

Binuclear Palladium Complexes with Bridging Hydrides. Unusual Coordination Behavior of LiBEt₄ and NaBEt₄

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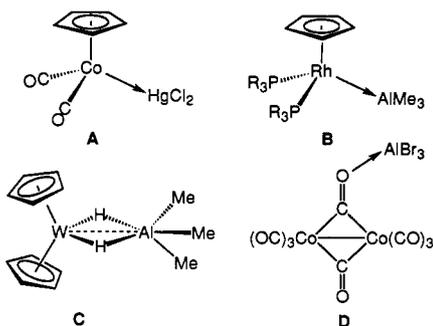
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Abstract: The reaction of Pd(dipp)Cl₂ (dipp = 1,3-bis(diisopropylphosphino)propane) with a 1:1 mixture of LiBEt₂H₂ and LiBEt₄ in THF generates the binuclear hydride derivative [(dipp)Pd]₂(μ-H)₂LiBEt₄ (**1**) in which the LiBEt₄ is bound to the palladium hydride core. The bare palladium hydride dimer [(dipp)Pd]₂(μ-H)₂ (**2**) was prepared by reaction of 2 equiv of KBET₃H in toluene with Pd(dipp)₂I₂. Addition of LiBEt₄ to the bare palladium dimer **2** generates the LiBEt₄ adduct **1**; this approach has been extended to the preparation of [(dipp)Pd]₂(μ-H)₂NaBEt₄ (**3**) and [(dipp)Pd]₂(μ-H)₂LiAlEt₄ (**4**) by the addition of NaBEt₄ and LiAlEt₄ respectively to **2**. On the basis of NMR spectroscopy, there is no evidence for dissociation of the lithium or sodium borate or aluminate salts from the hydride dimer but the ME'Et₄ (M = Li, Na; E' = B, Al) units are labile on the basis of exchange studies and variable temperature NMR data. Crystals of [(dipp)Pd]₂(μ-H)₂LiBEt₄·0.5(C₆H₁₄) (**1**) are monoclinic, *a* = 11.537(2) Å, *b* = 19.114(2) Å, *c* = 24.020(1) Å, β = 98.674(9)°, *Z* = 4, space group *P*2₁/*n*; those of [(dipp)Pd]₂(μ-H)₂ (**2**) are monoclinic, *a* = 13.128(1) Å, *b* = 14.362(4) Å, *c* = 20.353(1) Å, β = 99.593(6)°, *Z* = 4, space group *P*2₁/*n*; and those of [(dipp)Pd]₂(μ-H)₂NaBEt₄ (**3**) are monoclinic, *a* = 20.099(2) Å, *b* = 11.457(5) Å, *c* = 21.600(3) Å, β = 92.87(1)°, *Z* = 4, space group *P*2₁/*c*. The structures were solved by the Patterson method and were refined by full-matrix least-squares procedures to *R* = 0.033, 0.052, and 0.033 (*R*_w = 0.029, 0.054, and 0.028) for 5954, 4560, and 5018 reflections with *I* ≥ 3σ(*I*), respectively. In the solid-state structure of **1**, there are three C–H...Li interactions from the ethyl groups attached to boron whereas in the solid-state structure of **3** there are four such C–H...Na interactions.

Introduction

The concept of metal basicity was introduced over twenty years ago by Shriver¹ and has since been updated by Werner.² In this formalism, a metal complex acts as a Lewis base and formally donates a pair of electrons to a Lewis acid. Although the idea can be applied to oxidative addition chemistry, wherein the Lewis acid component is an electrophilic species such as H⁺, O₂, organic halides, or electron-deficient olefins such as tetracyanoethylene, it is also applicable to neutral Lewis acid acceptor molecules such as the group 13 derivatives, BF₃ and Al₂Me₆, and mercury halides. Some of the typical neutral Lewis acids that have been shown to interact with metal complexes are the following: Al₂Br₆ in Co₂(CO)₈·AlBr₃,³ HgCl₂ in a variety of complexes of the type (η⁵-C₅H₅)Co(CO)₂·HgCl₂ and Fe(CO)₃(PPh₃)₂·HgCl₂; Al₂Me₆ in (η⁵-C₅H₅)₂WH₂·AlMe₃,⁴ (η⁵-C₅H₅)₂ZrH·AlMe₃,⁵ and (η⁵-C₅H₅)₂ReH·AlMe₃,⁶ BF₃ in (η⁵-C₅H₅)₂WH₂·BF₃ and (η³-C₅H₅)₂ReH·BF₃,⁷ and Al₂Me₄Cl₂ in (η⁴-C₅H₅)Rh(PMe₃)₂·Al₂Me₄Cl₂.⁸ While this list is not comprehensive, it does focus on the main types of interactions possible; these are illustrated by the structures A–D below.



In general, the Lewis acid can be associated with the metal center

density (cf. A and B) or with the ligands, generally the hydrides (cf. C) or the carbonyls (cf. D).³ For example, in (η⁵-C₅H₅)₂WH₂·AlMe₃ (C), the nature of the interaction of the AlMe₃ unit with (η⁵-C₅H₅)WH₂ was only resolved with the aid of a low-temperature X-ray crystal structure. Formally d⁰ metal complexes can also engage in interactions with Lewis acids as evidenced by recent work in which zirconium methyl and hydride derivatives generate cationic, base-free derivatives by reaction with B(C₆F₅)₃.^{9,10}

Recently, we discovered a new type of complexation that uses a palladium dimer with bridging hydrides as the Lewis base and salts of the general formula M⁺ER₄⁻ (M = Li, Na; E = B, Al; R = alkyl) as the Lewis acids.¹¹ That alkali metal salts of group 13 "ate" compounds, such as LiBEt₄ and LiAlEt₄, could act as Lewis acids was unprecedented to our knowledge. Given the importance of Lewis acids in promoting reactions such as Ziegler–Natta polymerization of olefins, hydrocyanation of olefins,¹² dimerization of ethylene,¹³ and migratory insertion reactions,¹⁴ we began a systematic investigation of Lewis acid–Lewis base

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interactions using palladium hydride dimers and the simple alkali metal salts of peralkyl borates and aluminates. In this paper we report solid-state and solution structures of adducts of the general formula [(dipp)Pd]₂(μ-H)₂·ME'Et₄ (where dipp = 1,3-bis-(diisopropylphosphino)propane; M = Li or Na, E' = B or Al) as well as their relative stabilities. The solid-state structure of the parent palladium hydride dimer [(dipp)Pd]₂(μ-H)₂ is also included.

Experimental Section

Procedures. Unless otherwise stated all manipulations were performed under an atmosphere of dry, oxygen-free dinitrogen or argon by means of standard Schlenk or glovebox techniques. The glovebox used was a Vacuum Atmospheres HE-553-2 device equipped with a MO-40-2H purification system and a -40 °C freezer. ¹H and ³¹P{¹H} NMR spectroscopy were performed on a Varian XL-300 instrument operating at 300 MHz and 121.4 MHz, respectively. ²D NMR spectroscopy was also performed on the Varian instrument operating at 46 MHz. ¹H{³¹P} NMR spectroscopy was performed upon a Bruker AMX-500 instrument operating at 500.1 MHz. ¹H NMR spectra were referenced to internal C₆D₅H (7.15 ppm), C₆D₃CD₂H (2.09 ppm), or CHCl₃ (7.24 ppm). ³¹P NMR spectra were referenced to external P(OMe)₃ (141.0 ppm with respect to 85% H₃PO₄ at 0.0 ppm). Longitudinal relaxation times for the hydrides were measured by a standard inversion-recovery sequence supplied with Version 6.0c of the Varian VXR series software. Kinetic data were simulated by the DNMR-SIM program.¹⁵

Microanalyses (C, H, halogen) were performed by Mr. P. Borda of this department.

Materials. Dipp was prepared by a published procedure.¹⁶ EtLi was prepared by a published procedure¹⁷ and recrystallized from toluene. LiAlEt₄ and LiBEt₄ were prepared by adding AlEt₃ (Aldrich) or BEt₃ (Aldrich), respectively, to EtLi and recrystallized from toluene.¹⁸ NaBEt₄ (Strem) was used as supplied. KBET₃H was prepared by addition of BEt₃ to a slurry of KH (BDH) in toluene and was recrystallized from toluene; KBET₃D was prepared likewise from KD.¹⁹ PdCl₂ was obtained on loan from Johnson-Matthey and used to prepare Pd(C₆H₅C≡N)₂·Cl₂.²⁰

Hexanes, toluene, pentane, Et₂O, and THF were heated to reflux over CaH₂ prior to a final distillation from either sodium metal or sodium benzophenone ketyl under an Ar atmosphere. Acetone was dried over 4-Å sieves and sparged with dinitrogen. Deuterated solvents were dried by activated 3-Å molecular sieves; oxygen was removed by trap-to-trap distillation and 3 freeze-pump-thaw cycles.

Pd(dipp)Cl₂. To a solution of Pd(C₆H₅C≡N)₂Cl₂ (4.37 g; 11.4 mmol) in acetone (100 mL) was added dipp (3.15 g; 11.4 mmol) dropwise. With each drop of phosphine a yellow precipitate formed and the deep amber color of the solution discharged completely to give a clear supernatant. After 30 min of stirring the reaction mixture was exposed to the air and the fine yellow precipitate was collected upon a frit, washed with copious acetone (100 mL), and air-dried (4.34 g; 84% yield). Anal. Calcd for C₁₅H₃₄Cl₂P₂Pd: C, 39.71; H, 7.55; Cl, 15.63. Found: C, 40.00; H, 7.65; Cl, 15.63. ³¹P{¹H} and ¹H NMR assignments are reported elsewhere.¹⁶

Pd(dipp)I₂. To a slurry of Pd(dipp)Cl₂ (1.70 g; 3.75 mmol) in acetone (50 mL) was added NaI (1.50 g; 10.0 mmol). The color of the slurry deepened to ochre and stirring was continued for 2 h. Workup was as for Pd(dipp)Cl₂ giving Pd(dipp)I₂ as a fine ochre powder (2.12 g; 89% yield). Anal. Calcd for C₁₅H₃₄I₂P₂Pd: C, 28.30; H, 5.38; I, 39.87. Found: C, 27.98; H, 5.12; I, 40.05. ¹H NMR (CDCl₃): δ 2.90 (d hept, 4H, CHMe₂, J_{P-H} = 12.0 Hz, J_{H-Me} = 7.2 Hz), 2.25 (m, 2H, PCH₂CH₂CH₂P), 1.61 (m, 4H, PCH₂CH₂P), 1.41 (dd, 12H, CHMe, J_{P-Me} = 19.2 Hz, J_{Me-H} = 7.2 Hz), 1.24 (dd, 12H, CHMe', J_{P-Me'} = 13.8 Hz, J_{Me'-H} = 7.2 Hz). ³¹P{¹H} NMR (CDCl₃): δ 30.7. Pd(dipp)I₂ may also be prepared directly without isolation of Pd(dipp)Cl₂ (76% yield).

(15) Version 1.00 was obtained from Drs. G. Hägele and R. Fuhler of the Heinrich-Heine University, Düsseldorf, Germany; it will later be released as part of the WIN-NMR software package for the IBM PC.

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[(dipp)Pd]₂(μ-H)₂ (2). Pd(dipp)I₂ (1.15 g; 1.80 mmol) was slurried in toluene (100 mL) and cooled to -60 °C in a dry-ice/acetone bath. A solution of KBET₃H (0.499 g; 3.81 mmol) in toluene (10 mL) was added dropwise with stirring and the temperature was raised to -40 °C. A slight effervescence was noted and the red color of the dimer developed as the Pd(dipp)I₂ reacted. The temperature was maintained at -40 °C for 2 h after which time gas evolution had ceased and the solution was deep red in color. The temperature was further raised to -20 °C for 30 min after which the reaction mixture was passed through a frit lined with Celite. The solvent was removed *in vacuo* and the residue dissolved in pentane (9 mL). The filtered solution was cooled to -30 °C and deep-red crystals appeared after 24 h (0.300 g, 44% yield). ¹H{³¹P} NMR (C₆D₆): δ 1.93 (sept, 8H, CHMe₂, J_{H-Me} = 8.4 Hz), 1.90 (quin, 4H, PCH₂CH₂CH₂P, J_{H-H'} = 4.5 Hz), 1.32 (t, 8H, PCH₂CH₂CH₂P, J_{H-H'} = 4.5 Hz), 1.30 and 1.10 (d, 48H, CHMe₂, J_{Me-H} = 8.4 Hz), -2.50 (s, 2H, μ-H). ¹H NMR (C₆D₆): δ -2.52 (quin, μ-H, J_{P-H} = 34.9 Hz), other resonances appeared as multiplets, T₁(μ-H) = 0.62 s. ³¹P{¹H} NMR (C₆D₆): δ 27.0. Anal. Calcd for C₃₀H₇₀P₄Pd₂: C, 46.94; H, 9.19. Found: C, 47.22; H, 9.25.

[(dipp)Pd]₂(μ-D)₂ (2-d₂). The deuterium analogue was prepared by a procedure identical to that for **2** using KBET₃D (0.518 g; 3.72 mmol) and Pd(dipp)I₂ (1.16 g; 1.82 mmol). Recrystallization from pentane (10 mL) gave deep-red crystals (0.356 g, 51% yield). ¹H NMR (C₆D₆) δ 1.93 (m, 12H, PCH₂CH₂CH₂P, CHMe₂), 1.30 (m, 8H, PCH₂CH₂CH₂P), 1.30 and 1.10 (m, 48H, CHMe₂), -2.55 (quin of t, residual μ-(H-D), J_{P-H} = 35.0 Hz, J_{H-D} = 2.4 Hz). ²D NMR (C₇H₈): δ -2.52 (quin, μ-D, J_{P-D} = 5.5 Hz). ³¹P NMR (C₆D₆) δ 27.0 (t, J_{P-D} = 5.5 Hz). Anal. Calcd for C₃₀H₇₀P₄Pd₂: C, 46.94; H, 9.19. Found: C, 46.75; H, 9.10.

[(dipp)Pd]₂(μ-H)₂·LiBEt₄ (1). To a slurry of Pd(dipp)Cl₂ (0.398 g; 0.877 mmol) in THF (60 mL) at -60 °C was added a mixture of LiBEt₂H₂ and LiBEt₄ in THF (1.80 mL; 1.80 mmol Li⁺). The temperature was raised to -40 °C and the red color of the product developed as the Pd(dipp)Cl₂ reacted. A faint effervescence was also noted. The mixture was stirred for 2 h at the end of which time a deep red solution was observed and gas evolution had ceased. The temperature was further raised to -20 °C and stirring was continued for 1 h, after which the THF was removed under vacuum. The deep-red residue was extracted with toluene (30 mL) and the solution was passed through a frit lined with Celite to remove the precipitated LiCl. The toluene was removed by suction and the residue was dissolved in an extra volume of toluene (5 mL). This deep-red solution was layered with hexanes (10 mL) and yielded maroon crystals after 6 h at -40 °C (0.300 g; 68% yield). ¹H{³¹P} NMR (C₆D₆): δ 1.85 (sept, 8H, CHMe₂, J_{H-Me} = 8.4 Hz), 1.78 (quin, 4H, PCH₂CH₂CH₂P, J_{H-H'} = 4.4 Hz), 1.34 (br t, 12H, BCH₂CH₃, J_{H-H'} = 7.5 Hz), 1.24 (t, 8H, PCH₂CH₂CH₂P, J_{H-H'} = 4.4 Hz), 1.19 and 1.07 (d, 48H, CHMe₂, J_{Me-H} = 8.4 Hz), 0.42 (br q, 8H, BCH₂CH₃, J_{H-H'} = 7.5 Hz), -3.63 (br s, 2H, μ-H). ¹H NMR (C₆D₆): δ -3.66 (br quin, μ-H, J_{P-H} = 35 Hz), other resonances appeared as multiplets, T₁(μ-H) = 0.49 s. ³¹P{¹H} NMR (C₆D₆): δ 22.4. Anal. Calcd for C₃₈H₉₀BLiP₄Pd₂: C, 50.62; H, 10.06. Found: C, 50.57; H, 10.06.

Alternatively LiBEt₄ may be added to a solution of [(dipp)Pd]₂(μ-H)₂ in toluene as for **3**. Recrystallization from toluene/pentane gives the product in yields over 90%.

[(dipp)Pd]₂(μ-H)₂·NaBEt₄ (3). **2** (0.100 g; 0.130 mmol) and NaBEt₄ (0.020 g; 0.133 mmol) were treated as for the preparation of **4**. Upon adding the NaBEt₄ to the solution of **2** the color darkened to a bottle-green. Removal of the solvent gave a blue, crystalline residue. The residue was taken up in toluene (1.2 mL) and the green solution was layered with pentane (5.0 mL). Blue crystals appeared after 6 h (0.050 g; 41% yield). ¹H NMR (C₆D₆): δ 1.74 (m, 12H, PCH₂CH₂CH₂P, CHMe₂), 1.39 (t, 12H, BCH₂CH₃, J_{H-H'} = 7.0 Hz), 1.12 (m, 8H, PCH₂CH₂CH₂P), 1.10 and 0.99 (m, 48H, CHMe₂), 0.19 (q, 8H, BCH₂CH₃, J_{H-H'} = 7.0 Hz), -3.43 (quin, 2H, μ-H, J_{P-H} = 35.4 Hz), T₁(μ-H) = 0.18 s. ³¹P NMR (C₆D₆): δ 25.4. Anal. Calcd for C₃₈H₉₀BNaP₄Pd₂: C, 49.74; H, 9.89. Found: C, 50.00; H, 10.07.

[(dipp)Pd]₂(μ-H)₂·LiAlEt₄ (4). **2** (0.100 g; 0.130 mmol) and LiAlEt₄ (0.023 g; 0.133 mmol) were dissolved in toluene (10 mL) and stirred for 1 h. The red color of the solution becomes slightly less intense during this time. The solvent was removed by suction and recrystallization from pentane/toluene (3:1; 10 mL) gave purple crystals after 48 h (0.109 g; 89% yield). ¹H NMR (C₆D₆): δ 1.80 (m, 8H, CHMe₂), 1.75 (m, 4H, PCH₂CH₂CH₂P), 1.60 (t, 12H, AlCH₂CH₃, J_{H-H'} = 8.1 Hz), 1.16 (m, 8H, PCH₂CH₂CH₂P), 1.20 and 1.07 (m, 48H, CHMe₂), 0.05 (q, 8H, AlCH₂CH₃, J_{H-H'} = 8.1 Hz), -3.87 (quin, 2H, μ-H, J_{P-H} = 35.0 Hz).

Table 1. Crystallographic Data^a

compd	[(dipp)Pd] ₂ (μ-H) ₂ LiBEt ₄ ·0.5(C ₆ H ₁₄) (1)	[(dipp)Pd] ₂ (μ-H) ₂ (2)	[(dipp)Pd] ₂ (μ-H) ₂ NaBEt ₄ (3)
formula	C ₄₁ H ₉₇ BLiP ₄ Pd ₂	C ₃₀ H ₇₀ P ₄ Pd ₂	C ₃₃ H ₉₀ BNaP ₄ Pd ₂
fw	944.66	767.58	917.62
habit	prism	prism	hexagonal plate
cryst size, mm	0.20 × 0.30 × 0.35	0.15 × 0.30 × 0.40	0.20 × 0.45 × 0.45
cryst system	monoclinic	monoclinic	monoclinic
space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /c
a, Å	11.537(2)	13.128(1)	20.099(2)
b, Å	19.114(2)	14.362(4)	11.457(5)
c, Å	24.020(1)	20.353(1)	21.600(3)
b°	98.674(9)	99.593(6)	92.87(1)
V, Å ³	5236(1)	3784(1)	4968(2)
Z	4	4	4
T, °C	21	21	21
D _c , g/cm ³	1.198	1.347	1.227
F(000)	2012	1608	1944
m(Mo Kα), cm ⁻¹	8.33	11.22	8.72
transmission factors	0.92–1.00	0.83–1.00	0.82–1.00
scan type	ω–2θ	ω–2θ	ω–2θ
scan range, deg in ω	1.00 + 0.35 tan θ	1.21 + 0.35 tan θ	1.10 + 0.35 tan θ
scan speed, deg/min	16	16	32
data collected	+h,+k,±l	+h,+k,±l	+h,+k,±l
2θ _{max} , deg	55	55	55
cryst decay	negligible	4.5%	5.3%
total no. of reflns	12959	9441	12336
unique reflns	12356	9056	12005
R _{merge}	0.046	0.067	0.033
no. with I ≥ 3σ(I)	5954	4560	5018
no. of variables	451	329	425
R	0.033	0.052	0.033
R _w	0.029	0.054	0.028
gof	1.62	3.18	1.51
max D/s (final cycle)	0.05	0.02	0.04
residual density, e/Å ³	–0.34, 0.65 (both near Pd)	–1.0, 1.4 (near Pd)	–0.32, 0.27

^a Temperature 294 K, Rigaku AFC6S diffractometer, Mo Kα radiation, $l = 0.71069 \text{ \AA}$, graphite monochromator, takeoff angle 6.0° , aperture $6.0 \times 6.0 \text{ mm}$ at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), $s^2(F^2) = [S^2(C + 4B)]/Lp^2$ ($S = \text{scan speed}$, $C = \text{scan count}$, $B = \text{normalized background count}$), function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/s^2(F_o^2)$, $R = \sum |F_o| - |F_c| / \sum |F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, and $\text{gof} = [\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$. Values given for R , R_w , and gof are based on those reflections with $I \geq 3\sigma(I)$.

³¹P{¹H} NMR (C₆D₆): δ 23.3. Anal. Calcd for C₃₃H₉₀AlLiP₄Pd₂: C, 49.73; H, 9.88. Found: C, 49.48; H, 9.85.

Pd(dipp)(η²-H₂C=CH₂). To a solution of **2** (0.081 g; 0.106 mmol) in toluene (10 mL), subjected to several freeze–pump–thaw cycles was added ethylene (0.500 mmol) from a constant volume bomb. The initial red color of the solution rapidly discharged to give a colorless solution. The solvent was stripped off, the residue was dissolved in a minimum of pentane (2.5 mL), and the clear solution was cooled to -30°C . Colorless crystals appeared after 48 h (0.070 g; 80% yield). ¹H NMR (C₆D₆): δ 2.86 (d, 4H, H₂C=CH₂, $J_{\text{P-H}} = 1.5 \text{ Hz}$), 1.69 (sept, 4H, CHMe₂, $J_{\text{H-Me}} = 7.0 \text{ Hz}$), 1.68 (m, 2H, PCH₂CH₂CH₂P), 1.25 (m, 4H, PCH₂CH₂CH₂P), 1.08 and 0.96 (dd, 24H, CHMe₂, $J_{\text{P-H}} = 15.0 \text{ Hz}$, $J_{\text{Me-H}} = 7.0 \text{ Hz}$). ³¹P NMR (C₆D₆): δ 29.5. Anal. Calcd for C₁₇H₃₈P₂Pd: C, 49.70; H, 9.32. Found: C, 49.90; H, 9.41.

Pd(dipp)(PPh₃). To a solution of **2** (0.090 g; 0.117 mmol) in toluene (15 mL) was added PPh₃ (0.061 g; 0.233 mmol). The red color discharged rapidly and a vigorous evolution of gas was observed. The solvent was stripped off and the yellow residue taken up in Et₂O (15 mL). A yellow, microcrystalline powder deposited on standing (0.132 g; 87% yield). ¹H NMR (C₆D₆): δ 7.88 (m, 6H, *o*-Ph), 7.15 (m, 9H, *m*-, *p*-Ph), 1.75 (m, 6H, PCH₂CH₂CH₂P, CHMe₂), 1.23 (m, 4H, PCH₂CH₂CH₂P), 1.08 and 0.96 (dd, 24H, CHMe₂, $J_{\text{P-H}} = 9.6 \text{ Hz}$, $J_{\text{H-H}} = 3.0 \text{ Hz}$). ³¹P NMR (C₆D₆): δ 33.8 (t, 1P, $J_{\text{P-P}} = 88.5 \text{ Hz}$), 23.7 (d, 2P, $J_{\text{P-P}} = 88.5 \text{ Hz}$). Anal. Calcd for C₃₃H₄₉P₃Pd: C, 61.33; H, 7.66. Found: C, 61.52; H, 8.00.

Pd(dipp)(DMAD). To a solution of **2** (0.075 g; 0.098 mmol) in toluene (10 mL) was added DMAD in toluene (0.029 g; 0.200 mmol). The initial red color of the solution slowly discharged to give a colorless solution within 1 h. The solvent was stripped off, and the residue was dissolved in minimum pentane (5 mL). The colorless solution was cooled to -40°C and colorless crystals appeared after 48 h (0.087 g; 85% yield). ¹H NMR (C₆D₆): δ 3.54 (s, 6H, CO₂CH₃), 1.82 (sept, 4H, CHMe₂, $J_{\text{H-Me}} = 7.0 \text{ Hz}$), 1.51 (m, 2H, PCH₂CH₂CH₂P), 1.22 (m, 4H, PCH₂CH₂CH₂P), 1.11 and 0.87 (dd, 24H, CHMe₂, $J_{\text{P-H}} = 16.0 \text{ Hz}$, $J_{\text{Me-H}} = 7.0 \text{ Hz}$). ³¹P NMR (C₆D₆): δ 34.5. Anal. Calcd for C₂₁H₄₆P₂O₄Pd: C, 48.05; H, 7.68. Found: C, 48.27; H, 7.90.

X-ray Crystallographic Analyses of [(dipp)Pd]₂(μ-H)₂LiBEt₄·0.5(C₆H₁₄) (1), [(dipp)Pd]₂(μ-H)₂ (2), and [(dipp)Pd]₂(μ-H)₂NaBEt₄ (3). Crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least squares on the setting angles for 25 reflections with $2\theta = 20.5\text{--}28.4^\circ$, $30.0\text{--}39.4^\circ$, and $19.2\text{--}34.9^\circ$ respectively for 1–3. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, remained constant for 1 and decreased linearly by 4.5% for 2 and by 5.3% for 3. The data were processed²¹ and corrected for Lorentz and polarization effects, decay (for 2 and 3), and absorption (empirical, based on azimuthal scans for three reflections).

The three structures were solved by conventional heavy atom methods, the coordinates of the Pd and P atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. Disorder of one of the chelate ring carbon atoms in 3 (C(2)) was modeled by split-atom refinement. The site occupancy of the major component was refined with the constraint that the occupancy factors for the two sites sum to 1.00. The carbon atoms of the ligand containing P(3) and P(4) in 3 display a generally high degree of thermal motion that may be associated with some additional minor disordering. No attempt to model this possible disorder was made. The non-hydrogen atoms of all three structures were refined with anisotropic thermal parameters. The metal hydride atoms were refined with isotropic thermal parameters for 1, were placed in difference map positions but not refined for 3, and were refined with fixed thermal parameters near the end of the refinement but kept fixed during the final cycle due to a parameter oscillation problem for 2. All other hydrogen atoms were fixed in idealized positions (staggered methyl groups, C–H = 0.99 Å for 1 and 0.98 Å for 2 and 3, $B_{\text{H}} = 1.2 B_{\text{bonded atom}}$). A correction for secondary extinction was applied for 1, the final value of the extinction coefficient (Zaccharisen type) being $8.5(3) \times 10^{-8}$. The results for 1 presented here differ slightly from those reported earlier.¹¹ More accurate

(21) TEXSAN/TEXRAY: Crystal structure analysis package (VMS Version 5.1); Molecular Structure Corporation: The Woodlands, TX, 1985, 1991 (for 2 and 3). *teXsan*: Crystal structure analysis package (UNIX Version 1.6); Molecular Structure Corporation: The Woodlands, TX, 1985, 1992 (for 2).

Table 2. Selected Intramolecular Distances (Å) Observed in [(dipp)Pd]₂(μ-H)₂LiBEt₄ (1), [(dipp)Pd]₂(μ-H)₂ (2), and [(dipp)Pd]₂(μ-H)₂NaBEt₄ (3)

[(dipp)Pd] ₂ (μ-H) ₂ LiBEt ₄ (1)			
Pd(1)–Pd(2)	2.8248(5)	Pd(1)–H(1)	1.68(3)
Pd(1)–H(2)	1.70(3)	Pd(1)–P(1)	2.344(1)
Pd(1)–P(2)	2.337(1)	Pd(1)–Li	2.733(8)
Pd(2)–H(1)	1.79(4)	Pd(2)–H(2)	1.76(3)
Pd(2)–P(3)	2.336(1)	Pd(2)–P(4)	2.336(1)
Pd(2)–Li	2.635(8)	Li–B	2.275(9)
Li–H(1)	2.54(4)	Li–H(2)	2.25(3)
Li–C(31)	2.371(10)	Li–C(33)	2.339(9)
Li–C(35)	2.316(10)		
[(dipp)Pd] ₂ (μ-H) ₂ (2)			
Pd(1)–Pd(2)	2.8245(8)	Pd(1)–H(1)	1.67(5)
Pd(1)–H(2)	2.13(4)	Pd(1)–P(1)	2.304(2)
Pd(1)–P(2)	2.299(2)	Pd(2)–H(1)	2.11(5)
Pd(2)–H(2)	1.73(4)	Pd(2)–P(3)	2.306(2)
Pd(2)–P(4)	2.300(4)		
[(dipp)Pd] ₂ (μ-H) ₂ NaBEt ₄ (3)			
Pd(1)–Pd(2)	2.8169(6)	Pd(1)–H(1)	1.82(5)
Pd(1)–H(2)	1.79(4)	Pd(1)–P(1)	2.326(1)
Pd(1)–P(2)	2.325(1)	Pd(1)–Na	2.874(2)
Pd(2)–H(1)	1.74(5)	Pd(2)–H(2)	1.77(4)
Pd(2)–P(3)	2.324(3)	Pd(2)–P(4)	2.320(2)
Pd(2)–Na	2.897(2)	Na–B	3.329(2)
Na–H(1)	2.60(5)	Na–H(2)	2.56(5)
Na–C(31)	2.67(2)	Na–C(33)	2.78(2)

unit cell parameters, different weights, and the extinction correction have been employed. The crystal of **2** used for data collection was either twinned or fused to a fairly small satellite, resulting in relatively high residuals. Approximately 40 reflections with $|F_o| \gg |F_c|$, presumably resulting from overlapping reflections from the twin (or satellite) components, were omitted in the final stages of the refinement. Table 2 contains selected bond lengths while Table 3 reports selected bond angles for the complexes **1**, **2**, and **3**. Neutral atom scattering factors and anomalous dispersion corrections for all atoms were taken from the *International Tables for X-Ray Crystallography*.²² Final atomic coordinates and equivalent isotropic thermal parameters, complete tables of bond lengths and angles, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, least-squares planes, and measured and calculated structure factor amplitudes are included as supplementary material.

Results and Discussion

Our entry into this area came about during attempts to prepare a binuclear palladium complex that contained bridging hydrides. The initial intention was to complement work previously done in our laboratory on the corresponding binuclear rhodium complexes having chelating bidentate phosphine ancillary ligands and hydride bridges.^{23–26} However, it was also clear from examination of the literature that no palladium complexes bearing bridging hydrides had previously been unequivocally characterized,^{27–29} in spite of the fact that there were reports of nickel and platinum dimers of the general formula $[P_2M]_2(\mu-H)_2$ (P_2 = bidentate phosphine).^{30–32}

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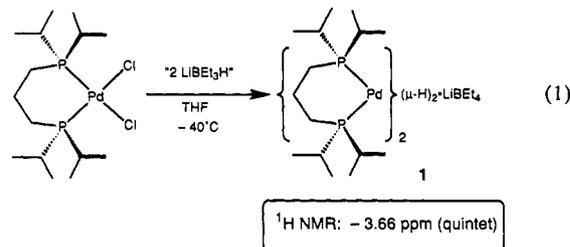
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The addition of a THF solution of LiBEt₃H (Aldrich Super Hydride) to a slurry of Pd(dipp)Cl₂ in THF at low temperature led to the formation of a deep red solution from which maroon crystals having the formula [(dipp)Pd]₂(μ-H)₂LiBEt₄ (**1**) could be isolated in 68% yield (eq 1). The ¹H NMR spectrum of **1**



exhibited a broad quintet at –3.66 ppm ($^2J_{P-H} = 35$ Hz), due to coupling to four equivalent phosphorus-31 nuclei, which clearly indicates the presence of bridging hydrides; furthermore, resonances due to a LiBEt₄ residue were observed at 1.30 and 0.42 ppm for the methyl and methylene resonances, respectively (cf. 1.29 and 0.21 ppm for crystalline LiBEt₄ in C₇D₈). The question of the origin of LiBEt₄ from a proprietary solution that was nominally LiBEt₃H was easily resolved by ¹¹B NMR spectroscopy; the spectrum of our particular bottle displayed two resonances: a singlet at –17.5 ppm, overlaid by a triplet at –17.8 ($J_{B-H} = 67.4$ Hz), attributed to LiBEt₄ and LiBEt₂H₂, respectively. Other bottles examined contained only authentic LiBEt₃H.

The X-ray crystal structure of **1** is shown in Figure 1. The binuclear structure is clearly evident as are the bridging hydrides which were located and refined. The palladium–hydride bond lengths range from 1.68(3) to 1.79(4) Å (cf., Pd(1)–H(1) 1.68(3) Å; Pd(1)–H(2) 1.70(3) Å; Pd(2)–H(1) 1.79(4) Å; Pd(2)–H(2) 1.76(3) Å); the Pd–H–Pd angle is 109(2)°. However, the most interesting feature of this structure is the presence of a coordinated LiBEt₄ unit having the lithium cation sandwiched between the Pd₂(μ-H)₂ core and the BEt₄ anion. The palladium–lithium distances are significantly different with the lithium being closer to Pd(2): Pd(1)–Li 2.733(8) Å and Pd(2)–Li 2.635(8) Å. Also noteworthy is the interaction of the lithium with the BEt₄ unit as the lithium binds to one C–H bond on each of three α-carbon ethyl substituents (Li–H = 1.69, 1.72 and 1.86 Å). The neutron diffraction study of LiBMe₄ shows similar Li–H–C interactions.³³

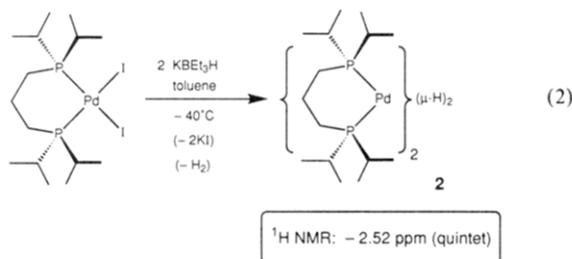
The unsymmetrical solid-state structure is not maintained in solution as evidenced by NMR spectroscopy. A symmetrical structure in solution is required since the two ends of the binuclear unit are spectroscopically equivalent, that is, a singlet in the ³¹P{¹H} NMR spectrum which indicates that all the phosphines are equivalent; in addition, the LiBEt₄ remains coordinated since the resonances due to the tetraethylborate unit are shifted in the ¹H NMR spectrum from those measured for pure LiBEt₄ in C₇D₈. Variable-temperature ¹H NMR studies show that, in solution, all four ethyl groups at boron are equivalent even at low temperatures, indicating that the BEt₄ unit is rather mobile. Moreover, from the variable-temperature NMR data, it is also evident that the top and the bottom of the binuclear palladium hydride are apparently equivalent, thus suggesting that the whole LiBEt₄ unit is labile. This feature will be discussed further below.

Clearly, any attempt to rationalize the nature of the bonding by the LiBEt₄ unit in the palladium–lithium adduct **1** could not be broached without the parent hydride dimer, [(dipp)Pd]₂(μ-H)₂. Unfortunately, attempts to prepare this complex by hydride metathesis of Pd(dipp)Cl₂ with pure LiBEt₃H were unsuccessful; however, treatment of the more soluble diiodide derivative Pd-

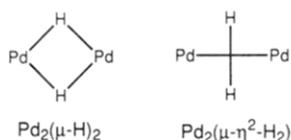
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(dipp)I₂ with 2 equiv of crystalline KBET₃H in toluene does give [(dipp)Pd]₂(μ-H)₂ (**2**), as shown in eq 2. Particularly, diagnostic of **2** is the hydride resonance in the ¹H NMR spectrum at -2.52 ppm which appears as a binomial quintet (*J*_{P-H} = 34.9 Hz).

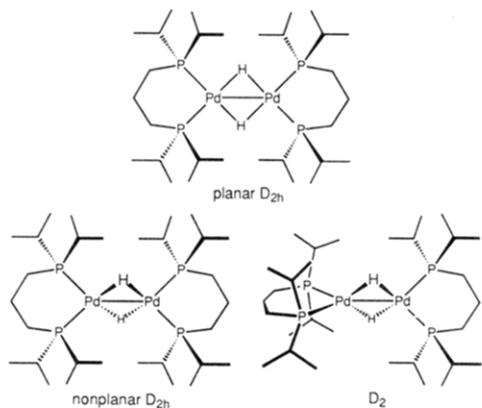


Typical formal oxidation states for palladium are +2 and 0.³⁴ However, both of the binuclear complexes, **1** and **2**, have formal oxidation states of +1, assuming that the hydrogens are bridging hydrides, Pd₂(μ-H)₂, and not a bridging dihydrogen unit, Pd₂(μ-η²-H₂).



From the X-ray structure of **1**, the presence of bridging hydrides is reasonable since the H-H separation is 2.00(5) Å, longer than the 1.6-Å distance normally ascribed as the cutoff for a η²-H₂ ligand.³⁵ Evidence that the parent binuclear complex **2** is also best described as a Pd(I) dimer comes from the formation of [(dipp)Pd]₂(μ-D)₂ by reaction of KBET₃D with the diiodide as before. The ¹H NMR spectrum of **2-d₂** shows a small quintet of 1:1:1 triplets at -2.55 ppm due to residual protons coupled to deuterium and four equivalent phosphorus-31 nuclei indicative of [(dipp)Pd]₂(μ-D)₂(μ-H) (**2-d₁**); the observed H-D coupling constant (*J*_{H-D}) of 2.4 Hz is much too small to be due to a η²-H₂ moiety.³⁵

The solution structure of bare palladium dimer **2** indicates that the phosphine donors are equivalent at all temperatures as are the hydrides; thus, any of the following geometries is appropriate for this molecule.



The X-ray crystal structure of this bare palladium hydride dimer **2** is shown in Figure 2. The Pd-Pd bond distance in **2** is 2.8245(8) Å, virtually identical to that found in the palladium-lithium adduct **1** (i.e. 2.8233(6) Å). What is striking, however, is the unsymmetrical nature of the hydride bridges between the two palladium atoms: the Pd(1)-H(1) distance is 1.67(3) Å while Pd(1)-H(2) is 2.13(4) Å; similarly, Pd(2)-H(2) is 1.73(3) Å and Pd(2)-H(1) is 2.11(3) Å. The shorter metal-hydride distances are similar to that found in the LiBE₄ adduct **1** but

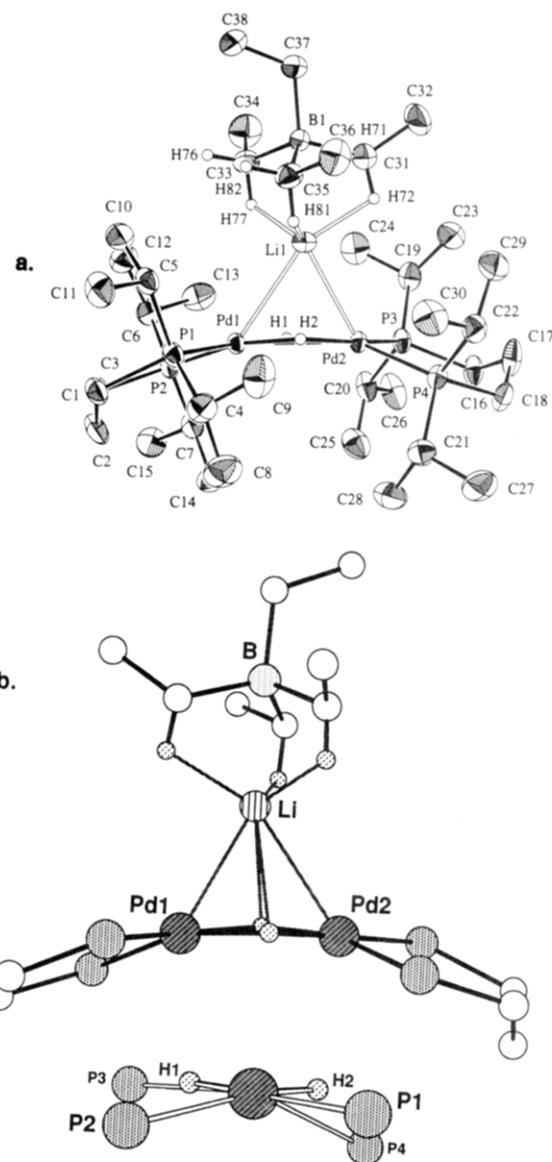


Figure 1. (a) Molecular structure and numbering scheme for [(dipp)Pd]₂(μ-H)₂LiBE₄ (**1**); (b) core view of **1** showing the interaction of the Li cation with the three α-C-H bonds in the ethyl groups, the bridging hydrides, and the palladium centres; and (c) a view looking down the Pd(1)-Pd(2) axis to show the nonplanar nature of the hydride and phosphorus core.

Table 3. Selected Intramolecular Angles (deg) Observed in [(dipp)Pd]₂(μ-H)₂LiBE₄ (**1**), [(dipp)Pd]₂(μ-H)₂ (**2**), and [(dipp)Pd]₂(μ-H)₂NaBE₄ (**3**)

[(dipp)Pd] ₂ (μ-H) ₂ LiBE ₄ (1)			
H(1)-Pd(1)-H(2)	72(2)	H(1)-Pd(2)-H(2)	68.5(1.5)
P(1)-Pd(1)-P(2)	99.91(4)	P(3)-Pd(2)-P(4)	100.54(5)
Pd(1)-Li-Pd(2)	63.5(2)	Pd(1)-H(1)-Pd(2)	109(2)
Pd(1)-H(2)-Pd(2)	109(2)	H(1)-Li-H(2)	49(1)
[(dipp)Pd] ₂ (μ-H) ₂ (2)			
H(1)-Pd(1)-H(2)	85.9(2)	H(1)-Pd(2)-H(2)	84.8(2)
P(1)-Pd(1)-P(2)	99.81(8)	P(3)-Pd(2)-P(4)	101.93(8)
Pd(1)-H(1)-Pd(2)	95.8(3)	Pd(1)-H(2)-Pd(2)	93.5(3)
[(dipp)Pd] ₂ (μ-H) ₂ NaBE ₄ (3)			
H(1)-Pd(1)-H(2)	73(2)	H(1)-Pd(2)-H(2)	76(2)
P(1)-Pd(1)-P(2)	100.49(5)	P(3)-Pd(2)-P(4)	100.95(6)
Pd(1)-Na-Pd(2)	58.43(4)	Pd(1)-H(1)-Pd(2)	104(2)
Pd(1)-H(2)-Pd(2)	105(3)	H(1)-Na-H(2)	49(3)

longer than the 1.531(11) Å found in the recently reported³⁶ cation {[(dipp)Pd]₂(μ-H)(μ-CO)}⁺.

The solid-state structure is not completely planar as evidenced by the end-on view in Figure 2b. Looking down the Pd(1)-Pd(2)

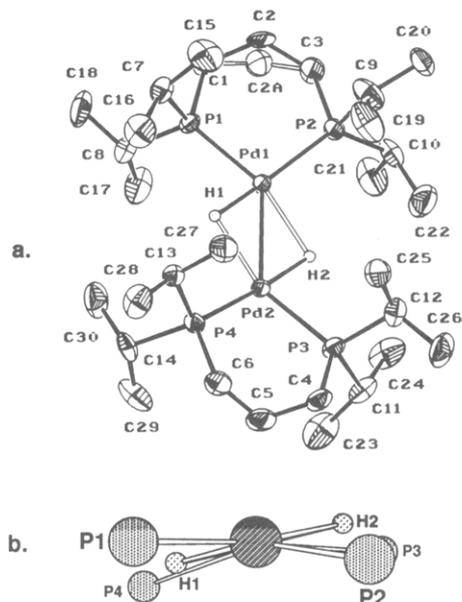


Figure 2. (a) Molecular structure and numbering scheme for $[(\text{dipp})\text{Pd}]_2(\mu\text{-H})_2$ (**2**); (b) a view looking down the Pd(1)–Pd(2) axis to show the nonplanar nature of the hydride and phosphorus core.

axis, the plane defined by the two palladium atoms and the two hydrides is canted by 19.5° to the P(1)–Pd(1)–P(2) plane and 15.1° to the P(3)–Pd(2)–P(4) plane. The analogous d^9 nickel dimer, $[(\text{dcypp})\text{Ni}]_2(\mu\text{-H})_2$ (dcypp = 1,3-bis(dicyclohexylphosphino)propane), has a solid-state structure³⁷ more resembling a D_2 symmetric species with the two Ni(dicypp) ends of the molecule staggered by 63.3° . However, a molecular orbital calculation performed upon the model complex $[(\text{H}_3\text{P})_2\text{Ni}]_2(\mu\text{-H})_2$ concluded that the energy minimum occurred for the completely planar D_{2h} structure, and thus the observed departure from planarity in $[(\text{dcypp})\text{Ni}]_2(\mu\text{-H})_2$ was proposed to be due to steric repulsion between the cyclohexyl groups on alternate ligands.³⁷ For the structure of the lithium adduct **1**, this angle is 34.6° , while for the hydride dimer **2**, this angle is 24.0° . Presumably, because of the larger size of Pd as compared to Ni, steric repulsion between isopropyl groups across the ends of the binuclear unit is minimal and the structure of the parent palladium hydride dimer **2** is nearly planar.

In solution, the structure of the bare palladium dimer **2** is completely symmetrical as evidenced by equivalent phosphines and hydrides by NMR spectroscopy at all temperatures. For this reason, a symmetrical, planar D_{2h} geometry is assumed for all discussions of the solution structure of this dimer **2**.

Examination of the ^1H NMR spectrum of the original reaction mixture of Pd(dipp) Cl_2 and the THF solution of LiBEt₂H₂/LiBEt₄ that ultimately produces **1** revealed a quintet at -2.52 ppm which is identical to that observed for the parent palladium hydride dimer **2**. This is strong evidence that the bare hydride dimer **2** is the initial product and only upon workup with removal of the THF, which was undoubtedly coordinated to the LiBEt₄, does coordination of free LiBEt₄ to the palladium–hydride dimer occur.

The proposal that the bare hydride dimer **2** is an intermediate in the formation of the palladium–lithium adduct **1** can be confirmed by the preparation of adduct **1** from dimer **2** by addition of LiBEt₄ in an aromatic solvent. Isolated yields of **1** by this procedure are in excess of 90%. This appears to be a general

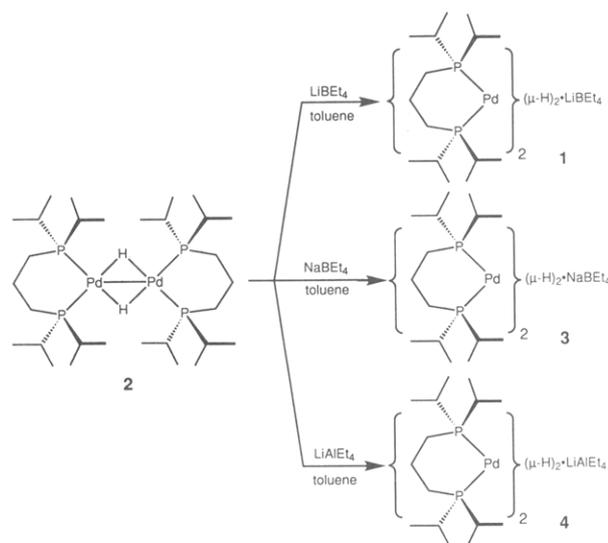
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Scheme 1



procedure since addition of the corresponding sodium salt, NaBEt₄, to the bare palladium dimer **2** generates the corresponding adduct $[(\text{dipp})\text{Pd}]_2(\mu\text{-H})_2\cdot\text{NaBEt}_4$ (**3**) while the addition of LiAlEt₄ also generates the related adduct $[(\text{dipp})\text{Pd}]_2(\mu\text{-H})_2\cdot\text{LiAlEt}_4$ (**4**). All of these transformations are summarized in Scheme 1.

The solid-state X-ray structure of the NaBEt₄ adduct **3** is shown in Figure 3. As can be seen from the ORTEP diagram, it displays similar features to that of the LiBEt₄ adduct **1**. The binuclear structure is apparent as are the bridging hydrides; the Pd–Pd distance of 2.8169(6) Å is very slightly shorter than either of the comparable Pd–Pd bond distances in **1** or **2** and the Pd–H bond lengths of 1.80(3) Å are long but within the range of 1.67(3)–2.13(4) Å observed for the bare dimer **2**.

The disposition of the tetraethylborate unit around the alkali metal constitutes the most important difference in the structures of adducts **1** and **3**. The lithium cation in **1** (Figure 1) is proximate to three of the α -carbons of the tetraethylborate unit, and a bridged interaction with one C–H bond of each of the three methylene units is inferred. It should be noted that the methylene hydrogens are in calculated positions based on the observed C–C angle of the ethyl group; nonetheless, only one C–H unit points at the Li cation. The Li–C separation (2.32–2.37 Å) is comparable to the corresponding distances in the structures of LiBMe₄ and LiAlEt₄ (2.36 and 2.37 Å, respectively).^{33,38} The sodium nucleus in the solid-state structure of **3** (Figure 3) is contiguous to only two α -carbons, but now positioned to interact with four α -C–H bonds; again, the hydrogens are placed in calculated positions based on the observed C–C bond angle of the ethyl group. The difference in the interaction of Na⁺ and Li⁺ with the tetraethylborate unit may be attributed to some peculiarity of the solid state; however, it may also reflect that sodium ion is larger than lithium ion and thus prefers a higher coordination number. The average Na–C distance is 2.67 Å.

Other distances of note are the lithium–hydride bond lengths of 2.25(3) and 2.54(4) Å and the lithium–palladium separations of 2.733(8) and 2.635(8) Å, the differences again indicative of the unsymmetrical structure in the solid-state structure of **1**. The observed sodium–hydride distances are 2.56(5) and 2.60(4) Å and the sodium–palladium lengths are 2.90(5) and 2.87(3) Å.

Variable-temperature, ^1H NMR experiments on the NaBEt₄ adduct **3** show no inequivalence among the ethyl groups of the tetraethylborate groups, even at -90°C , similar to that observed for the LiBEt₄ adduct **1**; this is consistent with the tetraethylborate

(38) Gerteis, R. L.; Dickerson, R. E.; Brown, T. L. *Inorg. Chem.* **1964**, *3*, 872.

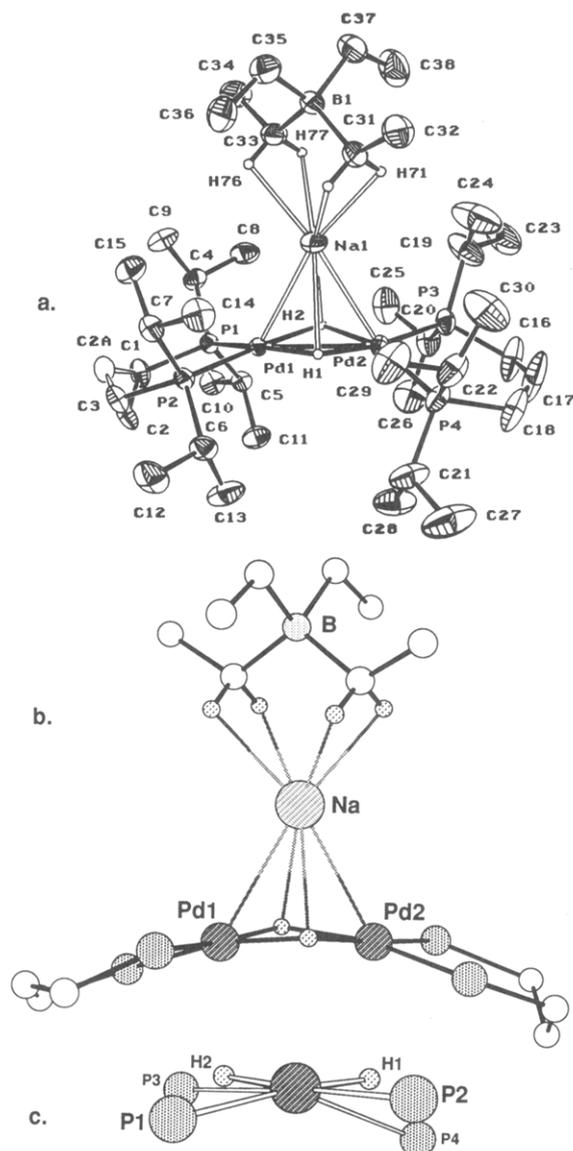


Figure 3. (a) Molecular structure and numbering scheme for $[(\text{dipp})\text{Pd}]_2(\mu\text{-H})_2\cdot\text{NaBEt}_4$ (**3**); (b) core view of **3** showing the interaction of the Na cation with the four $\alpha\text{-C-H}$ bonds in the ethyl groups, the bridging hydrides, and the palladium centers; and (c) a view looking down the Pd(1)–Pd(2) axis to show the nonplanar nature of the hydride and phosphorus core.

anion undergoing a rapid tumbling motion in solution interchanging all the methylene protons. Also comparable to **1** is the fact that, in the sodium adduct **3**, the top and bottom of the binuclear hydride unit are equivalent by ^1H NMR spectroscopy even at low temperature which is a feature consistent with a labile NaBEt_4 unit.

As outlined in Scheme 1, upon addition of stoichiometric amounts of solid LiBEt_4 to a benzene or toluene solution of the parent hydride dimer **2**, the LiBEt_4 adduct **1** is produced as determined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. How strong, thermodynamically, is the interaction of the perethylborate and aluminate salts with the palladium hydride dimer **2**? Attempts to measure the equilibrium constant for adduct **1** in the presence of **2** by NMR spectroscopy have so far failed presumably because the adduct forms completely even at low concentrations of LiBEt_4 . In addition, if a mixture of adduct **1** and the bare hydride dimer **2** are mixed together, exchange of the LiBEt_4 unit occurs as evidenced by broad resonances in the hydride region of the ^1H NMR spectrum (Figure 4); as the temperature is lowered, this particular exchange process becomes slow and the separate signals due to the hydride resonances of **1** and **2** are observed *in the exact*

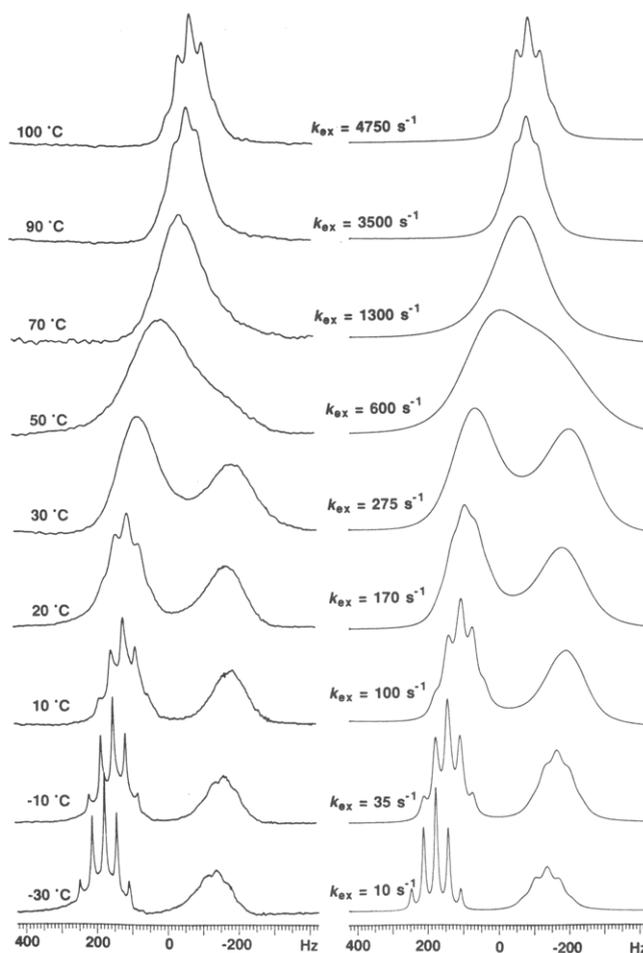


Figure 4. Experimental (left) and simulated (right) variable-temperature ^1H NMR spectra of an equimolar mixture of $[(\text{dipp})\text{Pd}]_2(\mu\text{-H})_2\cdot\text{LiBEt}_4$ (**1**) and $[(\text{dipp})\text{Pd}]_2(\mu\text{-H})_2$ (**2**) in the hydride region ($0\text{ Hz} = -3.0\text{ ppm}$; $[\text{Pd}] = 4.20 \times 10^{-2}\text{ mol L}^{-1}$); the very sharp quintet at low temperatures is due to **2** while the broader resonance is due to LiBEt_4 adduct **1**.

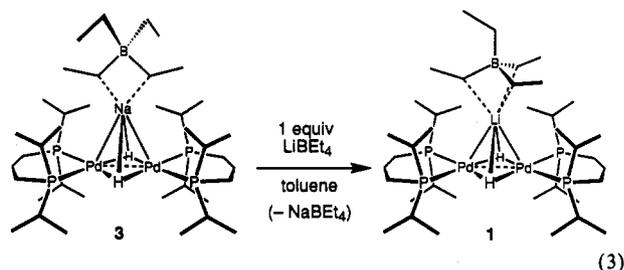
ratio that they were originally mixed. As the temperature is raised, the peaks coalesce to eventually generate a single resonance (at $100\text{ }^\circ\text{C}$) due to averaged intermolecular exchange. The kinetics of the exchange reaction have been estimated by variable-temperature ^1H NMR spectroscopy in C_7D_8 , followed by simulation of the experimental spectra. A graph of the interpolated rate constant, k_{ex} , versus inverse temperature gave an exponential dependence over a temperature range of $243\text{--}373\text{ K}$. The rate of exchange, R_{ex} , was found to vary as the concentration of adduct **1** and was insensitive to the concentration of the bare hydride dimer **2**. A simple first-order dissociative mechanism is proposed and the rate law is formulated as $R_{\text{ex}} = k_{\text{ex}}[\mathbf{1}]$. The Eyring activation parameters may be extracted from a plot of $\ln(k_{\text{ex}}T^{-1})$ versus T^{-1} : $\Delta H_{\text{ex}}^\ddagger = 7.9 \pm 1.0\text{ kcal mol}^{-1}$ and $\Delta S_{\text{ex}}^\ddagger = -13.6 \pm 4.0\text{ cal K}^{-1}\text{ mol}^{-1}$.³⁹ The negative value of $\Delta S_{\text{ex}}^\ddagger$ is troublesome for what is suggested to be a dissociative mechanism; however, if solvent molecules participate in the activated complex by solvating free LiBEt_4 , then this negative $\Delta S_{\text{ex}}^\ddagger$ can be rationalized. A more comprehensive kinetic analysis, embracing solvents other than C_7D_8 , could not be performed due to the insolubility of **1** in aliphatic solvents, and its complete decomposition in chlorinated solvents. As expected, in the presence of donor solvents such as THF or Et_2O , adduct formation is disrupted and the bare palladium dimer **2** is produced as evidenced by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

These experiments provide further evidence that, thermodynamically, the adduct **1** is favored yet, kinetically, the LiBEt_4 is

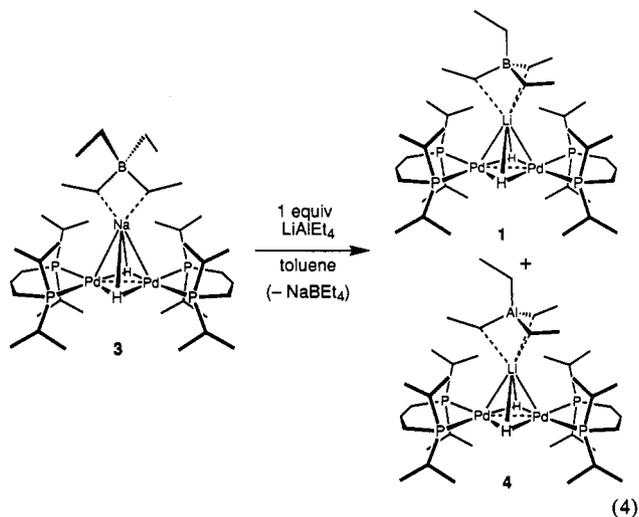
(39) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill Book Company: New York, 1981; pp 50–55.

rather labile; this latter point corroborates the ^1H NMR spectral data concerning the equivalence of both the ethyl groups at boron and the isopropyl substituents at phosphorus at low temperatures mentioned earlier.

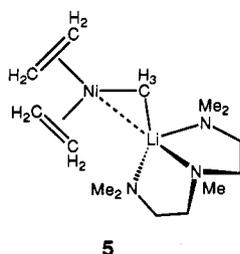
The addition of LiBEt_4 to the sodium adduct **3** results in virtually quantitative formation of the lithium adduct **1** (eq 4). Although 1 equiv of LiBEt_4 added to the sodium adduct **3** is enough to generate the lithium adduct **1** as the only detectable product, this is an equilibrium process since addition of ~ 5 equiv of NaBEt_4 to the lithium adduct **1** does result in the formation of a mixture of **1** and **3** in a 2:1 ratio; in other words, the reaction shown in eq 3 can be reversed to some extent by the addition of an excess of NaBEt_4 .



Interestingly, if LiAlEt_4 is added to the sodium tetraethylborate adduct **3**, an equal mixture of the lithium adducts **1** and **4** is obtained indicating that there is little preference for the anion portion of the adduct (eq 4).

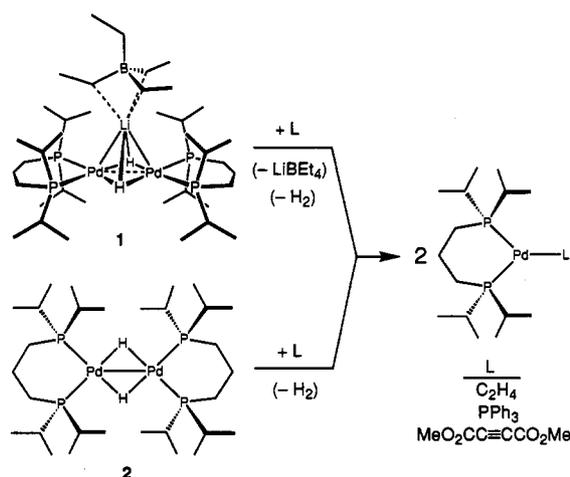


Bonding Considerations. With regard to the nature of the bonding in complexes **1**, **3**, and **4**, we have been unable to find another derivative with a similar type of interaction. Complexes that contain lithium are quite well known.⁴⁰⁻⁴² Examples range from ionic derivatives such as the tetrameric $\{[(\eta^5\text{-C}_5\text{H}_5)_2\text{MoH}]\text{-Li}\}_4$ to organolithium adducts of $\text{Ni}(0)$ similar to **5** which are considered to be ion pairs.⁴³⁻⁴⁵



It should be stressed that the interaction of the lithium ion with the metal complex in **5** is fundamentally different than in the

Scheme 2



palladium- LiBEt_4 adduct **1** or the corresponding NaBEt_4 derivative **3** since, in **5**, the methyl anion is directly attached to the metal center, whereas in the latter molecules, the anionic BEt_4 moiety coordinates only to the Li^+ or Na^+ ions. If the interaction of the LiBEt_4 with the palladium hydride dimer is not ionic then it must be an ion-dipole type bond (i.e., the lithium ion is electrostatically attracted to electron density) since it is fairly well established that the bonding in organolithium derivatives is largely ionic.^{40,46}

Reactivity Studies. Reactions of ethylene (or propylene) with the lithium adduct **1** result in the loss of H_2 (detected by ^1H NMR spectroscopy) and the release of the LiBEt_4 unit to generate the three-coordinate $\text{Pd}(0)$ adduct $\text{Pd}(\eta^2\text{-C}_2\text{H}_4)(\text{dipp})$; a similar reaction ensues when PPh_3 is allowed to react with **1** since $\text{Pd}(\text{PPh}_3)(\text{dipp})$ is obtained, and the reaction with dimethyl acetylenedicarboxylate, $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$, also generates the corresponding $\text{Pd}(0)$ adduct $\text{Pd}(\eta^2\text{-MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me})(\text{dipp})$. The same sequence of reactions carried out with the bare palladium dimer **2** produces the exact same palladium(0) adducts in virtually identical yields; all of this is summarized in Scheme 2. Thus, these formally palladium(I) hydride derivatives would appear to be sources of $\text{Pd}(0)$ since H_2 elimination is observed rather than any insertion type chemistry. In the case of the Li adduct **1**, the presence of the Lewis acidic LiBEt_4 moiety does not apparently influence any of the simple reaction types shown here since it is liberated along with the H_2 . There is precedent for the release of H_2 from formally $\text{Ni}(I)$ hydride dimers upon addition of olefins as well as liberation of alkylaluminum fragments from adducts of $\text{Ni}(0)$ derivatives.¹³ In retrospect, it is difficult to imagine how the Lewis acidic portion of **1**, the LiBEt_4 unit, could have any influence on these types of reactions since the particular substrates used would be expected to be relatively innocuous to group 13 "ate" species. In addition, the similarity in the reaction outcomes shown in Scheme 2 is consistent with the lability of the LiBEt_4 unit in that it is the palladium hydride dimer portion of adduct **1** that is undergoing the H_2 displacement and ligand addition reactions.

Conclusions

The interaction of Lewis acids with transition-metal complexes is manifested in a number of significant reaction types. Shown

(40) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

(41) Darensbourg, M. Y.; Ash, C. E. *Adv. Organomet. Chem.* **1987**, *27*, 1.

(42) Jonas, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 520.

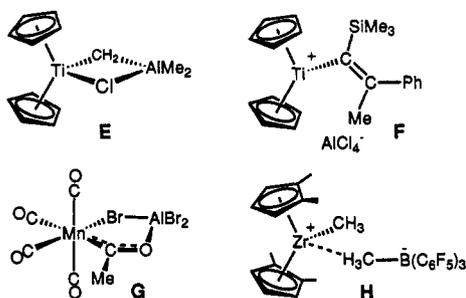
(43) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185.

(44) Poerschke, K. R.; Wilke, G. *J. Organomet. Chem.* **1988**, *358*, 519.

(45) Poerschke, K. R.; Wilke, G. *J. Organomet. Chem.* **1988**, *349*, 257-61.

(46) Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1988**, *27*, 169.

below (E–H) are some illustrative examples^{9,14,47,48} of how Lewis acids can influence the structure and reactivity of metal complexes.



These examples illustrate that Lewis acids cannot only remove a ligand from the coordination sphere of a metal thereby generating a open site (e.g. F and H) but can also bind to particular ligands in the coordination sphere and stabilize reactive fragments (e.g. the Ti=CH₂ unit in Tebbe's reagent E) and promote migratory insertion (e.g. the manganese acyl derivative G).

In the work reported in this paper, we document a whole new kind of Lewis acid–Lewis base interaction that involves a neutral, binuclear metal complex having bridging hydride ligands and alkali metal salts of group 13 tetraalkyl “ate” derivatives. By variable-temperature NMR studies, these adducts were shown

(47) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611.

(48) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219.

to be quite labile and this aspect is reflected in the reactivity of the hydride dimers with a variety of simple substrates. On the other hand, solution NMR experiments also show that the interaction is qualitatively quite strong since no evidence for dissociation of the adducts was found. In trying to gauge what promotes such an interaction, a number of features deserve mention: (a) the solution structures of the lithium and sodium tetraalkylborates (and aluminates) are not known; however, one might predict that the cation is labile and is involved in oligomeric aggregates; and (b) the palladium hydride dimer itself has very electron-rich metal centers [formally d⁹ for each Pd(I)] and bridging hydrides, both sources of electron density for an ion-dipole type interaction with soluble alkali metal cations. Taken together, it is not unreasonable to predict that other electron-rich metal complexes with and without hydrides should show adduct formation with species such as LiBEt₄ and NaBEt₄. Such studies are currently in progress.

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Supplementary Material Available: Final atomic coordinates and equivalent isotropic thermal parameters, complete tables of bond lengths and angles, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes for 1, 2, and 3 (110 pages); listing of measured and calculated structure factor amplitudes for 1, 2, and 3 (118 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.