $[(Ph_3P)_2PdCl_2]$ with Me_3GeH under similar conditions did not furnish any Pd hydride at all.[55]

$$[(Et_3P)_2PdX_2] + Me_3GeH \longrightarrow [(Et_3P)_2Pd(H)X] + Me_3GeX \quad (1)$$

$$X = Cl, Br$$
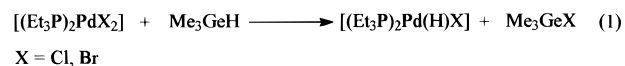
These first experiments clearly demonstrated[55] that unlike Pt complexes, $[(R_3P)_2Pt(H)Cl]$, the palladium analogues do not survive under strongly acidic (see section II.A.b and eq 5 below) or basic conditions (presumably, due to the elimination of HCl; see section V). Among the reducing agents that have been successfully used in the preparation of various Pd hydrides are $[(Cy_3P)_2Ni(H)(BH_4)]$,[58,59] $NaBH_4$,[60−64] and $LiHBEt_3$ (Super-Hydride).[65] The palladium hydrido complexes prepared this way are listed in Table 1. It is noteworthy that reducing agents should be carefully chosen for every particular

Table 1. Neutral Mononuclear Pd Hydrides Synthesized via Reduction Methods

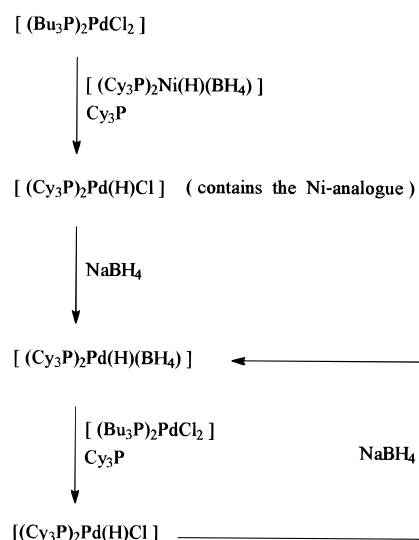| hydride	starting complex	reducing agent	isolated yield, %	characterization[a]	ref
[(Et$_3$P)$_2$Pd(H)Cl]	[(Et$_3$P)$_2$PdCl$_2$]	Me$_3$GeH	65	EA, IR, ^{1}H NMR	55
[(Et$_3$P)$_2$Pd(H)Br]	[(Et$_3$P)$_2$PdBr$_2$]	Me$_3$GeH[b]	95[c]	EA, IR, ^{1}H NMR	55
[(i-Pr$_3$P)$_2$Pd(H)Cl]	[(Bu$_3$P)$_2$PdCl$_2$]	[(i-Pr$_3$P)$_2$Ni(H)BH$_4$] + NaBH$_4$ + i-Pr$_3$P[d]	51	EA,[e] IR, ^{1}H NMR	59
[(Cy$_3$P)$_2$Pd(H)Cl]	[(Bu$_3$P)$_2$PdCl$_2$]	[(Cy$_3$P)$_2$Ni(H)BH$_4$] + NaBH$_4$ + Cy$_3$P[d]	68	EA, IR, ^{1}H NMR	59
[(Cy$_3$P)$_2$Pd(H)Cl]	[(Bu$_3$P)$_2$PdCl$_2$]	NaBH$_4$ + Cy$_3$P	50	EA, IR, ^{1}H NMR	62, 63
[(Cy$_3$P)$_2$Pd(H)NO$_3$]	[(Cy$_3$P)$_2$Pd(NO$_3$)$_2$]	NaBH$_4$	93	EA, IR, ^{1}H NMR	62
(structure: Pd–H with two P(t-Bu)$_2$ groups)	(structure: Pd–Cl with two P(t-Bu)$_2$ groups)	NaBH$_4$	96	EA,[e] IR, ^{1}H NMR	64
[(Me$_2$NCS$_2$)Pd(PEt$_3$)H]	[(Me$_2$NCS$_2$)Pd(PEt$_3$)Cl]	LiHBEt$_3$	NA[f]	^{1}H NMR	65

^{a} EA = elemental analysis. ^{b} The reduction is catalyzed with Pd metal. ^{c} Crude material. ^{d} The "cyclic" procedure. See text and Scheme 1. ^{e} Unsatisfactory elemental analysis. ^{f} The hydride is unstable above −25 °C and was not isolated.

Pd precursor. For instance, the reduction of [(R$_3$P)$_2$-PdCl$_2$] (R = i-Pr or Cy) with borohydride reagents resulted in no hydride species,[58,59] although similar reactions of nickel complexes furnished [(R$_3$P)$_2$Ni(H)-Cl] in satisfactory yield.[59,66] At the same time, the reaction between [(Bu$_3$P)$_2$PdCl$_2$] and NaBH$_4$ gave rise to the corresponding chloro hydrido complex which was converted *in situ* to [(Cy$_3$P)$_2$Pd(H)Cl] upon addition of tricyclohexylphosphine.[63] The reduction of [(t-Bu$_3$P)$_2$Pt(H)Cl] with NaBH$_4$ afforded the corresponding dihydride, [(t-Bu$_3$P)$_2$Pt(H)$_2$],[67] whereas treatment of [(t-Bu$_3$P)$_2$Pd(H)Cl] with NaBH$_4$ under similar conditions gave the zero-valent complex, [(t-Bu$_3$P)$_2$-Pd].[68] Complex mixtures of hydrido species were obtained by the treatment of [(R$_3$P)$_2$PdX$_2$] (R = Et, Bu; X = Cl, Br) with [(R′$_3$P)$_2$M(H)(BH$_4$)] (R′ = Cy, i-Pr; M = Ni, Pd). The reaction involved the reduction, followed by phosphine exchange. Although the resulting hydrides, [(Et$_3$P)$_2$Pd(H)Cl], [(Bu$_3$P)$_2$Pd(H)-Cl], [(Bu$_3$P)$_2$Pd(H)Br], [(Et$_3$P)(Cy$_3$P)Pd(H)Cl], [(Bu$_3$P)-(Cy$_3$P)Pd(H)Cl], [(Bu$_3$P)(Cy$_3$P)Pd(H)Br], and [(Bu$_3$P)-(i-Pr$_3$P)Pd(H)Cl], were not isolated, they were reliably characterized *in situ* by ^{1}H NMR.[59] The addition of excess Cy$_3$P (or i-Pr$_3$P) to such mixtures of Pd hydrides resulted in the isolation of the [(R$_3$P)$_2$Pd-(H)Cl] (R = Cy$_3$P or i-Pr$_3$P) contaminated with the corresponding Ni hydrides. These mixtures were then treated with NaBH$_4$ to give crude [(R$_3$P)$_2$Pd(H)-(BH$_4$)] which were subsequently converted to the pure chloro hydrido complexes by treatment with [(Bu$_3$P)$_2$PdCl$_2$] and excess Cy$_3$P (or i-Pr$_3$P).[58,59] While apparently tedious, this so-called "cyclic route" (see Scheme 1) can be useful for the preparation of pure [(R$_3$P)$_2$Pd(H)Cl] (R = Cy, i-Pr) on a gram scale.
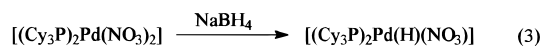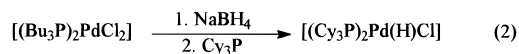
Much more simple and very efficient procedures have been developed by Saito and co-workers[60−63] for the synthesis of [(Cy$_3$P)$_2$Pd(H)X] (X = Cl, NO$_3$) in 50 and 93% yield, respectively (eqs 2 and 3). Interestingly, only the yellow form of [(Cy$_3$P)$_2$Pd(NO$_3$)$_2$] gave the hydride upon treatment with NaBH$_4$ in ethanol, whereas no hydride formed when the green form of the same precursor was used.[62] It is noteworthy that the (hydrido)palladium nitrate, [(Cy$_3$P)$_2$Pd(H)NO$_3$], is an exceptionally convenient reagent for the preparation of various neutral and cationic Pd hydrides via metathesis (see sections II.A.e and II.B.a).

Superhydride (LiHBEt$_3$), was found the best among other reagents, including Li(sec-Bu)$_3$BH and sodium cyanoborohydride, for the synthesis of [(Me$_2$NCS$_2$)-

Scheme 1

[(Bu$_3$P)$_2$PdCl$_2$]

↓ [(Cy$_3$P)$_2$Ni(H)(BH$_4$)] Cy$_3$P

[(Cy$_3$P)$_2$Pd(H)Cl] (contains the Ni-analogue)

↓ NaBH$_4$

[(Cy$_3$P)$_2$Pd(H)(BH$_4$)] ←

↓ [(Bu$_3$P)$_2$PdCl$_2$] Cy$_3$P   NaBH$_4$

[(Cy$_3$P)$_2$Pd(H)Cl] ————

Pd(H)(Et$_3$P)] from the corresponding chloride.[65] Although the hydride was not isolated (it is stable only below −25 °C) it was reliably characterized by low-temperature ^{1}H NMR spectral data.

$$[(Bu_3P)_2PdCl_2] \xrightarrow[\text{2. Cy}_3\text{P}]{\text{1. NaBH}_4} [(Cy_3P)_2Pd(H)Cl] \quad (2)$$

$$[(Cy_3P)_2Pd(NO_3)_2] \xrightarrow{\text{NaBH}_4} [(Cy_3P)_2Pd(H)(NO_3)] \quad (3)$$

b. Oxidative Addition of Strong Acids

Most tertiary phosphine palladium(0) complexes are very reactive toward HCl. One of the very few exceptions is the water-soluble [Pd(P(CH$_2$OH)$_3$)$_4$] whose ^{31}P NMR chemical shift does not change significantly upon addition of HCl to its aqueous solution.[69,70] In fact, 10^{-2} M aqueous solutions of [M(P(CH$_2$OH)$_3$)$_4$] are strongly alkaline if M = Pt (pH = 10−11), but almost neutral when M = Pd (pH = 7−8).[69] This ideally demonstrates that in zero-valent Pt and Pd complexes of similar structure, platinum is much more basic than palladium.

The first (triarylphosphine)palladium hydride was prepared in 1970 by the oxidative addition of HCl to [(Ph$_3$P)$_3$Pd(CO)] or [(Ph$_3$P)$_4$Pd] (eq 4).[71] It is worth noting at this point that Brooks and Glockling's attempt to synthesize [(Ph$_3$P)$_2$Pd(H)Cl] from [(Ph$_3$P)$_2$-PdCl$_2$] and trimethylgermane failed.[55] A number of

Table 2. Neutral Mononuclear Pd Hydrides Synthesized via Oxidative Addition of HCl to Pd(0) Complexes

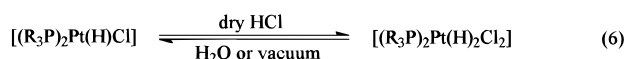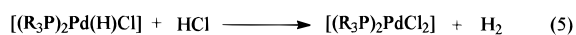| hydride	starting Pd(0) Complex	T, °C	isolated yield, %	characterization[a]	ref
[(Me$_3$P)$_2$Pd(H)Cl]	[(Me$_3$P)$_4$Pd]	−50	23	EA, IR, MS, ^{1}H NMR	72
[(Ph$_3$P)$_2$Pd(H)Cl]	[(Ph$_3$P)$_4$Pd]	−50	NR[b]	EA, IR	71
[(Ph$_3$P)$_2$Pd(H)Cl]	[(Ph$_3$P)$_3$Pd(CO)]	−50	57	EA, IR	71
[(Ph$_3$P)$_2$Pd(H)Cl]	[(Ph$_3$P)$_4$Pd]	−55	NR[b]	IR	73
[(Cy$_3$P)$_2$Pd(H)Cl]	[(Cy$_3$P)$_2$Pd]	−50	40	EA, IR	71
[(Cy$_3$P)$_2$Pd(H)Cl]	[(Cy$_3$P)$_2$Pd]	NR[b]	~100	IR, ^{1}H NMR	75
[(t-Bu$_3$P)$_2$Pd(H)Cl]	[(t-Bu$_3$P)$_2$Pd]	20	~100	EA, IR, ^{1}H NMR	76
[(t-Bu$_3$P)$_2$Pd(H)Cl]	[(t-Bu$_3$P)$_2$Pd]	20	~100	EA, IR, ^{1}H and ^{31}P NMR	68, 77
[(t-Bu$_2$PhP)$_2$Pd(H)Cl]	[(t-Bu$_2$PhP)$_2$Pd]	20	~100	EA, IR, ^{1}H NMR	76
[((PhCH$_2$)$_3$P)$_2$Pd(H)Cl]	[((PhCH$_2$)$_3$P)$_2$Pd(CH$_2$=CH$_2$)][c]	20	56[d]	IR, ^{1}H and ^{31}P NMR	78
[(i-Pr$_3$P)$_2$Pd(H)Cl]	[(i-Pr$_3$P)$_3$Pd]	−50	77	EA, IR, MS, ^{1}H and ^{31}P NMR	72
[(MePh$_2$P)$_2$Pd(H)Cl]	[(MePh$_2$P)$_4$Pd]	−50	91	EA, IR, ^{1}H NMR	72
[(MePh$_2$P)$_2$Pd(H)Cl]	[(MePh$_2$P)$_2$Pd(styrene)][c]	−78	45	EA, IR, ^{1}H NMR	79
[(Et$_2$PhP)$_2$Pd(H)Cl]	[(Et$_2$PhP)$_2$Pd(styrene)][c]	−78	66	IR, ^{1}H NMR	79
[(EtPh$_2$P)$_2$Pd(H)Cl]	[(EtPh$_2$P)$_2$Pd(styrene)][c]	−78	42	IR, ^{1}H NMR	79

[a] EA = elemental analysis; MS = mass spectrum. [b] NR = not reported. [c] Generated *in situ*. [d] Yield of impure complex; pure compound was not obtained.

$$[(Ph_3P)_3PdL] + HCl \longrightarrow [(Ph_3P)_2Pd(H)Cl] + PPh_3 + L \quad (4)$$
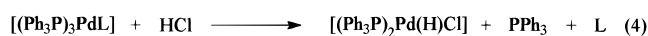
L = PPh$_3$ or CO

chloro(hydrido)palladium complexes, [L$_2$Pd(H)Cl] (L = tertiary phosphine), have been prepared by oxidative addition of HCl to the following Pd(0) compounds: [(Me$_3$P)$_4$Pd],[72] [(Ph$_3$P)$_4$Pd],[71,73,74] [(Ph$_3$P)$_3$Pd(CO)],[71] [(Cy$_3$P)$_2$Pd],[71,75] [(t-Bu$_3$P)$_2$Pd],[68,76,77] [(t-Bu$_2$PhP)$_2$Pd],[76] [(i-Pr$_3$P)$_3$Pd],[72] [(MePh$_2$P)$_4$Pd],[72] [((PhCH$_2$)$_3$P)$_2$Pd(CH$_2$=CH$_2$)],[78] [(MePh$_2$P)$_2$Pd(olefin)],[79] [(EtPh$_2$P)$_2$Pd(olefin)],[79] and [(Et$_2$PhP)$_2$Pd(olefin)][79] (olefin = styrene, methyl methacrylate). In all these cases, the resulting products were *trans*. The hydrido complexes were isolated in modest to excellent yield (see Table 2).

The oxidative addition reactions of HCl with Pd(0) complexes are normally conducted at low temperature (from −50 to −78 °C). However, in some cases[68,76−78] the synthesis can be carried out at room temperature. It is crucial to introduce only 1 equiv of HCl, otherwise the hydride reacts with excess HCl to give [L$_2$PdCl$_2$] and H$_2$ quantitatively (eq 5).[55,71,72,76,79,80] This is in sharp contrast with the behavior of chloro hydrido complexes of Pt which reversibly add HCl to give the corresponding Pt(IV) species (eq 6).[2b,57,81] The octahedral Pt(IV) dihydrides easily lose one molecule of HCl in the presence of water or under vacuum, but do not undergo reductive elimination of H$_2$. Reaction 5 likely occurs via similar Pd(IV) dichloro dihydrido complexes, from which H$_2$, not HCl, eliminates rapidly and irreversibly.
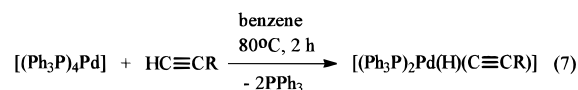
$$[(R_3P)_2Pd(H)Cl] + HCl \longrightarrow [(R_3P)_2PdCl_2] + H_2 \quad (5)$$

$$[(R_3P)_2Pt(H)Cl] \underset{H_2O \text{ or vacuum}}{\overset{dry \text{ } HCl}{\rightleftharpoons}} [(R_3P)_2Pt(H)_2Cl_2] \quad (6)$$

One reaction of HBr with [(t-Bu$_3$P)$_2$Pd] to give [(t-Bu$_3$P)$_2$Pd(H)Br] has been described with no experimental details.[77] No reports have appeared on reactions of Pd(0) complexes with HI or HF, furnishing hydrides. The reaction of [(Ph$_3$P)$_4$Pd] with HF yielded [(Ph$_3$P)$_4$Pd$_2$F$_2$]F$_2$, but no hydrido species emerged.[82] Trifluoroacetic acid oxidatively added to [(t-Bu$_3$P)$_2$Pd],[68,76,77] [(t-Bu$_2$PhP)$_2$Pd],[76] and [(i-Pr$_3$P)$_3$Pd][72] to give the corresponding *trans*-[(R$_3$P)$_2$Pd(H)(CF$_3$COO)]. The reaction between [(Cy$_3$P)$_2$Pd] and

formic acid afforded *trans*-[(Cy$_3$P)$_2$Pd(H)(HCOO)] which was isolated in 73% yield.[83] The formato hydride was not characterized by elemental analysis; a strange pattern was reported for the hydrido resonance in the ^{1}H NMR spectrum showing a triplet of doublets at −17.27 ppm with J_{P-H} = 6.3 Hz and J_{Pd-H} (?) = 5.1 Hz.[83]

c. Oxidative Addition of C–H, N–H, O–H, S–H, Ge–H Bonds, and the C–F Bond of FCHO

It was communicated[84] that terminal acetylenes oxidatively added to [(Ph$_3$P)$_4$Pd] to give [(Ph$_3$P)$_2$Pd-(H)(C≡CR)] (eq 7). The complexes were isolated in 55−90% yield and characterized by elemental analysis and IR, but no NMR data was reported. The same complexes were obtained independently by treatment of the corresponding chloro hydrides with sodium acetylides in liquid ammonia (see section II.A.e).[84] There has been no evidence reported for *trans* or *cis* geometry of the complexes.
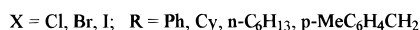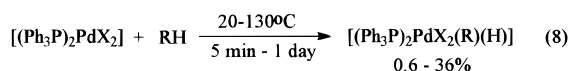
$$[(Ph_3P)_4Pd] + HC\equiv CR \xrightarrow[\text{- 2PPh}_3]{\overset{\text{benzene}}{\underset{\text{80°C, 2 h}}{}}} [(Ph_3P)_2Pd(H)(C\equiv CR)] \quad (7)$$

R = Ph, Bu, t-Bu, CH$_2$=C(Me)

Unlike the (triphenylphosphine)ethynylpalladium hydrides, their triethylphosphine counterparts are exceedingly unstable and therefore cannot be isolated. Nonetheless, they can be generated and used *in situ* (see section V).[85,86]

The addition reactions of HCN to zero-valent Ni complexes have been studied in detail and are well-documented.[87] However, no reports have appeared on synthesis of (cyano)palladium hydrides from Pd(O) compounds and HCN. An intermediate was observed by ^{1}H NMR in the reaction between [(diop)Pd-(norbornene)] and HCN, which was formulated as [(diop)Pd(H)CN].[88] Doyle[89] reported that mixing [(Ph$_3$P)$_4$Pd] with HCOF leads to oxidative addition of the C−F bond, followed by decarbonylation and the formation of [(Ph$_3$P)$_2$Pd(H)F]. Although the latter was characterized by elemental analysis, no evidence was presented for the hydridic nature of the material isolated.[89]

Recently, Vedernikov et al.[90a] briefly communicated their striking observations of the oxidative addition of various nonactivated, aliphatic and aromatic C–H bonds to $[(Ph_3P)_2PdX_2]$ (X = Cl, Br, I) under exceedingly mild conditions (20–130 °C). Although the reaction (eq 8) cannot be used for the synthesis of

$$[(Ph_3P)_2PdX_2] + RH \xrightarrow[\text{5 min - 1 day}]{20\text{-}130^\circ\text{C}} [(Ph_3P)_2PdX_2(R)(H)] \quad (8)$$
$$0.6 - 36\%$$

X = Cl, Br, I; R = Ph, Cy, n-C_6H_{13}, p-$MeC_6H_4CH_2$

pure Pd hydrides, the process is obviously of exceptional interest. In a few cases (R = Cy, X = Br, I) the organopalladium(IV) hydrides were isolated in admixtures with the starting Pd(II) complexes. The presence of the Pd–H bond in the complexes was established by some chemical reactions and confirmed by the IR (2190 cm^{-1}) and ^{1}H NMR ($\delta = -6$ and -18 ppm) data. The formation of Pd–H species from the hydrocarbons is in accord with the catalytic activity of $[(Ph_3P)_2PdX_2]$ in the chlorination of various RH with CCl_4 to RCl.[90b] Chloroform formed as the byproduct in this catalytic process.

In 1970, Roundhill[91] reported that $[(Ph_3P)_4Pd]$ reacted with imides to give $Pd(imido)_2$-type complexes and no palladium hydrides. At the same time, treatment of $[(Cy_3P)_2Pd]$ with succinimide furnished $[(Cy_3P)_2Pd(H)(N(COCH_2)_2)]$, albeit in only 15% yield.[92] The (hydrido)nickel analogue was obtained in a much better yield (74%) after a 1:2:1 mixture of $[Ni(COD)_2]$, Cy_3P, and succinimide in THF was stirred at ambient temperature.[92]

Normally, the O–H bond of alcohols does not add to Pd(0) complexes. It has recently been reported,[93,94] however, that bis(tricyclohexylphosphine)palladium-(0) readily reacts with 2 equivalents of PhOH or C_6F_5-OH to give *trans*-$[(Cy_3P)_2Pd(H)(OAr)]\cdot ArOH$ (Ar = Ph, C_6F_5) in ca. 55–60% isolated yield. The molecule of ArOH is coordinated to the metal-bonded aryloxo ligand through the Pd-O(Ar)···H—OAr hydrogen bond. It is believed that this hydrogen bond makes the ArO ligand "softer" and therefore more compatible with the metal center.[94] The role of the hydrogen bond in stabilizing the whole molecule was clearly demonstrated by the formation of the $[(Cy_3P)_2Pd(H)(OAr)]\cdots$ ArOH even when the reactants were used in a 1:1 ratio for the reaction. Both aryloxy hydrides were characterized by the IR and NMR spectral data, elemental analysis, and single-crystal X-ray diffraction. It is remarkable that the crystallographic studies resulted in localization of the hydrido ligands, thus making the complexes the first (and the only) mononuclear neutral palladium hydrides fully characterized by X-ray analysis (see section VI). Aliphatic alcohols like MeOH and *i*-PrOH do not add to $[(Cy_3P)_2Pd]$.[94] Interestingly, the reaction between $[(t\text{-}Bu_3P)_2Pd]$ and PhOH did not result in the anticipated hydride, giving instead the binuclear complex, $[(t\text{-}Bu_2PH)_2Pd(\mu\text{-}t\text{-}Bu_2P)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}OPh)]\cdot 3PhOH$.[95] Oxidative addition of ArSH (Ar = Ph, p-MeC_6H_4, p-$MeOC_6H_4$) to $[(Cy_3P)_2Pd]$ resulted in the smooth formation of the $[(Cy_3P)_2Pd(H)(SAr)]$ in 44–82% yield.[96] The reported IR and ^{1}H NMR data were not sufficient for distinguishing between *cis* and *trans* geometries for the (thiolato)palladium hydrides. In fact, the proton

resonances of the Pd–H appeared as upfield singlets presumably due to small J_{P-H} values. However, the complexes are likely *trans* since *trans* structures have been established for all their nickel[96] and (aryloxy)-palladium[93,94] counterparts. Studying the $[(Cy_3P)_2\text{-}Pd(H)(SAr)]$ by ^{31}P NMR spectroscopy would easily remove all doubts.

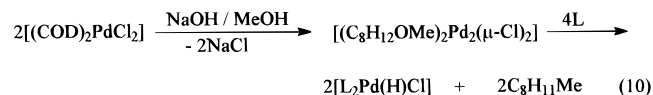Bochkarev et al.[97] reported the synthesis of $[L_2M\text{-}(H)(Ge(C_6F_5)_3)]$ (L = PPh_3; M = Pd, Pt) from $(C_6F_5)_3$-GeH and $[L_nM]$ (n = 3,4). The yield of the Pd complex (17%) was much lower than that of the Pt derivative (62%). Both IR data and elemental analysis were consistent with the formulation. Unfortunately, no NMR data were published.

d. β-Elimination Reactions

These reactions are not widely used for the preparation of Pd hydrides, though some of them are very clean and convenient to conduct. In the early 1970s, Hosokawa and Maitlis[98] demonstrated that $[(Ph_3P)_2\text{-}Pd(H)Cl]$ can be generated by the β-hydride elimination process (eq 9). The tricyclohexylphosphine complex can be prepared similarly.[99,100]

$$[(Ph_3P)_2Pd(H)Cl] + \quad (9)$$
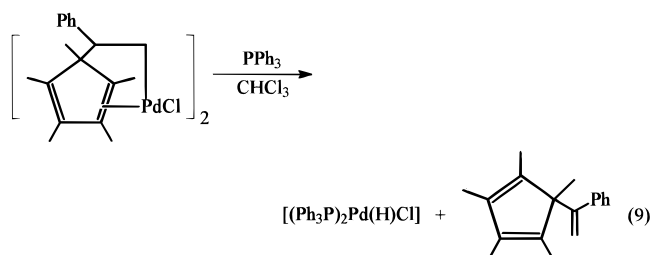
A very efficient procedure was developed by Goel and Goel[101] for the preparation of various $[L_2Pd(H)\text{-}Cl]$ (L = Cy_3P, *i*-Pr_3P, *t*-Bu_2BuP, *t*-Bu_2MeP, and *t*-Bu_3P) according to eq 10. In all cases the yields were almost quantitative, except for L = *t*-Bu_3P. The very low yield of the (tri-*tert*-butylphosphine)palladium hydride was obviously due to the facile intramolecular metalation of the ligand methyl groups (section V.E).[68,77,101] Among the numerous advantages of the method is that the hydrido complexes precipitate from the reaction mixtures in analytically pure form, and do not require any additional purification. Unfortunately, this nice piece of work[101] was communicated only briefly, with no experimental details.

$$2[(COD)_2PdCl_2] \xrightarrow[\text{- 2NaCl}]{\text{NaOH / MeOH}} [(C_8H_{12}OMe)_2Pd_2(\mu\text{-}Cl)_2] \xrightarrow{4L}$$
$$2[L_2Pd(H)Cl] + 2C_8H_{11}Me \quad (10)$$

Before reacting *in situ* with an acetylene (See section 5.A.a),[86] the intermediate, $[(Et_3P)_2Pd(H)\text{-}(C\equiv CPh)]$, was generated from $[(Et_3P)_2Pd(Cl)(C\equiv CPh)]$ and BuLi via ligand exchange, followed by β-elimination of butene (detected) from the resulting (σ-butyl)-palladium acetylide.[85]

e. Ligand Exchange

Ligand metathesis has been frequently applied to the synthesis of new cationic (section II.B.a) and neutral Pd hydrides from (hydrido)palladium precursors (see Table 3). This way, for instance, the first

Table 3. Neutral Mononuclear Pd Hydrides Synthesized via Ligand Metathesis

$$[(R_3P)_2Pd(H)] + MY \rightarrow [(R_3P)_2Pd(H)Y] + MX$$
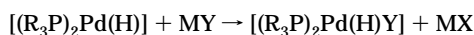
$[(R_3P)_2Pd(H)Y]$	X	MY^a	isolated yield, %	characterization^b	ref
$[(Et_3P)_2Pd(H)I]$	Cl	KI	NR^{c,d}	IR	55
$[(Cy_3P)_2Pd(H)I]$	Cl	LiI	65	EA, IR, ^{1}H NMR	59
$[(i\text{-}Pr_3P)_2Pd(H)I]$	Cl	mI	63	EA, IR, ^{1}H NMR	62
$[(Cy_3P)_2Pd(H)Br]$	Cl	LiBr	55	EA, IR, ^{1}H NMR	59
$[(i\text{-}Pr_3P)_2Pd(H)Br]$	Cl	mBr	36	EA, IR, ^{1}H NMR	62
$[(Cy_3P)_2Pd(H)Cl]$	NO$_3$	Et$_4$NCl	76	NR^c	103
$[(Cy_3P)_2Pd(H)CN]$	Cl	mCN	16	EA, IR, ^{1}H NMR	62
$[(i\text{-}Pr_3P)_2Pd(H)CN]$	Cl	mCN	34	EA, IR, ^{1}H NMR	62
$[(Cy_3P)_2Pd(H)SCN]$	Cl	KSCN	46	EA, IR, ^{1}H NMR	59
$[(i\text{-}Pr_3P)_2Pd(H)SCN]$	Cl	mSCN	55	EA, IR, ^{1}H NMR	62
$[(Cy_3P)_2Pd(H)BH_4]$	Cl	NaBH$_4$	85	EA, IR, ^{1}H NMR	59, 104
$[(i\text{-}Pr_3P)_2Pd(H)BH_4]$	Cl	NaBH$_4$	84	EA, IR, ^{1}H NMR	59
$[(Cy_3P)_2Pd(H)Me]$	Cl	MeMgBr	100^{e,f}	^{1}H NMR	102
$[(i\text{-}Pr_3P)_2Pd(H)Me]$	Cl	MeMgBr	>90	IR, ^{1}H NMR	102
$[(Ph_3P)_2Pd(H)C\equiv CR']^g$	Cl	NaC$\equiv$CR'	80–90	EA, IR,	84
$[(Cy_3P)_2Pd(H)NHPh]$	Cl	NaNHPh	51	^{1}H and ^{31}P NMR	78
$[(i\text{-}Pr_3P)_2Pd(H)NHPh]$	Cl	NaNHPh	NR^{c,e}	^{1}H and ^{31}P NMR	78

^{a} m = alkali metal (not specified in ref 62). ^{b} EA = elemental analysis. ^{c} NR = not reported. ^{d} Isolated complex was impure. ^{e} Complex was not isolated. ^{f} NMR yield. ^{g} R' = Ph, Bu, t-Bu, CH$_2$C=C(Me).

methylpalladium hydrides, $[L_2Pd(H)Me]$ (L = Cy$_3$P, i-Pr$_3$P), were prepared from the corresponding chloro hydrido complexes and MeMgBr.[102] The (triisopropylphosphine)(σ-methyl)palladium hydride was isolated (> 90% yield), whereas its tricyclohexylphosphine counterpart, albeit formed quantitatively, was only characterized in solution. The chloro and nitrato ligands in various $[L_2Pd(H)X]$, where L = tertiary phosphine and X = Cl or NO$_3$, were metathetically replaced by I,[55,59,62] Br,[59,62] Cl,[103] CN,[62] SCN,[59,62] BH$_4$,[58,59,104] RC$\equiv$C,[84] Me,[102] and PhNH.[78] Unfortunately, some of these reports lack experimental details.

f. Miscellaneous Methods

Treatment of aryl- and benzoylpalladium complexes with H$_2$ (80 atm) in THF-d_8 at 60 °C led to the hydrogenolysis of the Pd–C bond and clean formation of the hydrides (eq 11).[105] The complexes were characterized by solution NMR and IR, but not isolated in pure form. It is believed that the hydrogenolysis proceeds via oxidative addition of H$_2$ to the organopalladium complex, followed by reductive elimination of RH from the resulting Pd(IV) species.

$$[(Ph_3P)_2Pd(R)X] + H_2 \longrightarrow [(Ph_3P)_2Pd(H)X] + RH \quad (11)$$
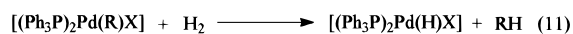
R = Ph, PhCO; X = Cl, Br

A diamagnetic solid material was isolated from the reaction between [Pd(acac)$_2$], nitrobenzene, and H$_2$ in ethanol/pyridine.[106] The compound was formulated as [(acac)Pd(H)(PhNO$_2$)(Py)] on the basis of microanalysis and IR data. The complex was also studied by ^{1}H NMR spectroscopy, but, surprisingly, the hydrido region of the spectrum was not explored.

Heating mixtures of t-Bu$_3$P with chloropalladium complexes, such as [(PhCN)$_2$PdCl$_2$], PdCl$_2$, or Na$_2$[PdCl$_4$], in benzene[76] or DMF[107] afforded [(t-Bu$_3$P)$_2$Pd(H)Cl] in 32 and 90% yield, respectively. Kudo et al.[33] reported that complexes [(Cy$_3$P)$_2$M(H)$_2$] (M = Pd, Pt) were prepared from [M(acac)$_2$] and AlR$_3$ in the presence of Cy$_3$P. Both dihydrides were almost

insoluble in common organic solvents thus preventing their characterization by NMR. The synthesis of the Pd dihydride was then repeated and the product was demonstrated to contain a Pd–H bond.[34] However, the samples of [(Cy$_3$P)$_2$Pt(H)$_2$] prepared by other, independent methods,[76,108–110] while being identical with each other, exhibited totally different solubility and IR pattern from those reported for the compound made of [Pt(acac)$_2$], AlR$_3$, and Cy$_3$P. Hence, it is conceivable that the hydrido Pd complex formulated as [(Cy$_3$P)$_2$Pd(H)$_2$],[33] possessed another composition and structure.

Unlike dicoordinate [L$_2$Pt] (L = bulky phosphine), complexes [L$_2$Pd] do not add H$_2$ to give square-planar dihydrides.[76] An attempt to make [(t-Bu$_3$P)$_2$Pd(H)$_2$] from [(t-Bu$_3$P)$_2$Pd] and H$_2$ under UV failed, although the resulting impure amorphous brown solid showed ν(Pd–H) = 2260 cm^{-1} and δ(Pd–H) = 847 cm^{-1} in the IR spectrum.[76]

B. Cationic Hydrides

The first cationic Pd hydrides were synthesized by Green and Munakata in the early 1970s.[111,112] There are two methods to prepare cationic hydrido complexes of palladium: (i) the removal of an anionic ligand in neutral Pd hydrides, or its replacement by a neutral ligand, and (ii) protonation of zero-valent Pd complexes.

a. Ligand Exchange

These reactions are summarized in Table 4. Among the incoming ligands used for the synthesis are monodentate[72] and bidentate[111,112] phosphines, pyridine and its derivatives,[62] pyrazole,[62] imidazole,[62] and acetonitrile.[103] Both PF$_6^-$ and BPh$_4^-$ have been used as the counterions. Mabbott and Maitlis[99,100] generated [(dppe)Pd(H)]$^+$ and [(dpae)Pd(H)]$^+$ and used them *in situ*, without identification or characterization, for addition to di- and triolefins which were already present in the reaction mixture. The tricoordinate cationic species were generated by the treatment of [L$_2$Pd(H)Cl] (L = PPh$_3$, PCy$_3$) with

Table 4. Mononuclear Cationic Pd Hydrides Synthesized via Ligand Metathesis

$$[L_nPd(H)X] + L' \xrightarrow[-X^-]{A^-} [L_mPd(H)L']^+ A^-$$
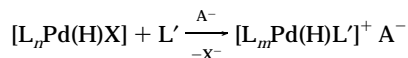
| cationic hydride	starting hydride	isolated yield, %	characterization[a]	ref
[(Cy₃P)₂Pd(H)(dppe)]⁺ PF₆⁻	[(Cy₃P)₂Pd(H)Cl]	8	EA, IR, ¹H NMR	112
[(i-Pr₃P)₂Pd(H)(dppe)]⁺ PF₆⁻	[(i-Pr₃P)₂Pd(H)Cl]	NR[b]	EA, IR, ¹H NMR	112
[(Me₃P)₃Pd(H)]⁺BPh₄⁻	[(Me₃P)₂Pd(H)Cl]	NR[b]	IR, ¹H NMR	72
[(Cy₃P)₂Pd(H)(MeCN)]⁺PF₆⁻	[(Cy₃P)₂Pd(H)Cl]	79	NR[b]	103
[(Cy₃P)₂Pd(H)(Py)]⁺BPh₄⁻	[(Cy₃P)₂Pd(H)(NO₃)]	92	EA, IR, ¹H NMR	62
[(Cy₃P)₂Pd(H)(2-MePy)]⁺BPh₄⁻	[(Cy₃P)₂Pd(H)(NO₃)]	68	EA, IR, ¹H NMR	62
[(Cy₃P)₂Pd(H)(3-MePh)]⁺BPh₄⁻	[(Cy₃P)₂Pd(H)(NO₃)]	54	EA, IR, ¹H NMR	62
[(Cy₃P)₂Pd(H)(4-MePy)]⁺BPh₄⁻	[(Cy₃P)₂Pd(H)(NO₃)]	65	EA, IR, ¹H NMR	62
[(Cy₃P)₂Pd(H)(4-PhPy)]⁺BPh₄⁻	[(Cy₃P)₂Pd(H)(NO₃)]	41	EA, IR, ¹H NMR	62
[(Cy₃P)₂Pd(H)(4-Py-methanol)]⁺BPh₄⁻	[(Cy₃P)₂Pd(H)(NO₃)]	80	EA, IR, ¹H NMR	62
[(Cy₃P)₂Pd(H)(2,4,6-Me₃Py)]⁺BPh₄⁻	[(Cy₃P)₂Pd(H)(NO₃)]	64	EA, IR, ¹H NMR	62
[(Cy₃P)₂Pd(H)(3,5-Me₂Py)]⁺BPh₄⁻	[(Cy₃P)₂Pd(H)(NO₃)]	77	EA, IR, ¹H NMR	62
[(Cy₃P)₂Pd(H)(pyrazole)]⁺BPh₄⁻	[(Cy₃P)₂Pd(H)(NO₃)]	86	EA, IR, ¹H NMR	62
[(Cy₃P)₂Pd(H)(imidazole)]⁺BPh₄⁻	[(Cy₃P)₂Pd(H)(NO₃)]	83	EA, IR, ¹H NMR	62

[a] EA = elemental analysis. [b] NR = not reported.

dppe or dpae and AgPF₆. At the same time, it is known[111,112] that the complexes, [L₂Pd(H)Cl], transform to [LPd(H)(dppe)]⁺ upon addition of dppe and NH₄PF₆. Therefore, the "tricoordinate" cations generated in solution[99,100] may exist in equilibrium with the corresponding tetracoordinate, square-planar complexes, [(dppe)Pd(L)(H)]⁺ and [(dpae)Pd(L)(H)]⁺.

b. Protonation of Zero-Valent Complexes

It has been established beyond any doubt that in Pd(0) complexes the metal centers are significantly less basic than those in their Pt (0) congeners.[69,76,113−116] For example, solutions of [(Et₃P)₃Pt] in aqueous THF were estimated to have pH of ∼14,[114] whereas saturated solutions of [(Et₃P)₃Pd] in water have pH = 9.5.[115] Despite the lower basicity of the Pd center in various LₙPd(0) complexes, it can be protonated thus giving rise to the corresponding cationic hydrides.

In 1976 Schunn[117] reported an efficient and simple method for the synthesis of [(Et₃P)₃PdH]⁺ BPh₄⁻ in almost quantitative yield, according to eq 12. A modification of this method was later used for the preparation of [(Me₃P)₃PdH]⁺ BPh₄⁻.[118]

$$[(Et_3P)_3Pd] \xrightarrow[\text{2. HCl}]{\text{1. NaBPh}_4 \text{ / EtOH}} [(Et_3P)_3PdH]^+ BPh_4^- \quad (12)$$
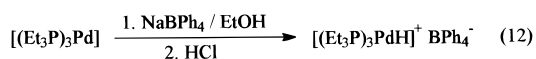
Siedle et al.[119] used a strong C−H acid, H₂C(SO₂-CF₃)₂, for the protonation of [L₄Pd] (L = Ph₃P, Ph₂-MeP) as well as some zero-valent complexes of Ni and Pt. The resulting Pd(II) hydrides, [L₃PdH]⁺ HC-(SO₂CF₃)₂⁻, were isolated in 62−69% yield as white crystalline solids. Zudin et al.[120−122] demonstrated that treatment of palladium acetate with H₂ and excess PPh₃ in aqueous CF₃COOH resulted in the formation of [(Ph₃P)₃PdH]⁺ which was not isolated but thoroughly investigated by ¹H and ³¹P NMR spectroscopy in solution. The hydrido cation was found to be quite stable under the acidic conditions, provided the concentration of water in the mixture was more than 20%. At lower concentrations of H₂O, the hydride decomposed rapidly, whereas in 70% and 60% aqueous CF₃COOH, the complex was stable for several hours and days, respectively.[120−122] Addition of strongly coordinating anions (e.g., Br⁻) to the

solution caused an immediate decomposition of the hydride, accompanied by the evolution of H₂. It is proposed[121,122] that the cationic hydride is formed due to the interaction between the [(Ph₃P)₂PdX₂] (X = AcO or CF₃COO) and H₂. However, in light of the recent reports by Amatore et al.[123,124] and Ozawa et al.,[125] another reaction path is worth considering. This involves the facile formation of Ph₃PO and (triphenylphosphine)palladium(0) complexes from [Pd(OAc)₂] and PPh₃, followed by proton transfer to the metal center. Various cationic hydrides, [L₃-PdH]⁺, where L = tertiary phosphine, have been studied by NMR spectroscopy by a number of research groups.[117−122,126]

Leoni et al.[127−129] described protonation of [L₂Pd] (L = Cy₃P, t-Bu₃P) with water in the presence of Lewis acids. No reaction was observed in the absence of acidic promoters. Treatment of the [L₂Pd] with H₃O⁺ X⁻ (X = HOBF₃ or BF₄) afforded *trans*-[L₂Pd-(H)(H₂O)]⁺ X⁻ which were exceptionally labile when L = t-Bu₃P,[127] but quite stable if L = Cy₃P.[128,129] However, addition of acetonitrile to the aquapalladium hydrides led to the formation of *trans*-[L₂Pd-(H)(MeCN)]⁺ which were all stable, regardless of the nature of the phosphine ligand.[127−129] The formation of a palladium hydride by reacting [(Cy₃P)₂Pd] with HBF₄ took place only in the presence of ligands capable of strongly binding to Pd (e.g., H₂O, MeCN, and Py, but not Et₂O).[129] For instance, [Et₂OH]⁺ BF₄⁻ did not react with [(Cy₃P)₂Pd] under rigorously dry conditions. However, when the above-mentioned ligands were present, the smooth formation of [(Cy₃P)₂-Pd(H)L]⁺ BF₄⁻ (L = H₂O, MeCN, Py) occurred. Remarkably, these hydrides can be isolated as tetraphenylborate salts when L = Py[62] or MeCN,[128] but not H₂O. The rapid decomposition of the BPh₄⁻ by the aqua(hydrido)palladium cation is rationalized in terms of the hydride acidity and the inability of the tetraphenylborate anion to stabilize the complex by hydrogen bonding. In fact, IR spectroscopic and X-ray diffraction studies of [(Cy₃P)₂Pd(H)(H₂O)]⁺ BF₄⁻ revealed the presence of strong hydrogen bonds between the aqua ligand and the anion. Conductivity experiments suggested that such hydrogen-bonded species might also exist in significant amounts in solution.[129]

III. Synthesis of Binuclear Palladium Hydrides

In 1976 Schunn[117] observed a high-field quintet at -3.56 ppm ($J = 32$ Hz) in the 210 K ^{1}H NMR spectrum of a toluene solution of $[(Et_3P)_3Pd]$ under hydrogen (150 psig). The signal was assigned to the binuclear hydride, $[(Et_3P)_4Pd_2(\mu\text{-}H)_2]$, which was not isolated. Soon after that, a report[130] appeared in which several binuclear palladium complexes were tentatively formulated as $[(\eta^5\text{-}Ar_5C_5)_2Pd_2(\mu\text{-}H)(\mu\text{-}X)]$ (Ar = Ph, p-Tol; X = Cl, Br). However, no high-field resonances were observed in the ^{1}H NMR spectra of these species. Since the early 1980s, several reports have been published on the synthesis and characterization of various binuclear hydrido complexes of palladium, both cationic and neutral. The most exciting and interesting results in this field have been obtained within last 10 years.

A. Dimerization of Mononuclear Pd Hydrides in the Presence of CO

In the late 1970s and early 1980s, Zudin et al.[120-122] reported that $[(Ph_3P)_3PdH]^+$ X^- (X = CF_3COO), generated *in situ*, reacted with CO to give the binuclear complex, $[(Ph_3P)_4Pd_2(\mu\text{-}H)(\mu\text{-}CO)]^+$ X^-, according to eq 13. This reaction is reversible, but in the presence of excess CO the equilibrium can be shifted almost entirely to the right. The cationic binuclear hydride was characterized by ^{1}H and ^{31}P NMR spectral data, but was not isolated.[121,122] Surprisingly, no reaction was observed when $[(Me_3P)_3\text{-}PdH]^+$ was treated with CO.[118]

$$2[(Ph_3P)_3PdH]^+ \; CF_3CO_2^- \underset{PPh_3}{\overset{CO}{\rightleftharpoons}} [(Ph_3P)_4Pd_2(\mu\text{--}CO)(\mu\text{--}H)]^+ \; CF_3CO_2^- \quad (13)$$
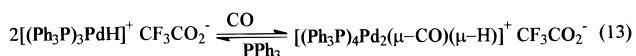
Similar complexes were obtained with X = ClO_4[131] and $HC(SO_2CF_3)_2$.[119] In the latter case, the analytically pure complex was isolated in 76% yield. The binuclear carbonyl(hydrido)palladium cation is fluxional over a wide range of temperatures, becoming stereochemically rigid only at -110 °C.[119] Both $\Delta H^{\ddagger}$ (9.5 ± 0.4 kcal/mol) and $\Delta S^{\ddagger}$ (8 ± 4 eu) have been determined for the permutation of chemically nonequivalent ^{31}P environments of the $[(Ph_3P)_4Pd_2(\mu\text{-}CO)(\mu\text{-}H)]^+$ in solution. The positive entropy of activation found is consistent with the proposal of cleavage of either a Pd−H or a Pd−C bridge with subsequent rotation about the remaining Pd−H−Pd or Pd−C−Pd bond.[119] It has been proposed that the $[(Ph_3P)_4Pd_2(\mu\text{-}H)(\mu\text{-}CO)]^+$ plays the key role in a number of catalytic processes including olefin carbonylation reactions, water gas shift reaction, and the reduction of nitrobenzene with CO.[122,131-133]

B. Reduction Methods

Various techniques and reducing agents have been used for converting mono- and binuclear non-(hydrido)palladium complexes to binuclear hydrides. An interesting complex was obtained quantitatively by Rimml and Venanzi,[134] according to eq 14. It is remarkable that the binuclear cation, which contains just one H bridge and no Pd−Pd bond, is very stable when the counterion, X, is CF_3SO_3 but decomposes (albeit slowly) in solution when X = BPh_4, to give Pd

metal. The reaction likely involves the formation of a neutral Pd formate, followed by its decarboxylation and coordination of the Pd hydride to the as yet unreacted mononuclear cationic Pd complex, with concomitant loss of acetone.
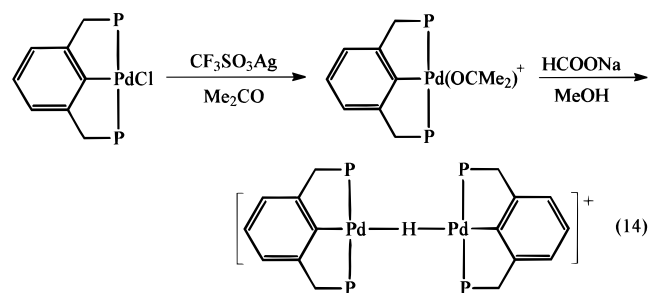
$$P = PPh_2$$

Fryzuk and co-workers[135] accidently synthesized an exceptionally remarkable binuclear hydride in which the Pd core is coordinated to $LiBEt_4$ (eq 15). "Fortuitously",[135] the stock bottle of the Superhydride reagent that was used for the reduction, contained no $LiBEt_3H$ at all, but a 1:1 mixture of $LiBEt_2H_2$ and $LiBEt_4$ instead. Similar complexes with $NaBEt_4$ and $LiAlEt_4$ were also prepared and exhaustively characterized.[135,136] The "free" hydride, $[(dippp)_2Pd_2(\mu\text{-}H)_2]$ (44% yield), was synthesized by the reduction of $[(dippp)PdI_2]$ with $LiBEt_3H$ (eq 16). The chloropalladium analogue did not give the hydride under the same conditions, presumably because of poor solubility.[136] Treatment of the "free" Pd hydride with $LiBEt_4$, $NaBEt_4$, or $LiAlEt_4$ gave rise to the corresponding adducts in over 90%, 41%, and 89% yield, respectively. The structures of these interesting complexes will be discussed below (section VI). A similar binuclear Pd dihydride, $[(dcpe)_2Pd_2(\mu\text{-}H)_2]$, was prepared in 85% yield from $[(dcpe)Pd(C_2O_4)]$ and H_2 under UV irradiation.[137]
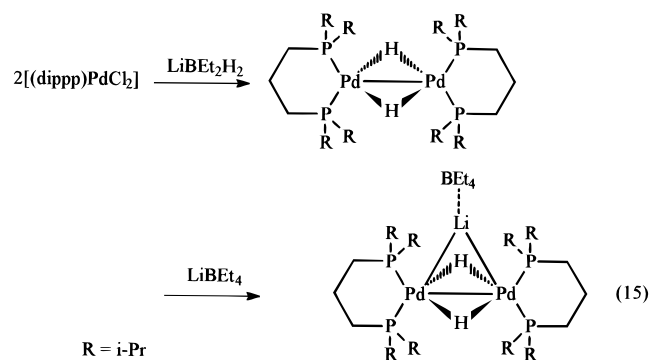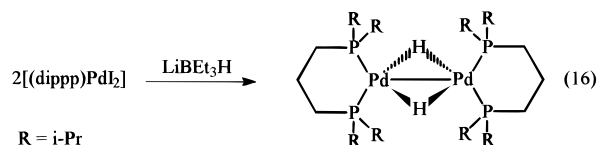
The methanolysis of $[(dippp)Pd(Ph)Cl]$ in the presence of Et_3N furnished the cationic dimer, $[(dippp)_2\text{-}Pd_2(\mu\text{-}CO)(\mu\text{-}H)]^+$ Cl^-, in 71.6% yield (eq 17).[138,139] An alternative way for making this complex employs the reaction between $[(dippp)_2Pd]$, HCl, and CO.[139] The binuclear hydride was characterized by single-crystal diffraction (see section VI).[138] A related complex,

[{(*S,S*)-bdpp}₂Pd₂(*μ*-CO)(*μ*-H)]⁺ Cl⁻, was prepared by the reaction of [{(*S,S*)-bdpp}Pd(COMe)Cl] with MeOH in the presence of CO.[140] Plausible mechanistic schemes accounting for both methanolysis reactions have been proposed.[138−140]

$$2[(dippp)Pd(Ph)Cl] + 2MeOH + Et_3N \longrightarrow 2PhH + CH_2O +$$

(17)

$$H_2 + [Et_3NH]^+ Cl^- +$$
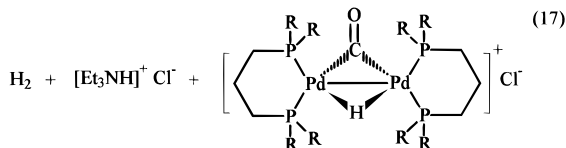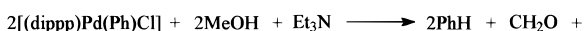
R = i-Pr

A very simple and efficient method was recently reported by Xu and Anderson[141] for the synthesis of binuclear organopalladium hydrides, [(*μ*-dppm)₂Pd₂R₂-(*μ*-H)]⁺ PF₆⁻ (R = Me or Ph), from the corresponding chloro-bridged dimers and NaBH₄. The yields were 86% and 70% for the methyl and phenyl complexes, respectively. This method is more convenient and efficient than that suggested by Stille's group for the preparation of the methyl complex (see section III.C).

A deep-green complex was isolated from the hydrogenation of nitrobenzene in the presence of palladium(II) acetylacetonate, and tentatively formulated as [Pd(acac)(acacH)(H)(PhNO₂)]₂.[142] The IR band at 2138 cm⁻¹ was assigned to a Pd−H vibration; no other evidence was obtained in support of the proposed structure.

C. Oxidative Addition Reactions

In 1980, Goel and Ogini[143] briefly reported on the dimerization of [(*t*-Bu₃As)₂Pd(H)Cl] (eq 18), and the resulting mixture of *cis* and *trans* isomers was characterized by analytical and ¹H NMR spectral data. Interestingly, the phosphine analogues, [(*t*-Bu₃P)₂Pd(H)X], underwent rapid metalation resulting in the cleavage of the Pd−H bonds (section V.E).[69,77] While leading to different cyclometalated products, both reactions likely occur via oxidative addition of the C−H bond to the electron-rich palladium center.

(18)

+ cis-isomer
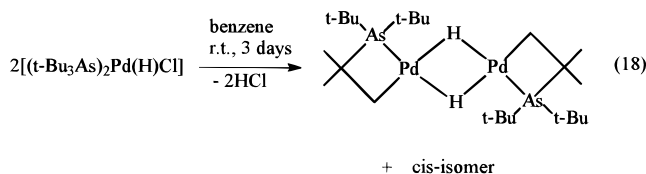
Binuclear oxidative addition of HCl[144−147] and H₂S[148−150] across the Pd−Pd bond in various (dppm)-Pd(I) complexes led to hydrido complexes, only a few of them having been isolated. Mixing equimolar amounts of [(*μ*-dppm)₂Pd₂Cl₂] and Me₃Al in CH₂Cl₂ gave Me₂AlCl and the unstable monomethylated Pd(I) complex which was transformed to the cationic Pd(II) binuclear hydride upon addition of EtOH at −78 °C (eq 19). The reaction presumably involves oxidative addition of the HCl generated *in situ* from the Me₂AlCl and ethanol. When the reaction was conducted with a 10−20-fold excess Me₃Al, the dimethyl complex with bridging hydrido ligand, [(*μ*-dppm)₂Pd₂(Me)₂(*μ*-H)]⁺ was formed. Both hydrides

(19)
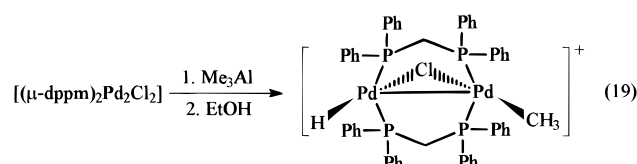
were isolated as tetraphenylborate salts in 83% and 70% yield, respectively. The monomethylated complex was structurally characterized by single-crystal X-ray diffraction; the hydrido ligand was located and its position was refined (see section VI).

Hydrido mercapto intermediates (e.g., [(*μ*-dppm)₂-Pd₂X₂(H)(SH)], where X = Br, I)[148] were detected by low-temperature ¹H NMR technique in reactions between binuclear dppm palladium (I) complexes and H₂S.[148−150] Because of the thermal lability of all these hydrido complexes, none of them were isolated.

One of the most exciting recent discoveries in the chemistry of palladium hydrides was made by Leoni et al.[151−153] who synthesized and characterized phosphido-bridged palladium(I) dimers with η^2 Pd−H−P interactions. Protonation of the nonhydrido binuclear precursor with CF₃SO₃H or HBF₄ in dimethoxyethane afforded the binuclear cation with the previously unknown Pd−H−P bridging unit (eq 20).[151,152]

(20)
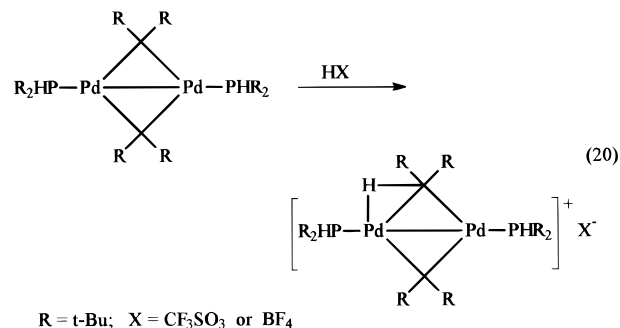
R = t-Bu; X = CF₃SO₃ or BF₄

Both the trifluoromethanesulfonate and tetrafluoroborate were isolated in over 70% yield and thoroughly characterized. Although it appeared impossible to locate the hydride in the X-ray structure of the CF₃SO₃ salt,[152] convincing evidence for the Pd−H−P fragment stemmed from the exhaustive NMR studies of the complex.[151,152] In the ¹H NMR spectrum, the "hydride" was found at −0.16 ppm as a doublet of doublets due to the coupling to two nonequivalent P nuclei of the bridging ligands. Another complex of similar structure was prepared by the route shown in eq 21.[153] The solution ¹H NMR pattern for the hydride (doublet of doublets at δ = −0.35 ppm) is very close to that previously observed for the *tert*-butylphosphine complex.

(21)

X = CF₃SO₃⁻

IV. Synthesis of Heterobinuclear, Polynuclear, and Solid-State Ternary Palladium Hydrides

Braunstein and co-workers[154] presented a detailed investigation of the reactions between acids (HBF$_4$ and HCl) and heterobimetallic Pd−M (M = Cr, Mo, W, Mn, Fe, Co) complexes with bridging phosphido ligands. When HBF$_4$ in ether was used, the corresponding cationic hydrides were obtained (eq 22). Most complexes were isolated as analytically and spectroscopically pure compounds in 48−86% yield, whereas the hydride with M = Mo(CO)$_2$ and R = Ph was only identified spectroscopically; no yields were reported for the manganese (R = Ph) and iron complexes.

$$\text{(22)}$$

M = Cr(CO)$_2$Cp; R = Cy
M = Mo(CO)$_2$Cp; R = Cy, Ph
M = W(CO)$_2$Cp; R = Cy, Ph

M = Mn(CO)$_4$; R = Cy, Ph
M = Fe(CO)Cp; R = Cy
M = Co(CO)$_3$; R = Cy

Using HCl instead of HBF$_4$ in this reaction furnished neutral complexes due to protonation, followed by the replacement of one of the phosphine ligands by the Cl$^-$ (eq 23). It was shown that the protonation step precedes the ligand exchange. When the Mo−Pd complex with R = Ph reacted with HCl under the same conditions, the resulting neutral hydride was found to exist in equilibrium with the cationic hydrido species containing two phosphines and Cl$^-$ in the outer coordination sphere (compare with eq 22). No hydrides were detected in the reaction between HCl and the Mn−Pd or Co−Pd complexes.[154]

$$\text{(23)}$$

M = Cr(CO)$_2$Cp; R = Cy
M = Mo(CO)$_2$Cp; R = Cy
M = W(CO)$_2$Cp; R = Cy

Several Pd−Pt hydrido-bridged complexes have been synthesized by various methods. For instance, Grove et al.[155] reported the preparation of one such complex in which the metal atoms are held in one molecule by two hydrido bridges (eq 24).

$$\text{(24)}$$

A number of organometallic Pd−Pt hydrides were very recently prepared by the borohydride reduction of their chloro precursors in 45−96% isolated yield (eq 25).[141] All these remarkably air and thermally

stable complexes, as well as their dipalladium analogues (section III.B), have been characterized by elemental analysis and ^{1}H and ^{31}P NMR spectral data. The Pd−Pt analogue of the dipalladium hydride shown in eq 14 was prepared by reacting the acetone solvate, [LPd(OCMe$_2$)]$^+$, with the platinum hydride, [LPtH], (L = 2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$).[134]

$$\text{(25)}$$

P = PPh$_2$
R = Me, Et, Ph; R' = Me, Ph

Only a few polynuclear palladium hydrides have been reported thus far, none of them having been structurally characterized. Puddephatt's trinuclear hydride (eq 26) likely possesses the structure of its platinum congener that has been characterized by a single-crystal X-ray diffraction.[156,157] The red trinuclear Pd hydride was isolated in 97% yield, but due to instability decomposed in the solid state, thus preventing characterization by elemental analysis.[157] However, the NMR and IR spectral data ideally confirmed the proposed structure.

[(μ-dppm)$_3$Pd$_3$(μ3-CO)]$^{2+}$ (PF$_6^-$)$_2$ $\xrightarrow[\text{-H}^+, \text{-CO}]{\text{H}_2\text{S}}$

$$\text{(26)}$$

P = PPh$_2$

Moiseev and Vargaftik[158] have published an account of their research in the field of Pd-catalyzed oxidation reactions, which includes a section describing hydrido clusters of palladium. The reduction of Pd(OAc)$_2$ with H$_2$ in acetic acid in the presence of L (L = Phen or Bipy) resulted in the formation of X-ray amorphous brown solids which were formulated as [Pd$_4$L(OAc)$_2$H$_4$]$_n$[159] with $n = \sim100$.[159,160] These clusters were characterized by elemental analysis, high-resolution electron microscopy, electron diffraction, IR, ^{1}H NMR, and EXAFS spectral techniques.[158,159] In addition, their reactions with a number of reagents (e.g., Hg, PPh$_3$, O$_2$, NO, quinones, tetracyanoethylene, H$_2$NCON(Me)NO, and PhenH$^+$) have been studied.[158,160−163] The reaction of the polynuclear hydrido species with CO gave rise to the new carbonyl hydrido clusters formulated as [Pd$_4$L$_3$(CO)$_3$(H)$_2$-(OAc)$_3$]$_n$ ($n = 2, 3$).[158,164] Bubbling CO through a solution of Pd(OAc)$_2$ and Phen (1:1) in AcOH at 20

°C, gave a nonhydrido Pd(I) cluster formulated as [(Phen)Pd(CO)OAc]$_n$, in quantitative yield.[164,165] When the reaction was conducted at 50 °C, other things being equal, a polymeric hydrido complex, [(Phen)$_2$Pd$_2$-(CO)H(OAc)·AcOH]$_m$ was obtained with $\delta = -15.5$ ppm (^{1}H NMR). Finally, treatment of Pd(OAc)$_2$ and Phen in AcOH with an H$_2$/CO mixture furnished a hydrido cluster which was formulated as [(Phen)$_3$Pd$_4$-(CO)$_3$H$_2$(OAc)$_2$·AcOH].[165] In addition to elemental analysis and molecular weight measurements, the carbonyl hydrides were studied by IR, ^{1}H NMR, and EXAFS spectroscopy. A tetrahedral structure with inner-sphere chelating Phen ligands, bridging carbonyl, and hydrido ligands was assigned to the tetranuclear clusters. All these complexes were shown to be stable electrolytes which lose the [H(OAc)$_2$]$^-$ anions upon dissolution in water or ethanol.[165] However, no structural formulas were suggested. It was reported that similar carbonyl hydrido clusters were synthesized with Bipy and the diisoamyl ester of bicinchoninic acid as the ligands, but no experimental details were communicated.[165]

Interestingly, treatment of the [Pd$_4$(Phen)$_4$(CO)$_4$-(OAc)$_4$] with H$_2$ in MeOH at ambient temperature furnished a hydride identified as [(Phen)$_2$Pd$_2$(CO)H-(OAc)·AcOH].[165] The molecular weight determination indicated that this binuclear complex is monomeric, unlike its polymeric counterpart (see above). The stoichiometrically identical Pd$_2$ monomer and Pd$_2$ polymer displayed similar patterns in their IR and ^{1}H NMR spectra. At the same time, their electronic absorption parameters were found to be somewhat different.

More recently, the reaction between [(Ph$_3$P)Pd-(OAc)$_2$] and formic acid was described,[166,167] furnishing a hydride formulated as [Pd$_2$(PPh$_2$)H$_x$]$_n$ as the main product in 60−70% yield. A broad signal centered at −9.5 ppm was observed in the ^{1}H NMR spectrum of the isolated complex indicating the presence of hydrido ligands. The EXAFS and SAXS studies suggested that the molecule is spherical (15.6 ± 0.5 Å in diameter) containing ∼10 Pd atoms arranged in a linear polymeric chain and linked by Pd−Pd bonds and bridging diphenylphosphido and hydrido ligands.[166,167]

In general, the results obtained by Moiseev, Vargaftik, and co-workers[158−167] are of significant interest. It has been certainly established that these polynuclear systems contain Pd−H bonds. Unfortunately, the exact structures of the (hydrido)- and carbonyl(hydrido)palladium clusters still remain obscure, despite the fact that the complexes have been meticulously investigated by nearly all applicable techniques including the most modern and powerful ones.

A number of solid-state ternary hydrides, M−Pd−H (M = alkali or alkaline earth metal), were recently prepared via the high-temperature reaction between palladium sponge, hydrogen, and the corresponding M hydride under pressure.[168−177] Examples of such solid-phase hydrides include Li$_2$PdH$_2$,[169] Na$_2$PdH$_2$,[170] CaPdH$_2$,[171] Na$_2$PdH$_4$,[172] K$_2$PdH$_4$,[173] Rb$_2$PdH$_4$,[174] Cs$_2$-PdH$_4$,[174] K$_3$PdH$_3$,[175] Rb$_3$PdH$_3$,[176] Rb$_3$PdH$_5$,[176] and NaPd$_3$H$_2$.[177] Analogous deuterides were prepared similarly and characterized by powder neutron diffraction, exhibiting in many cases the linear [PdH$_2$]$^{2-}$ and square-planar [PdH$_4$]$^{2-}$ structures (see section VI). The reaction conditions required for the solid state synthesis are quite drastic in terms of both temperature (up to 850 °C) and pressure (up to 1800 bar), indicating the thermal stability of the products. Among all ternary metal hydrides, the sodium derivative of the [PdH$_2$]$^{2-}$ anion is certainly unique as it melts at 408 °C without decomposition.[170] This dihydride was characterized by powder X-ray, neutron (the deuterio derivative), and single-crystal X-ray diffraction.[170] Remarkably, the Na$_2$PdH$_2$/Na$_2$-PtH$_4$ system readily underwent the Pd/Pt exchange which led to partial substitution of the metal in each hydride by that of the other.[178] The first mixed alkali−alkaline earth transition metal hydride, LiSr$_2$-PdH$_5$, was recently prepared by the slow (10−14 days) reaction between H$_2$ and a Li−Sr−Pd alloy at 520−530 °C and 75 bar.[179] When a Sr−Pd alloy was treated with hydrogen at 200 °C, the SrPdH$_{2.7}$ phase of perovskite-type structure was obtained,[180] similar to the palladium−lanthanide nonstoichiometric hydrides, EuPdH$_{2.9}$,[181] and YbPdH$_{2.7}$,[182] reported earlier. Structural studies of some of the solid-state ternary hydrides merit separate consideration and will be discussed in section VI.

V. Reactions of Palladium Hydrides

Hydrido complexes of palladium are reactive species. All reactions of Pd hydrides can be subdivided into two major categories: (i) reactions that result in the Pd−H bond cleavage and (ii) reactions in which the Pd−H bond remains intact. The latter can be regarded as methods to prepare new palladium hydrides from precursors which already contain the Pd−H bond. Such reactions can be found in sections II.A.e and II.B.a. In this section, we will review various reactions of palladium hydrides, which proceed with the Pd−H bond dissociation. Many of these transformations are of relevance to catalysis, because Pd hydrides have been proposed as catalytic intermediates in a variety of catalytic reactions including industrially important processes.[87,183] Let us first touch on some of these reactions and their mechanisms which apparently involve (hydrido)palladium complexes.

The Wacker Oxidation of Olefins. One of the most impressive examples is the Wacker oxidation of ethylene (eq 27), which nowadays accounts for ∼85% of all acetaldehyde produced worldwide.[183] The Wacker oxidation of various substrates has been extensively studied,[28−30,87,183−189] revealing the general mechanistic features of the process (Scheme 2).
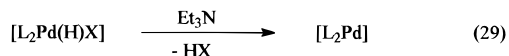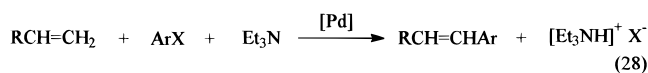
$$2\ CH_2{=}CH_2 \ +\ O_2 \ \xrightarrow[\text{HCl}]{\text{PdCl}_2,\ \text{CuCl}_2} \ 2\ CH_3CHO \qquad (27)$$
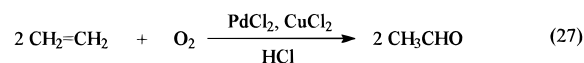
As can be seen from Scheme 2, the Wacker oxidation involves replacement of a chloride ion in [PdCl$_4$]$^{2-}$ (depicted as Pd^{2+}) by the olefin, followed by the formation of the hydroxyethyl intermediate. During these steps, more chloro ligands are likely substituted by water or hydroxo ligands. No unambiguous direct proof has been obtained for the subsequent steps, i.e., β-elimination to give a palladium hydride, its decom-

Scheme 2
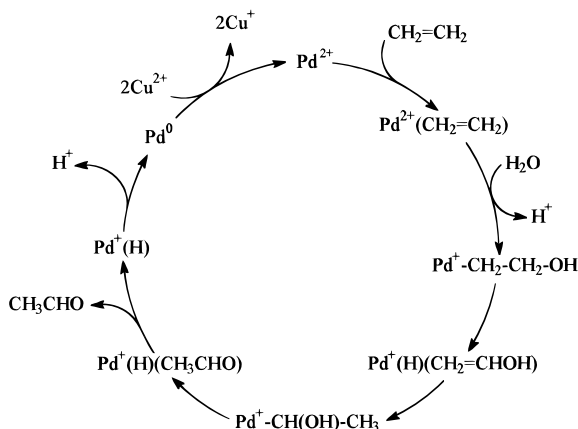
position via reductive elimination, and the formation of Pd metal. It is still questionable whether a hydroxyethyl intermediate emerges due to intermolecular attack of H_2O on the coordinated olefin[190,191] or via migratory insertion.[192,193] It is also unclear whether Pd metal does form in the catalytic reaction.[194] However, these steps have been meticulously studied, and a considerable amount of information has been obtained. In contrast, neither β-elimination nor reductive elimination of HCl from the resulting hydride (H^+ loss) have been investigated to a point at which firm conclusions could be drawn regarding these steps. One of the most striking observations made in this field is the fact that no deuterium was incorporated into the product when the oxidation was conducted in D_2O.[87,195] This indicates that if some hydrido species do mediate the process, (i) the hydrides are not capable of undergoing any exchange with water, (ii) they do not add across the carbon–carbon double bond of the as yet unreacted olefin, and (iii) when both processes are possible, β-hydrogen elimination from the oxygen, not the carbon, is preferred. Clearly, the nature of the hydrido species participating in the oxidation of ethylene is insufficiently understood and should be explored. This is also true for other Wacker-type oxidation reactions leading to ketones, acetals, vinyl acetate, glycol acetates, and other valuable products.

The Heck Arylation of Olefins. This process (eq 28)[29,30] has no analogues in noncatalytic synthetic chemistry and is therefore of considerable interest. It is believed that the final step of the catalytic cycle is the base-induced reductive elimination of the hydrogen halide, HX, from the corresponding Pd(II) hydrido intermediate, resulting in regeneration of the catalytically active Pd(0) species (eq 29).

$$RCH=CH_2 \ + \ ArX \ + \ Et_3N \ \xrightarrow{[Pd]} \ RCH=CHAr \ + \ [Et_3NH]^+ \ X^-$$
$$(28)$$

$$[L_2Pd(H)X] \ \xrightarrow[- HX]{Et_3N} \ [L_2Pd] \qquad (29)$$

L = tertiary phosphine

Unlike the Wacker oxidation, the arylation of olefins is usually conducted in the presence of tertiary phosphines, L, which stabilize Pd hydrides. In fact, complexes of the general formula $[(R_3P)_2Pd(H)X]$ (X = halogen) are the most frequently encountered

palladium hydrides (see section II). It is surprising that there have been no reports in the literature describing a detailed study of reductive elimination of HX from halo(hydrido)palladium complexes. At the same time, the reductive elimination of HCl from similar chloro(hydrido)platinum compounds has been studied by a number of research groups and found to be quite facile under both homogeneous and phase-transfer conditions.[19]
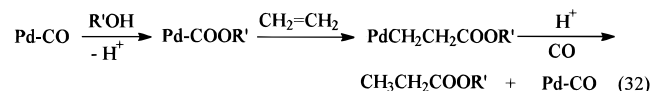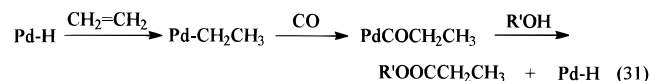
It was mentioned that $[(t\text{-}Bu_3P)_2Pd]$ formed upon treatment of $[(t\text{-}Bu_3P)_2Pd(H)Cl]$ with n-BuLi in hexane.[69] Different mechanisms could be operative in this dehydrochlorination. For instance, the Pd–Cl bond might be alkylated with n-BuLi to give a (σ-butyl)palladium hydride which would lose butane (reductive elimination) or butene (β-elimination). Should the latter occur, the resulting dihydrido complex would instantly eliminate H_2, thus transforming to the Pd(0) complex that was isolated. No studies have been reported on dehydrohalogenation of $[L_2Pd(H)X]$ with nonalkylating bases like alkali, amines, proton sponge, etc. Mechanistic considerations[19] predict that base-promoted eliminations of HX would be more feasible for Pd hydrides because, as compared to their Pt analogs, they are (i) more acidic and (ii) more reactive toward ligand exchange. Some research is definitely required to find out if relatively stable and certainly accessible complexes $[L_2Pd(H)X]$ can eliminate HX in the presence of various bases.

The Hydrocarbalkoxylation and Hydrocarboxylation of Olefins. There have been numerous debates whether these important catalytic reactions (eq 30)[196–201] occur via a Pd–H or a Pd–COOR′ (Pd–COOH) intermediate.

$$RCH=CH_2 \ + \ R'OH \ + \ CO \ \xrightarrow{[Pd]}$$
$$RCH_2CH_2COOR' \ + \ CH_3CH(R)COOR' \qquad (30)$$
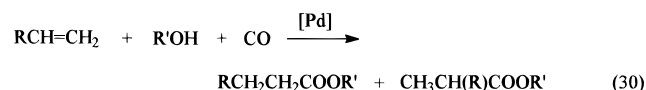
R' = Alk or H

Two mechanisms (eqs 31 and 32) have been proposed, with indirect evidence having been found for both. At present, however, most researchers agree that the hydrido mechanism (eq 31) is more plausible than the alkoxycarbonyl path (eq 32).[202–205] Catalytic reaction 30 was discussed in the most recent review of transition metal hydrides in organic synthesis,[200] implying that the authors accepted the hydrido mechanism which was originally proposed by Knifton.[206]

$$Pd\text{-}H \xrightarrow{CH_2=CH_2} Pd\text{-}CH_2CH_3 \xrightarrow{CO} PdCOCH_2CH_3 \xrightarrow{R'OH}$$
$$R'OOCCH_2CH_3 \ + \ Pd\text{-}H \quad (31)$$

$$Pd\text{-}CO \xrightarrow[-H^+]{R'OH} Pd\text{-}COOR' \xrightarrow{CH_2=CH_2} PdCH_2CH_2COOR' \xrightarrow[CO]{H^+}$$
$$CH_3CH_2COOR' \ + \ Pd\text{-}CO \quad (32)$$

Cavinato and Toniolo[202] reported interesting results and convincing arguments in support of the hydrido mechanism (eq 31). For instance, when $[(Ph_3P)_2Pd(Cl)(COOMe)]$ was treated with 1-hexene under the catalytic reaction conditions but in the absence of CO, no ester formation was observed. On

the other hand, the closely related [(Ph$_3$P)$_2$Pt(Cl)-(COOEt)] readily underwent displacement of the chloro ligand by CO,[207] suggesting that the Pd counterpart would also do so. The resulting cationic Pd species, especially in the presence of CO, may be more reactive toward the olefin than the [(Ph$_3$P)$_2$Pd-(Cl)(COOMe)]. Earlier, it was demonstrated that heating [(Me$_3$P)$_2$Pd(CH$_2$Ph)(COOMe)] at 80 °C did not cause reductive elimination of the ester,[208] whereas the methyl phenylacetate and Pd(0) readily formed upon treatment of [L$_2$Pd(Cl)CH$_2$Ph] with MeOH and CO in the presence of triethylamine.[202,208] No reaction occurred when [(Ph$_3$P)$_2$Pd(Cl)(COOMe)] was used as the catalyst for the carbonylation of 1-hexene in the presence of sodium carboxylates or Et$_3$N and in the absence of PPh$_3$.[202] However, this observation cannot completely rule out the nonhydrido mechanism (eq 32) as most catalytic runs, with [(Ph$_3$P)$_2$-PdCl$_2$] as added catalyst, were conducted in the presence of extra triphenylphosphine.[202]

Among other factors pointing to the hydrido mechanism (eq 31) is the enhanced catalytic activity in the presence of H$_2$ which could favor the formation of Pd hydrides (see ref 202 and references cited therein). Formic acid[203] is perhaps beneficial for the same reason. Labeling,[209a] *in situ* IR,[209b] and kinetic studies[209c,d] strongly support the hydrido mechanism for the closely related hydrocarboxylation of styrene. Palladium hydrides likely mediate the Pd-catalyzed water gas shift reaction in the presence of HCl.[210] It is possible that oligomerization and polymerization of ethylene with CO to polyketones[211] also involve Pd hydrides as intermediates. On the other hand, a nonhydrido mechanism may govern the Pd-catalyzed hydroalkoxycarbonylation of olefins under certain conditions, e.g., in the absence of chloride anions.[212]

A wide variety of other important Pd-catalyzed processes seem to proceed via palladium hydrides as intermediates, e.g., the allylic alkylation reactions[213] which involve the formation of π-allylic Pd complexes from olefins, the telomerization reactions of conjugated dienes,[29] the water gas shift reaction[43] and reduction of various substrates with CO/H$_2$O,[214] the isomerization of epoxides to carbonyl compounds,[215] the reductive dehalogenation of aromatic halides,[216] the recently reported hydrophosphorylation of alkynes,[217] and others. All these examples demonstrate the significance of (hydrido)palladium chemistry for homogeneous catalysis. However, for most of the above cases, there has been no direct evidence for Pd hydrides; they were merely proposed as key catalytic intermediates by logically applying the fundamentals of modern organometallic and inorganic chemistry. Palladium hydrides have rarely been observed in catalytic reaction mixtures. A few cases in which the hydrido species were detected and characterized, merit special consideration.

When the water gas shift reaction, with [Pd$_2$(μ-dmpm)$_2$Cl$_2$] as added catalyst, was quenched to 25 °C and the ^{31}P NMR spectrum was measured in D$_2$O, two signals were observed.[43] One of those was a singlet at 3.6 ppm which was assigned to [Pd$_2$(μ-dmpm)$_2$(μ-CO)(OD)$_2$]. The other signal was a 1:2:3:2:1 quintet assigned to the dideuteride, [Pd$_2$(μ-dmpm)$_2$(μ-CO)(D)$_2$]. Further support for the mech-

Scheme 3

P = PMe$_2$
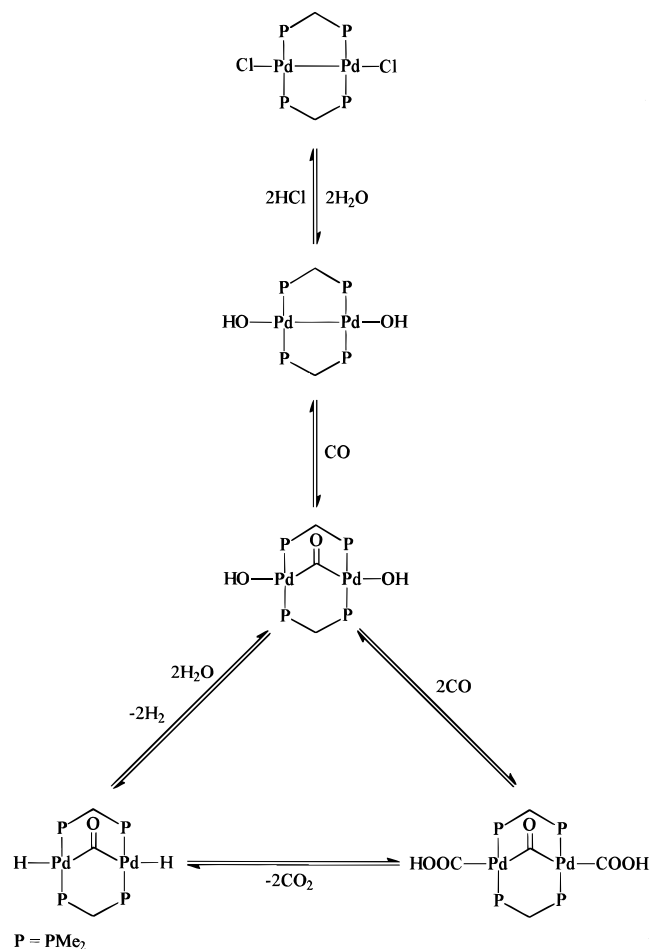
anism was found by obtaining [Pd$_2$(μ-dmpm)$_2$(μ-CO)-(Ph)$_2$] by the decomposition of [Pd$_2$(μ-dmpm)$_2$(μ-CO)-(COOPh)$_2$] under nitrogen. Other intermediates suspected of being involved in the catalytic cycle were also detected and meticulously and reliably characterized by spectral means. This work by Kullberg and Kubiak[43] is a rare and probably one of the most impressive examples of a successfully elucidated catalytic mechanism involving palladium hydrides (Scheme 3).

Zudin et al.[122] demonstrated that the cationic hydride, [(Ph$_3$P)$_3$PdH]$^+$, generated in the Pd(OAc)$_2$/PPh$_3$/CF$_3$COOH/H$_2$O system (section II.B) catalyzed the water gas shift reaction and the carbonylation of ethylene to diethyl ketone. In the water gas shift reaction, the key step involving the hydride was the acidolysis of the Pd-H bond to give H$_2$. When ethylene was introduced to the system, hydropalladation of the C=C bond was observed (see below). A number of interesting observations were made regarding other steps of the catalytic cycle.

Portnoy and Milstein[139] reported the catalytic transfer deuteration of cyclooctene and ethyl vinyl ether with acetone-d_6 in the presence of [(dippp)$_2$Pd$_2$-(μ-H)(μ-CO)]$^+$. Monitoring the reaction by ^{31}P NMR spectroscopy revealed the presence of only two complexes in the mixture, namely the cationic hydride and small amounts of its deuterio derivative. The reaction apparently occurred via a series of hydropalladation and β-elimination processes involving the olefin and the acetone enol form. No hydropallada-

tion products were observed by NMR, suggesting that the equilibrium between the hydride and a palladium alkyl species was shifted toward the hydride. In other words, β-elimination processes occurred at a considerably higher rate than the addition of the Pd–H bond across the C=C double bonds.

Three different palladium hydrides were detected by ^{1}H and ^{31}P NMR spectroscopy when a solution of [Pd(dpba)Cl][+] Cl^{−} was treated with H$_2$ prior to catalyzing the hydrogenation of cyclohexene.[218] In line with the proposed structures were the observed ^{1}H NMR chemical shifts ($-25.8 \div -31.2$ ppm) and the multiplicity of the hydrido resonances. Both ^{1}H NMR and kinetic studies suggested that of the three hydrido species observed, the highest catalytic activity was exhibited by a monohydride formulated as [Pd(dpba)H][+] Cl^{−}. Unfortunately, this compound was not isolated from the mixture, although, according to the ^{31}P NMR spectrum, it accounted for ~50% of all phosphine palladium species present.

Very recently, Bruk et al.[219] reported that a weak, broad resonance centered at -1.9 ppm was observed in the ^{1}H NMR spectrum of a reaction mixture rapidly cooled to -40 °C. The mixture was analyzed 10 min after the Pd-catalyzed reaction began, leading to succinic and maleic anhydrides from acetylene and CO. Remarkably, the active catalytic system (PdBr$_2$/LiBr/MeCN) did not employ tertiary phosphines or other ligands which would stabilize a palladium hydride. This shows that attempts to detect a hydrido Pd intermediate in a catalytic reaction mixture which lacks such ligands, should not be *a priori* regarded as worthless. On the other hand, although the catalytic process likely involves Pd hydrides as intermediates, the observed "hydrido" resonance may have been due to a hydroxo, not hydrido, species. For instance, chemical shifts of -1.5 and -1.8 ppm have been observed for the Pd–OH resonances in ^{1}H NMR spectra of *trans*-[L$_2$Pd$_2$-Ph$_2$(μ-OH)$_2$], where L = Ph$_3$P and Cy$_3$P, respectively.[46] It is worth noting that the carbonylation (20 °C, 1 atm) of the organopalladium hydroxide with L = PPh$_3$ smoothly and rapidly furnished benzoic anhydride in quantitative yield.[44] Therefore, additional studies would be required before the hydridic nature of the observed species could be unambiguously established. For instance, an attempt could be made to stabilize the species resonating at -1.9 ppm[219] by adding a tertiary phosphine to the reaction mixture, in hope that the resulting derivative would be isolable or suitable for further characterization in solution.

The fact that palladium hydrides were used as catalysts for some reactions, naturally makes it tempting to propose these very hydrido complexes as intermediates involved in the catalytic cycle. One should be careful about drawing such conclusions, however. No matter how plausible the participation of the species appears, supporting evidence must be obtained before the proposed route can be accepted. For instance, when [(Ph$_3$P)$_2$Pd(H)Cl] was generated *in situ* from the Pd(0) precursor and HCl (section II.A.b) the solution was successfully used for the carbonylation of 1-heptene.[73] Thus, it would be reasonable to propose the generated hydride as one

of the catalytically important species. On the other hand, it was found that the catalytic reaction readily occurred only when one extra equivalent of HCl was added to the mixture; no carbonylation took place when the Pd(0) complex and HCl were used in a 1:1 ratio.[73] As HCl destroys various palladium hydrido complexes ([(Ph$_3$P)$_2$Pd(H)Cl] included) rapidly and irreversibly (eq 5), the originally generated [(Ph$_3$P)$_2$-Pd(H)Cl] must have decomposed upon addition of the extra equivalent of HCl to the mixture. Therefore, it is questionable if that particular hydride was somehow involved in the catalytic cycle. This, however, does not rule out the possibility of other hydrido species (of different structures and composition) mediating the process.

In light of the above examples it is clear that studying reactions of hydrido palladium complexes is important for catalytic research. In particular, hydropalladation of multiple bonds and reductive elimination of HX are of considerable interest.

A. Addition of Palladium Hydrides across C–C Multiple Bonds

The number of papers describing detailed investigations of hydropalladation reactions of alkenes or alkynes is limited. As early as 1967, Brooks and Glockling[57] mentioned that [(Et$_3$P)$_2$Pd(H)Cl] readily reacted with acrylonitrile, phenylacetylene, tetrafluoroethylene, and butadiene to give a complexity of products which were not characterized. Green and Munakata[111,112] reported that the Pd–H bond of some cationic hydrides readily added across the double bonds of dienes thus causing the oligomerization reaction. Mabbott and Maitlis[99,100] found that the cationic palladium hydrides, [(dppe)PdH][+] and [(dpae)-PdH][+] generated *in situ* (see section II.B.a) reacted with acetylenes, but the reaction products were not characterized. The dehydrogenation reactions of rather ill-defined hydrido species with methyl acrylate[34] and dimethoxycarbonylacetylene[220] were reported to give a mixture of products and an alkenyl compound, respectively. Evidence has been obtained for the facile insertion reactions between mononuclear[121,122] or polynuclear[165] cationic palladium hydrides and various unsaturated hydrocarbons. Although it is clear that most palladium hydrides are, in general, quite reactive toward olefins, dienes, and acetylenes, there are some examples of Pd–H bonds whose reactivity toward such substrates seems to be rather low. For instance, the addition of acetylene to [(Cy$_3$P)$_2$Pd(H)(NHPh)] yielded the hydrido alkynyl complex, [(Cy$_3$P)$_2$Pd(H)(C≡CH)], and aniline; no insertion reaction was observed.[78] Ethylene and acrylonitrile induced the reductive elimination of aniline from the [(Cy$_3$P)$_2$Pd(H)(NHPh)]. Hence, no addition of the Pd–H bond across the C=C bonds was detected in this case, either.[78] The carbonyl hydrido binuclear complex, [L$_2$Pd$_2$(μ-CO)(μ-H)][+] where L = (*S,S*)-bdpp, was rather inert toward styrene, whereas the highly unstable analogous compound, [(bdpp)Pd-(H)Cl], that exists only at low temperatures, readily inserted styrene at -30 °C.[140] However, the fact that palladium alkyls cannot be isolated from, nor observed in these reactions, does not necessarily point to the low reactivity of the hydrides toward unsatur-
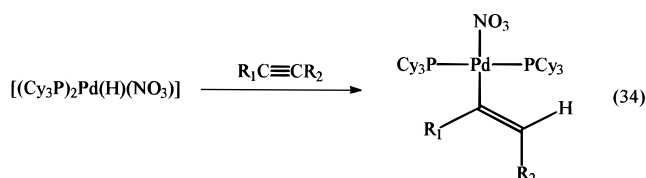
ated substrates. For instance, Milstein's complex, $[(dippp)_2Pd_2(\mu\text{-}H)(\mu\text{-}CO)]^+$,[139] would have been considered unreactive toward the C≡C bonds if no labeling experiments (see above) had been conducted. Similarly, the incorporation of deuterium into unreacted styrene was observed in the Pd-catalyzed hydrocarboxylation of PhCH=CH$_2$ in the presence of D$_2$O, indicating that a series of hydropalladation and β-elimination reactions occurred in the system.[209a] Clearly, if the equilibrium (eq 33) is shifted to the hydride, no hydropalladation may be observed, unless isotope labeling is employed for the study. Indeed, the fact that some $[(R_3P)_2Pd(H)Cl]$ can be efficiently prepared by β-elimination reactions (see section II.A.d)[99−101] demonstrates that equilibrium 33 between the metal alkyl and hydride can be shifted almost entirely to the latter.

$$\text{Pd-H} \quad + \quad \text{C=C} \quad \rightleftharpoons \quad \text{Pd-C-C-H} \qquad (33)$$
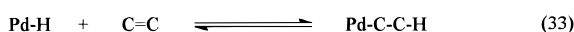
The lability of some hydropalladation products makes it difficult, if not impossible, to study reactions between Pd hydrides and unsaturated compounds. In some cases, however, the adducts were stable enough for isolation and exhaustive characterization.

a. Hydropalladation of Alkynes

The first detailed study of the Pd−H bond addition across the C≡C bond of acetylenes was reported by Clark and Milne.[103] It was found that although the $[(Cy_3P)_2Pd(H)X]$ did not react with the alkynes when X = Cl, complexes with weakly bound ligands (X = NO$_3$ or MeCN) were very reactive toward various electron-deficient acetylenes. Both nitrato and acetonitrile hydrides smoothly added alkynes containing one electron-withdrawing group to give alkenyl complexes in high yields. The vinylic complexes were found to be all *trans* (eq 34). Similar complexes were obtained when the cationic hydride was employed (X = MeCN). In this case, the alkenyl products were isolated as neutral chlorides by quenching the reaction solutions with LiCl. Hence, the addition was always *cis* and the hydridic H added exclusively to the acetylenic carbon containing the electron-withdrawing group.

$$[(Cy_3P)_2Pd(H)(NO_3)] \xrightarrow{R_1C\equiv CR_2} \begin{array}{c} NO_3 \\ | \\ Cy_3P-Pd-PCy_3 \\ \diagdown \\ R_1 \quad H \\ R_2 \end{array} \qquad (34)$$

R$_1$ = Me; R$_2$ = COOMe
R$_1$ = Ph; R$_2$ = COOMe
R$_1$ = Ph; R$_2$ = CF$_3$
R$_1$ = H; R$_2$ = COOMe

In contrast, the vinylic complexes derived from the *cis* addition of similar Pt hydrides to acetylenes often incorporated the more electron-withdrawing substituent of the acetylene on the α-carbon atom.[221] No firm conclusion was drawn regarding mechanisms of the Pd−H bond addition to the triple bond. However, it was demonstrated that the insertion occurred via an intermediate in which the hydrido ligand remained on the metal.[103] Unlike the reactions of

Scheme 4

$[(Me_2NCS_2)Pd(PEt_3)H]$ + $R_1\text{-}C\equiv C\text{-}R_2$ $\xrightarrow{-78^\circ C}$
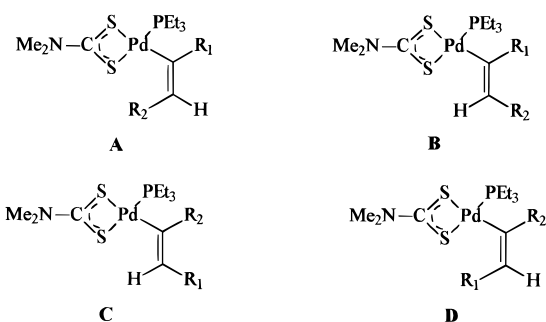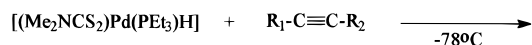
R$_1$	R$_2$	Ratio:	A	B	C	D
MeO$_2$C	MeO$_2$C		4	1	-	-
MeO$_2$C	Me		1	4	1	1
Pr	H		4	-	1	traces

acetylenes containing one electron-withdrawing group, the interaction between the Pd hydrides and RC≡CR, where R = MeOOC or CF$_3$, was much more complicated, leading to mixtures of unidentified products. Interestingly, when mixed in the presence of proton sponge, the same reactants gave Pd(0) complexes in high yield, due to reductive elimination of HCl from the metal center (see below).[103] On the other hand, $[(Et_3P)_2Pd(H)(C\equiv CH)]$,[85] generated *in situ*, smoothly reacted with MeOOCC≡CCOOMe to give the *cis* insertion product, $[(Et_3P)_2Pd(MeOOC=CHCOOMeO-(C\equiv CH)]$, in good yield.[86] The adduct was characterized by a single-crystal X-ray diffraction.[86]

Portnoy and Milstein[139] recently reported the hydropalladation of diphenylacetylene and phenylacetylene with $[(dippp)_2Pd_2(\mu\text{-}H)(\mu\text{-}CO)]^+$ Cl$^-$. In both cases, the stereochemistry of the addition was *cis*. The reaction with PhC≡CPh led to the formation of three palladium complexes, $[(dippp)Pd(\eta^2\text{-}PhC\equiv CPh)]$, $[(dippp)Pd(Cl)(C(Ph)=CHPh)]$, and $[(dippp)Pd(Cl)-(C(O)C(Ph)=CHPh)]$. The latter apparently formed due to the release of CO in the course of the reaction and the subsequent carbonylation of the vinylic adduct.[139] It was proposed that the acetylene induced the splitting of the dimeric hydride to $[(dippp)Pd(H)-Cl]$ and $[(dippp)Pd(CO)]$. The former added across the triple bond of the alkyne, while the latter lost CO and formed the (η^2-acetylene)palladium(0) complex. Similar results were obtained with phenylacetylene which added to the Pd center exclusively via the more sterically hindered, Ph-substituted carbon atom.

In contrast with the selective *cis* hydropalladations described above, low-temperature reactions between the labile $[(Me_2NCS_2)Pd(PEt_3)H]$ and various alkynes furnished all possible adducts (Scheme 4).[65] Interestingly, the reaction with 3-hexyne did not afford isolable products. It is likely that the hydropalladation reactions with $[(Me_2NCS_2)Pd(PEt_3)H]$ involve electron-transfer processes due to which the *trans*-addition products emerge.[222] On the other hand, *cis*-addition is indicative of synchronous, four-centered mechanism. Having considered and analyzed their

own and literature data, Portnoy and Milstein[139] concluded that the mode of hydropalladation of alkynes is mostly governed by electronic rather than steric factors.

b. Hydropalladation of Olefins

Only a few reactions of this kind have been reported. Reger and Garza[65] found that the unstable hydride, $[(Me_2NCS_2)Pd(PEt_3)H]$, readily reacted with acrylonitrile to give specifically the branched isomer, $[(Me_2NCS_2)Pd(PEt_3)(CH(CN)CH_3)]$, in 86% yield. This complex is thermodynamically more stable than the linear isomer, $[(Me_2NCS_2)Pd(PEt_3)(CH_2CH_2CN)]$, which was prepared independently.[223] However, the branched isomer is certainly the primary, not secondary product of the reaction, because the temperature required for the isomerization is at least 100 °C above that used for the hydropalladation. No products were isolated from reactions of the same hydride with 1,4-butadiene, styrene, 1-hexene, allene, and allyl methyl ether.

The (hydrido)palladium dimer, $[(dippp)_2Pd_2(\mu\text{-}H)\text{-}(\mu\text{-}CO)]^+ Cl^-$, readily underwent H/D exchange of the hydride in the presence of acetone-d_6.[139] When the exchange was conducted in the presence of cyclooctene or ethyl vinyl ether, the catalytic transfer deuteration of the olefins was observed. Although no palladium alkyls were isolated due to the facile β-elimination, the H/D exchange experiments clearly indicated anti-Markovnikov addition of the Pd−H(D) bond to the olefins. No H/D exchange was observed when norbornene was employed under identical conditions. Instead, the formation of the mononuclear norbornyl palladium complex and its CO insertion product was observed. Obviously, the rate of β-H elimination determines the mode of the reaction between the binuclear hydride and unsaturated hydrocarbons.[139]

It was demonstrated that the cationic hydride, $[(Ph_3P)_3PdH]^+$, generated from $[(Ph_3P)_4Pd]$ in 70% aqueous trifluoroacetic acid readily reacted with ethylene at −25 °C to give a (σ-ethyl)palladium complex, presumably $[(Ph_3P)_2PdEt]^+$.[122] At this temperature, protons of the ethyl group underwent a slow (on the NMR time scale) exchange which became fast at +25 °C. Although equilibrium 33 in this system was almost entirely shifted toward the palladium alkyl, β-elimination processes certainly occurred causing the exchange that was observed in the NMR experiments. Both stereochemistry and mechanism of hydropalladation reactions with the $[(Ph_3P)_3PdH]^+$ remain unknown, as no reactions with unsaturated hydrocarbons, other than ethylene, were reported.[122]

c. Hydropalladation of Dienes and Polyenes

Although $[(Ph_3P)_2Pd(H)Cl]$ was found unreactive toward isoprene (see above), the cationic species generated by treatment of this hydride with dppe or dpae in the presence of $AgPF_6$ readily added to various dienes and trienes.[100] It was proposed that the reactive species were tricoordinate cationic hydrides, $[Pd(dppe)H]^+$ and $[Pd(dpae)H]^+$ which can easily add across the carbon−carbon double bond of polyenes to give the corresponding η^3-allylic complexes (e.g., eq 35). Both methyls in the molecule were found to be *syn*.

$$\text{\char94\char94\char94\char94} \quad + \quad [(dppe)PdH]^+ \quad \longrightarrow \quad \left[(dppe)Pd\text{---} \right]^+ \quad (35)$$
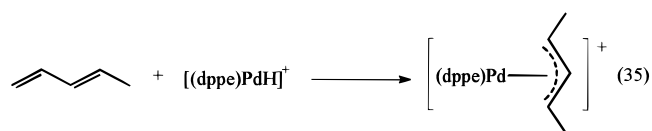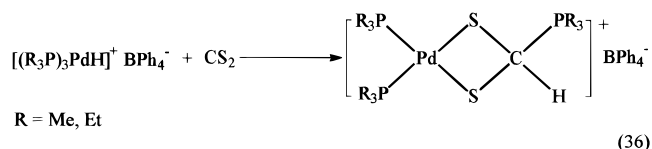
Similar η^3-allylic complexes were obtained with other dienes, including isoprene, cyclopentadiene, 1,3-cyclohexadiene, 1,3-COD, and 1,5-COD. The reactions with the two isomeric cyclooctadienes furnished the same allylic complex, due to the double-bond isomerization in the 1,5-COD. Trienes, like cycloheptatriene and 1,5,9-cyclododecatriene, also reacted with these hydrides to give allylic compounds. When norbornadiene and 2-butyne were reacted under the same conditions, only polymeric materials formed which were not studied. However, the majority of the π-allylic complexes obtained in that work were reliably characterized.[100]

In closing this section, it is worth noting that the data available on hydropalladation reactions of unsaturated hydrocarbons is not sufficient to draw firm conclusions. First of all, some palladium hydrides do not form stable adducts with various olefins, acetylenes, and polyenes. This fact can be rationalized in terms of either the poor reactivity of some hydrides toward carbon−carbon multiple bonds, or the facile β-elimination which determines the position of equilibrium 33. Second, it is still not very clear how the nature of ligands on the Pd center, the electronic and steric properties of the unsaturated substrate, the solvent, and reaction conditions influence the reactivity of the system and govern the selectivity of hydropalladation reactions. Extensive and meticulous research is needed to clarify these points. Finally, new palladium hydrides have to be synthesized for modeling various Pd-catalyzed reactions of unsaturated organic substrates.

B. Addition of Palladium Hydrides across Carbon–Heteroatom Multiple Bonds

Evidence was obtained for the fast exchange between $^{13}CO_2$ and $[(Cy_3P)_2Pd(H)(O_2CH)]$, indicating the facile insertion of carbon dioxide into the Pd−H bond.[83] Carbon disulfide smoothly reacted with $[(R_3P)_3PdH]^+ BPh_4^-$ (R = Me or Et) to give the 4-membered palladacycles (eq 36).[224] Interestingly, the reaction between the trimethylphosphine cationic hydride and COS was not as clean, giving rise to many complexes.[225] One of them was isolated and formulated as $[(Me_3P)_6Pd_3(\mu\text{-}S)_2]^{2+} (BPh_4^-)_2$.

$$[(R_3P)_3PdH]^+ BPh_4^- \; + \; CS_2 \longrightarrow \left[\begin{array}{c} R_3P \\ R_3P \end{array} Pd \begin{array}{c} S \\ S \end{array} C \begin{array}{c} PR_3 \\ H \end{array} \right]^+ BPh_4^-$$

R = Me, Et

$$(36)$$

C. Reductive Elimination of HX and Deprotonation

As mentioned above, chloro hydrido complexes of palladium, $[(R_3P)_2Pd(H)Cl]$, are the most frequently

encountered palladium hydrides. Although they likely participate in various catalytic processes (e.g., the Heck arylation of olefins), reductive elimination of HCl from these hydrides still remains unexplored. A few base-promoted reductive elimination reactions have been reported for both neutral and cationic Pd hydrides. For instance, mixing $[(Cy_3P)_2Pd(H)NO_3]$ with proton sponge in the presence of MeOOC-C≡COOMe furnished the zero-valent Pd complex, $[(Cy_3P)_2Pd(MeOOCC≡COOMe)]$, in quantitative yield.[103] The cationic hydride, $[(Cy_3P)_2Pd(H)(MeCN)]^+$, reacted with proton sponge and the acetylene similarly. It is remarkable that when acetylenes containing only one electron-withdrawing group were used, no zero-valent complexes emerged. Alkenyl complexes formed instead due to the facile and irreversible hydropalladation reaction (section V.A.a).[103] The treatment of $[(Cy_3P)_2Pd(H)(H_2O)]^+$ with bases, like Ph_3C^-, OH^-, Et_3N, and Cy_3P, caused deprotonation of the Pd−H bond and the generation of $[(Cy_3P)_2Pd]$ in high yield.[129] Interestingly, the Pd−H bond in the $[(Cy_3P)_2Pd(H)(H_2O)]^+$ was found to be more acidic than O−H bonds of the aqua ligand.[129]

A number of π-acid-promoted reductive elimination reactions have been described for various Pd hydrides. For instance, bubbling CO through a solution of $[(Cy_3P)_2Pd(H)(succinimido)]$ resulted in the elimination of succinimide in 85% yield.[92] Similarly, ethylene and acrylonitrile caused the elimination of aniline from $[(Cy_3P)_2Pd(H)(NHPh)]$ and concomitant formation of the corresponding Pd(0) olefin complexes.[78] The CO-promoted elimination and deprotonation reactions have been reported for $[(Cy_3P)_2Pd(H)(OAr)]\cdot ArOH$ (Ar = Ph, C_6F_5)[94] and $[(t-Bu_3P)_2Pd(H)(H_2O)]^+$.[127] The resulting Pd(0) complexes, presumably trinuclear carbonyl phosphine clusters, were characterized by elemental analysis and IR spectra.

Osakada et al.[96] reported that the thermal decomposition of $[(Cy_3P)_2Pd(H)(SAr)]$ at 200 °C gave rise to $Cy_3P=S$ and ArH as the major products. The Pd-(0) species formed were not characterized. Some palladium hydrides undergo spontaneous reductive elimination reactions at ambient and even lower temperatures. Examples include the elimination of RH from the ill-defined organopalladium(IV) hydrides, $[(Ph_3P)_2Pd(H)(R)X_2]$ (X = I, Br, Cl),[90] the elimination of aniline from $[(Cy_3P)_2Pd(H)(NHPh)]$,[78] and the binuclear elimination of MeCHO from the cationic complexes, $[Pd_2(H)(MeCO)(\mu\text{-}Cl)(\mu\text{-}dppm)_2]^+$ and $[Pd_2(MeCO)_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$.[145] Jones and Cole-Hamilton[226] proposed that the photochemical production of H_2 from $[(Et_3P)_3PdH]^+$ in water involved the intermediate formation of the Pd (IV) dihydride, $[(Et_3P)_3Pd(H)_2]^{2+}$, followed by reductive elimination of H_2.
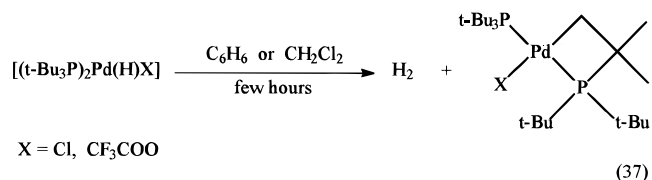
D. Oxidation and Reduction Reactions

Hydrido complexes of palladium are usually air-sensitive compounds which give complex mixtures of products upon oxidation. Clearly, the oxidation reactions proceed with Pd−H bond cleavage. To our knowledge, there have been no publications describing an investigation of such oxidation reactions, except for one example which is certainly of consider-

able interest. A decade ago Vargaftik and his group found that the polynuclear hydrido complex, $[Pd_4\text{-}(Phen)(OAc)_2H_4]_n$ (see section IV) reacted with O_2 to give the giant palladium cluster, $[Pd_{570\pm30}(Phen)_{63\pm3}\text{-}(OAc)_{190\pm10}]$.[158,227] This unique giant cluster was thoroughly and meticulously studied by various physical methods and found to possess catalytic activity in a number of reactions.[158]
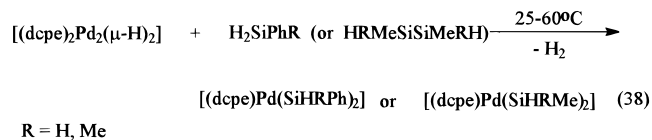
The attempted preparation of $[(t\text{-}Bu_3P)_2Pd(H)_2]$ through the reduction of $[(t\text{-}Bu_3P)_2Pd(H)Cl]$ with $NaBH_4$ in EtOH furnished the zero-valent complex, $[(t\text{-}Bu_3P)_2Pd]$, in good yield.[68,77] Treatment of the tetraphenylborate salt of $[(Et_3P)_3PdH]^+$ with sodium or magnesium amalgam in THF resulted in the evolution of H_2 (90−91% yield) and precipitation of an unidentified Pd-containing material.[115] The cation, $[(Et_3P)_3PdH]^+$, can also be reduced electrochemically[228] or with the photochemically produced $[Ru(Bipy)_3]^+$.[229] However, zinc amalgam failed to reduce the $[(Et_3P)_3PdH]^+$.[115]

E. Palladation of C−H and Si−H Bonds

Clark, Goel, and Goel[68,77,101] reported the facile intramolecular metalation of the tributylphosphine ligands in $[(t\text{-}Bu_3P)_2Pd(H)X]$, where X = Cl or CF_3-COO, according to eq 37. The resulting palladacycles lost the *tert*-butylphosphine ligand and dimerized upon standing in solution for one day. The metalation likely involved oxidative addition of a C−H bond of the phosphine ligand to the electron-rich palladium center, followed by reductive elimination of H_2 from the dihydrido intermediate.

$$[(t\text{-}Bu_3P)_2Pd(H)X] \xrightarrow[\text{few hours}]{C_6H_6 \text{ or } CH_2Cl_2} H_2 \quad + \quad \text{[palladacycle structure]}$$

X = Cl, CF_3COO

(37)

Stable bis(silyl)palladium complexes were prepared by reacting $[(dcpe)_2Pd_2(\mu\text{-}H)_2]$ with H_2SiPhR or $HRMeSiSiMeRH$, where R = H, Me, or Ph (eq 38).[137]

$$[(dcpe)_2Pd_2(\mu\text{-}H)_2] \quad + \quad H_2SiPhR \text{ (or } HRMeSiSiMeRH) \xrightarrow[-H_2]{25\text{-}60^oC}$$

$$[(dcpe)Pd(SiHRPh)_2] \quad \text{or} \quad [(dcpe)Pd(SiHRMe)_2] \quad (38)$$

R = H, Me

VI. Structural, Spectral, and Theoretical Studies

The first single-crystal X-ray structure of a palladium hydrido complex was reported by Schneider and Shearer[56] in 1973. However, it is noteworthy that relatively short Pd−H contacts (2.84−2.85 Å) were found even earlier in the red form of $[(PhMe_2P)_2PdI_2]$ where the ortho-phenyl hydrogens "complete" the square-planar coordination sphere of Pd to octahedral.[230] Similar Pd−H contacts were also found in other complexes, e.g., $[(Ph_3P)_2PdI_2]$[231] and $[(t\text{-}Bu_2PhP)_2Pd]$.[232] A very interesting structure was reported by Roe et al.,[233] revealing a short (2.3 Å) contact between the Pd atom and the vinylic hydrogen in $[(Ph_3P)_2Pd(Br)(C(R)=C(R)C(R)=C(R)H)]$, where R = COOMe (Figure 1). The vinyl proton in this and
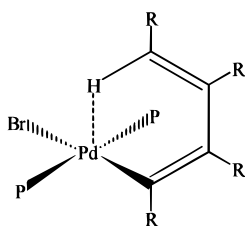
Figure 1. The short Pd−H contact in bromobis(triphenylphosphine)[1,2,3,4-tetrakis(methoxycarbonyl)buta-1,3-dienyl]palladium (ref 233).

other similar complexes resonated at very low field (δ = 8.1−8.6 ppm), exhibiting triplet patterns (J = 1.4 Hz) due to the coupling to the two P nuclei. Other examples of similar axial agostic interactions in Pd complexes are known.[45a]

Although the hydrido ligand was not located in the X-ray structure of trans-[(Et$_3$P)$_2$Pd(H)Cl],[56] its presence was confirmed by the elongated Pd−Cl bond (2.427 Å) due to the strong trans influence. The two P atoms, trans to each other, and one Cl ligand occupied three other sites of the distorted square centered on the Pd atom. Both P−Pd−Cl angles (95.2° and 95.3°) were found noticeably bigger than the ideal value of 90°.

Over 10 years had passed since the crystallographic study of [(Et$_3$P)$_2$Pd(H)Cl],[56] before Kellenberger et al.[144] reported the first full structural characterization of a palladium hydride, including location of the hydrido ligand. A Pd−H bond length of 1.56 (4) Å was found in the structure of [Pd$_2$(H)(CH$_3$)(μ-Cl)(μ-dppm)$_2$]$^+$ BPh$_4^-$,[144,145] with the Pd−Pd distance being 3.01 Å. Since the mid-1980s, a number of palladium hydrides have been crystallographically studied by Braga et al.,[93,94,129] Fryzuk et al.,[135,136] and Portnoy et al.[138] The hydrido ligands in all these structures have been located, and the Pd−H bond distances are given in Table 5. In the X-ray structure of trans-[(t-Bu$_3$P)$_2$Pd(H)(MeCN)]$^+$ BPh$_4^-$,[127] the hydride H-atom was directly located in the difference Fourier map, but not refined, except for its isotropic thermal parameter; the Pd−H bond length was not reported. The crystallographic data on one (hydrido)(mercapto)palladium complex, [(Cy$_3$P)$_2$Pd(H)(SH)], can be obtained through the Cambridge Crystallographic Data Bank.[234] It is remarkable that all structurally characterized mononuclear[93,94,127,129,234] and binuclear[135,136,138] hydrido complexes of palladium are stabilized by electron-rich, bulky phosphine ligands.

The Pd−H bond distances in palladium hydrides structurally characterized to date are in the range of 1.46 (2)−2.13 (4) Å. The shortest Pd−H bond distance (1.46 (2) Å) was found in the square-planar trans-[(Cy$_3$P)$_2$Pd(H)(C$_6$F$_5$O)]·C$_6$F$_5$OH[93,94] where the hydrido ligand is trans to the pentafluorophenoxy group. In the nonfluorinated analogue of this complex, trans-[(Cy$_3$P)$_2$Pd(H)(C$_6$H$_5$O)]·C$_6$H$_5$OH, the Pd−H bond length is significantly longer (1.57 (2) Å). This is obviously due to the difference in electronic properties of phenoxy and pentafluorophenoxy substituents, the latter being much more electron deficient and hence a weaker trans-influencing ligand. Analysis of the X-ray structures of [Pd$_2$(dippp)$_2$(μ-H)$_2$] and its adducts with LiBEt$_4$ and NaBEt$_4$[136] reveals the well-pronounced unsymmetrical nature of the hydrido

Table 5. The Pd−H Bond Distances in Crystallographically Characterized Pd Hydrides

complex	Pd−H, Å	refs
trans-[(Cy$_3$P)$_2$Pd(H)(OC$_6$H$_5$)]·C$_6$H$_5$OH	1.57 (2)	93, 94
trans-[(Cy$_3$P)$_2$Pd(H)(OC$_6$F$_5$)]·C$_6$F$_5$OH	1.46 (2)	93, 94
trans-[(Cy$_3$P)$_2$Pd(H)(H$_2$O)]$^+$BF$_4^-$	1.51 (1)	129
	1.56 (4)	144, 145
	1.62 (5) 1.62 (5) 1.78 (4) 1.79 (4)	135
	1.68 (3) 1.70 (3) 1.76 (3) 1.79 (4)	136
	1.74 (5) 1.77 (4) 1.79 (4) 1.82 (5)	136
	1.67 (5) 1.73 (4) 2.11 (5) 2.13 (4)	136
	1.54 (1) 1.53 (1)	138

bridges in all the three molecules (see Table 5). In solution, however, hydrido ligands within each of these molecules are equivalent, according to the NMR data. The Pd−Pd bond distances are virtually identical for these three complexes (2.8169 (6)−2.8248 (5) Å) and slightly longer than that found in the cationic [Pd$_2$(dippp)$_2$(μ-CO)(μ-H)]$^+$ (2.767 (4) Å).[138] Quite remarkably, the alkali metals (Li and Na) exhibit totally different coordination modes in the adducts between [Pd$_2$(dippp)$_2$(μ-H)$_2$] and LiBEt$_4$ or NaBEt$_4$.[136] In the lithium compound, the Li atom is contiguous to three of the methylene atoms of the BEt$_4$ fragment, interacting with one C−H bond of each of the α-carbons. The sodium atom, in the corresponding adduct, binds to all four hydrogens of only two α-carbons of the four ethyl groups.

Comparison of the Pd−P bond distances in [Pd$_2$-(dippp)$_2$(μ-CO)(μ-H)]$^+$ Cl$^-$ indicates that the CO ligand possesses a higher trans influence than the hydride.[138] This is in accord with the fact that bridging hydrogens usually exhibit noticeably lower trans influence than terminal hydrides.

Table 6. Solid-State Hydrides, M₂[PdD₄] (M = Alkali Metal), Studied by Powder Neutron Diffraction

hydride	T, K	structure type	Pd–D, Å	ref
K₂[PdD₄]	295	Na₂[PtH₄]	1.625 (8)	173
Rb₂[PdD₄]	15	Na₂[PtH₄]	1.674 (7)	174
			1.667 (4)	
Rb₂[PdD₄]	295	K₂[PtCl₆]	1.630 (6)	174
Cs₂[PdD₄]	15	Na₂[PtH₄]	1.60 (2)	174
			1.62 (2)	
Cs₂[PdD₄]	295	K₂[PtCl₆]	1.60 (2)	174

In general, single-crystal X-ray studies have shown no anomalous structural features for the Pd–H bond in the molecular hydrido complexes of palladium. No reports have yet appeared in the literature describing an investigation of palladium hydrides by single-crystal neutron diffraction. However, powder neutron diffraction has been fruitfully used in the structural investigations of ternary palladium hydrides (deuterides) described in section IV. To date, these studies have resulted in the most accurate data on the Pd–H(D) bond length.

The values obtained for the Pd–D bond distances in the linear [PdD₂]²⁻ units of Li₂[PdD₂],[168,169] Na₂-[PdD₂],[170] and KD·K₂[PdD₂][175] were 1.65 (determined by extrapolation), 1.68 (1), and 1.68 Å, respectively. The sodium palladium dihydride (isotypic with Na₂-HgO₂) was also studied by both powder and single-crystal X-ray diffraction, giving the slightly lower and certainly less accurate value of 1.64 (10) Å for the Pd–H bond distance.[170] The Ca[PdD₂] phase was found to have a perovskite-type structure with a ²/₃ occupation of the D position and an apparently statistical arrangement of linear [PdD₂]²⁻ units, the Pd–D bond length being 1.84 (1) Å.[171] The palladium atom in the linear [PdD₂] unit of LiSr₂PdD₅ (1.691 (4) Å) was also coordinated to another hydrogen atom which occupied one of the octahedral positions. An average value of 1.95 Å was found for this weaker contact, the local bond distances being presumably shorter.[179]

The Pd–D bond lengths have been accurately determined for M₂[PdD₄], where M = Na,[172] K,[173] Rb,[174] and Cs.[174] Some of these values are presented in Table 6. In the sodium (9–600 K) and potassium (295 K) tetrahydrido derivatives, the [PdH₄]²⁻ unit was found to be square-planar, of Na₂PtH₄-type,[172,173] whereas the Rb and Cs analogues exhibited this type of structure only at low temperatures (15 K).[174] The 295 K neutron diffraction study of Rb₂[PdD₄] and Cs₂[PdD₄] revealed the atomic arrangement isotypic with K₂PtCl₆. Statistic analysis of the data in Table 6 (kindly provided by referee no. 65) gave the averaged value of Pd–D = 1.63 (1) Å which is very close to that obtained for the corresponding solid-state Pt hydrides (1.614 (11) Å).

There have been no communications in the literature reporting systematic spectral studies of Pd hydrides. At the same time, both vibrational and NMR spectroscopy have been widely used for identification and characterization of various hydrido complexes of palladium.[235] Some spectral studies have been carried out on highly unstable Pd hydrides, like PdH, PdH₂⁺, and PdH₂ which exist under certain conditions in the gas-phase or in low-temperature noble gas matrices. The gas-phase ion beam experiments with PdH⁺ resulted in the determination of Pd–H bond dissociation energy values (45 ± 3[236] and 53 ± 3[237] kcal/mol) which are close to the most commonly cited value for a transition metal-hydrogen bond (∼60 kcal/mol).[238] Both PdH and PdD have been investigated by absorption spectroscopy in the gas phase,[239,240] and by EPR spectroscopy in Ar (Kr) matrices.[241] High-resolution mass-spectroscopy has been applied to the study of PdH₂⁺ generated in the field evaporation of Pd metal in the presence of H₂.[242] Both PdH₂⁺ and PdD₂⁺ have been isolated in noble gas matrices and studied by EPR.[243] Ozin and Garcia-Prieto[244] reported the low-temperature matrix isolation of the nonclassical PdH₂ and its characterization by vibrational spectroscopy.

A number of theoretical calculations on Pd hydrides and their reactions have been carried out over the last 20 years.[243,245–273] In one of the earliest *ab initio* MO studies[245] it was shown that the neutral NiH and PdH have different ground states, namely ²Δ and ²Σ, respectively, because in NiH the bonding is largely a 4s–1s interaction, whereas in PdH it is 4d–1s. Molecules such as PdH,[245,248,249,263,264] PdH₂,[250–259,265] PdH⁺,[265] and PdH₂⁺ [243] have been theoretically studied by various research groups. Among the reactions investigated, there have been the addition of hydrogen to palladium atoms, ions, naked 3-atomic clusters, and complexes,[243,257,250,252,254–258,271] activation of C–H and C–C bonds,[266,270,273] reductive elimination of H₂ and CH₄,[253,259] and various migratory insertion processes involving olefins and CO.[260–262,268,269] It is worth noting that the existence of transition metal dihydrogen complexes was first predicted on the basis of the theoretical studies of [(R₃P)₂Pd₂(H₂)][247] and [Pd(H₂)].[250] These calculations were performed and published a few years before the first dihydrogen complexes were isolated and unambiguously characterized.[20–27] Ironically, no stable molecular hydrogen complexes of palladium have been prepared thus far, although [Pd(H₂)] has been successfully isolated and characterized in frozen inert gas matrices.[244]

VII. Conclusions

The above material demonstrates that since the discovery of [(Et₃P)₂Pd(H)Cl] in 1965, considerable progress has been made in the chemistry of palladium hydrides. Both synthetic methods and chemical properties of palladium hydrides differ from those of analogous nickel and platinum compounds. Despite the instability of most (hydrido)palladium complexes, many of them have been prepared in good yields and investigated by diverse chemical and physical methods. At the same time, there is still a large number of blank spots in the hydrido chemistry of palladium. For instance, none of Pd hydrides have been studied by single-crystal neutron diffraction, the method which would provide us with the most accurate structural data regarding the Pd–H bond. There have been no systematic IR or NMR spectral studies of molecular palladium hydrides reported in the literature, thus far. Finally, the information accrued on the reactivity of palladium hydrides is certainly insufficient, although the demand for this knowledge is increasingly great in the catalytic world. The high reactivity of the Pd–H bond, along with the

unique catalytic properties of palladium, make Pd hydrides indispensable participants of many proposed (and plausible!) mechanisms for various important catalytic processes. With very few exceptions however, most of those mechanistic schemes are based on nothing but common sense and shaky analogy with the chemistry of platinum. From some examples discussed in this review, it is clear that such analogies might be deceptive.

Hence, one could foresee the following directions, in which this fascinating area of chemistry could develop. First, the synthetic chemistry of palladium hydrides is far from being exhausted and may surprise the chemists many more times. The recent results from Leoni's and Fryzuk's groups constitute evidence for this statement. Second, it is important to acquire more profound knowledge on both chemical and physical properties of palladium hydrides. Finally, it is believed that if inorganic, organometallic, catalytic, and theoretical lines of research in this field were more mutually encouraging and supportive to each other, the result of such collaborations could be splendidly fruitful.

VIII. Abbreviations

Ac	acetyl
acac	acetylacetonate
Alk	alkyl
Ar	aryl
bdpp	2,4-bis(diphenylphosphino)pentane
Bipy	2,2′-bipyridyl
Bu	butyl
COD	cyclooctadiene
Cy	cyclohexyl
dcpe	1,2-bis(dicyclohexylphosphino)ethane
diop	2,2-dimethyl-4,5-bis[(diphenylphosphino)methyl]-1,3-dioxacyclopentane
dippp	1,3-bis(diisopropylphosphino)propane
dmpm	bis(dimethylphosphino)methane
dpae	1,2-bis(diphenylarsino)ethane
dpba	bis[2-(diphenylphosphino)ethyl]benzylamine
dppe	1,2-bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
Et	ethyl
Me	methyl
Ph	phenyl
Phen	1,10-phenanthroline
Pr	propyl
Py	pyridine
Tol	tolyl

IX. Acknowledgments

X. References

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