reaction is a non-metal catalyzed version of eq 3, where we have chosen NH_3 as the catalyst. This synthetic strategy has broad potential for heterogeneous reactions beginning with metallic elements.

Perhaps the most interesting feature of the structure described here are the unusually low coordination numbers for a divalent cation as large[5] as Ba^{2+}. This again demonstrates the ability of the bis(trimethylsilyl)amido ligand to provide sufficient steric bulk as to stabilize low coordination numbers. The *variability* of the barium coordination number is also noteworthy. The systematic loss of THF along a series of *isolable* members is also presumably driven by the steric bulk of the $N(SiMe_3)_2$ group.

Another interesting feature is the trend shown by NMR spectroscopy as the number of coordinated THF molecules changes. The chemical shifts of the coordinated THF are shifted upfield compared to free THF in toluene-d_8 (δ 3.55, 1.46). The dimeric compound **2** has its THF resonances farther upfield than those of the bis(THF) monomer, **1**. Resonances for the methyl groups also show an upfield shift as one goes to fewer coordinated THF molecules. This is evident in both the ^1H and $^{13}C\{^1H\}$ NMR spectra.

A brief comparison of these structures to those of other divalent metal amido compounds is noteworthy. The chemistry of divalent metal bis(trimethylsilyl)amides includes monomers (M = Zn),[6] monomer/dimer equilibria involving $M_2(NR_2)_2(\mu\text{-}NR_2)_2$ (M = Mn, Fe, Co, Ni),[7-9] and formation of 1:1 mononuclear adducts with THF (Mn, Fe).[8] Chromium(II) forms a bis(THF) adduct.[10] The influence of still larger silyl groups has also been investigated.[11,12] In contrast to **3**, the metal is planar in $Cr_2(N^iPr_2)_4$[13] and in $\{M[N(SiMe_3)_2]_2\}_2$, M = Mn, Co.[8]

While the larger barium atom acquires three-coordination by dimerizing in compound **3**, the lighter group IIA atom, beryllium, is monomeric in $Be[N(SiMe_3)_2]_2$.[14]

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Supplementary Material Available: For compounds **1–3**, tables of crystallographic data, fractional coordinates, and isotropic and anisotropic thermal parameters and labeled figures (11 pages); listings of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Reactivity of Palladium(II) Complexes with Bidentate Bis(phosphine) Ligands toward the Octahydrotriborate(1−) Anion and Dependence of the Reaction upon Halide Arrangement: Molecular Structure of the *trans*-(bis(diphenylphosphino)hexane)palladium(II) Dichloride Dimer

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The reactivity of the palladium(II) bis(phosphine) complexes, $(Ph_2P(CH_2)_nPPh_2)PdCl_2$ (n = 1–6), toward the octahydrotriborate(1−) anion, $[B_3H_8]^-$, has been investigated. For n = 1–4, the metallaborane $(Ph_2P(CH_2)_nPPh_2)Pd(B_3H_7)$ is produced, although the yield depends upon the organic chain length of the phosphino ligand and is maximized when n = 2. Our observation that no reaction occurs between the $[B_3H_8]^-$ anion and (bis(diphenylphosphino)pentane)- or (bis(diphenylphosphino)hexane)-palladium(II) dichloride leads us to examine the structure of these starting materials. Unlike $(Ph_2P(CH_2)_nPPh_2)PdCl_2$ for n = 1–4, which are cis monomers, complexes with n = 5 or 6 are dimeric with a trans arrangement of chloro substituents; the molecular structure of *trans*-$[(Ph_2P(CH_2)_6PPh_2)PdCl_2]_2$ is presented: triclinic, $P\bar{1}$; a = 9.448 (2), b = 11.772 (2), c = 16.983 (3) Å; α = 74.18 (2), β = 87.14 (2), γ = 77.59 (2)°; V = 1774.9 (9) Å^3, Z = 2; R_F = 5.17%. A detailed comparison of this structure with those of related complexes is made.

The versatility of the triborane ligand with respect to bonding to metal fragments has been recognized for some years.[1-5] As the octahydrotriborate(1−) anion, $[B_3H_8]^-$, the triborane ligand tends to coordinate through terminal hydrogen atoms to generate M–H–B bridging interactions, e.g. $Cr(CO)_4B_3H_8$,[6] $Mn(CO)_3B_3H_8$,[7] and $(\mu\text{-}Br)Mn_2(CO)_6B_3H_8$.[8] On the other hand, in situ loss of a proton formally produces the "borallyl" $[B_3H_7]^{2-}$ ligand (not isolated as a free entity), as confirmed structurally in the complexes $(Me_2PhP)_2PtB_3H_7$,[9,10] $(Ph_3P)_2(CO)HIrB_3H_7$,[11,12] and $(dppf)PdB_3H_7$[13] (dppf − 1,1′-bis(diphenylphosphino)ferrocene). The preferred coordination mode of the triborane ligand is sensitive to the bonding capability of the metal fragment,[4] and clearly, as the $[B_3H_8]^-$ anion reacts with a given metal complex, it responds to the presence (or absence) of potential leaving groups present.

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Table I. Spectroscopic Properties of $L_2PdB_3H_7$ (L_2 = dppm, dppe, dppp, dppb, dppf)

compd	NMR spectra[a] $\delta(^{11}B)$	$\delta(^1H)$	$\delta(^{31}P)$	IR spectrum[b] ν(BH), cm^{-1}
(dppm)PdB_3H_7 (**1**)	+5.0 (2 B), +18.2 (1 B)	+3.5 (5 H), −2.8 (2 H)	*c*	*c*
(dppe)PdB_3H_7 (**2**)	+8.6 (2 B), +20.2 (1 B)	+3.5 (5 H), −2.8 (2 H)	+34.5	2498 s, 2460 s, 2409 s, 1863 m, 1585 m, 1571 m
(dppp)PdB_3H_7 (**3**)	+8.3 (2 B), +19.5 (1 B)	+3.1 (5 H), −2.9 (2 H)	−1.2	2480 s, 2415 s, 1870 m, 1587 m
(dppb)PdB_3H_7 (**4**)	+8.0 (2 B), +19.0 (1 B)	+3.2 (5 H), −2.9 (2 H)	+11.7	2490 s, 2425 s, 1881 m, 1571 m
(dppf)PdB_3H_7[d] (**5**)	+8.5 (2 B), +20.1 (1 B)	+2.9 (5 H), −2.8 (2 H)	+12.5	2498 s, 2421 s, 1890 m, 1543 m

[a] In CD_2Cl_2; at 293 K. [b] KBr disk. [c] Insufficient sample. [d] Reference 13.

Thus, in the preparation from $[B_3H_8]^-$ of complexes incorporating the $\{B_3H_7\}$ fragment, not only must substitution of a leaving group for $[B_3H_8]^-$ occur but elimination of HX (where X is typically halide) is also a prerequisite.[9,10]

With these observations in mind, we have investigated the reactivity of a series of palladium(II) complexes containing bidentate phosphino ligands, $(Ph_2P(CH_2)_nPPh_2)PdCl_2$ (n = 1–6), toward the $[B_3H_8]^-$ anion. The original aim of this study was to discover whether a systematic change in the steric requirements of the bidentate phosphine ligand would provide a correspondingly systematic change in the coordination mode of the triborane ligand. Could we force the triborane fragment to bind in a manner other than that previously observed? However, the investigation has led us into a detailed study of the bis(phosphino)palladium(II) chloride complexes themselves, since rather than reacting with $[B_3H_8]^-$ and giving rise to a change in bonding mode to the metal center, $(Ph_2P(CH_2)_nPPh_2)PdCl_2$ (n = 5, 6) failed to react at all.

Two palladium(II) derivatives have been reported and are pertinent to the present study. The synthesis and characterization by elemental and spectroscopic analysis of (dppe)PdB_3H_7 (dppe = bis(diphenylphosphino)ethane) have been described.[10] The dppf ligand is sterically more demanding than dppe, and yet, the π-borallyl bonding mode still persists, as is illustrated by the molecular structure of (dppf)PdB_3H_7 (Figure 1).[13] The ferrocene rings of the dppf ligand are able to twist with respect to one another, thereby providing this ligand with a high degree of flexibility and an ability to subtend a large P–Pd–P bond angle of 104.2 (1)° in (dppf)PdB_3H_7 while not perturbing the bonding mode of the triborane ligand. In contrast, terminally substituted bis(diphenylphosphino)alkane chelating ligands possessing relatively short, straight-chain alkane backbones are less flexible than the dppf ligand. Given a long enough backbone between the phosphorus donors, we considered that the coordination mode of the triborane fragment might eventually be hindered. The molecular structures of (dppm)$PdCl_2$, (dppe)$PdCl_2$, and (dppp)$PdCl_2$ confirm that the P–Pd–P angle increases with the length of the organic chain: ∠P–Pd–P = 72.68 (3)° in (dppm)$PdCl_2$, 85.82 (7)° in (dppe)$PdCl_2$, and 90.58 (5)° in (dppp)$PdCl_2$. The associated closure of the Cl–Pd–Cl angle is less pronounced: ∠Cl–Pd–Cl = 93.63 (3)° in (dppm)$PdCl_2$, 94.19 (7)° in (dppe)$PdCl_2$, and 90.78 (5)° in (dppp)$PdCl_2$, although deviation of the phosphorus (or chlorine) atoms from an ideal square plane (P_2PdCl_2) relieves strain in both (dppm)$PdCl_2$ and (dppp)$PdCl_2$.[14]

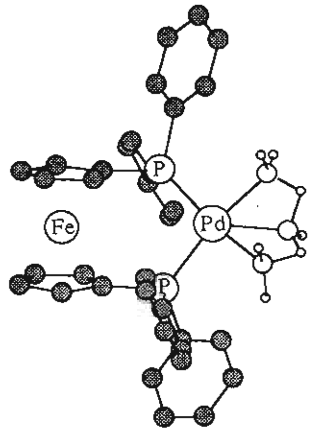

Figure 1. Schematic representation of the molecular structure of (dppf)PdB_3H_7 (**5**)[13] with phenyl and ferrocenyl H atoms omitted for clarity.

Experimental Section

General Data. FT-NMR spectra were recorded on a Bruker WM 250 or AM 400 spectrometer. ^1H NMR shifts are reported with respect to δ 0 for Me_4Si; ^{11}B NMR shifts with respect to δ 0 for $F_3B\cdot OEt_2$; ^{31}P NMR shifts with respect to δ 0 for H_3PO_4. All downfield chemical shifts are positive. IR spectra were recorded on a Perkin-Elmer FT 1710 spectrophotometer. FAB mass spectra were recorded on a Kratos MS 50TC, MS 902, or MS 890 instrument. Molecular weights were determined cryoscopically in dry benzene.

Unless otherwise stated, reactions were carried out under argon by using standard Schlenk techniques.[15] Solvents were dried over suitable reagents and freshly distilled under nitrogen before use. Chromatographic separations were carried out under nitrogen, by column with Kieselgel 70-230 mesh (Merck). Phosphines (Aldrich or Strem), $PdCl_2$ (Aldrich), and $[Me_4N][B_3H_8]$ (Strem or Alfa-Ventron) were used directly as supplied. Na_2PdCl_4 was prepared by a method analogous to that described for the preparation of $K_2Pd(CN)_4$.[16]

Ligands are abbreviated as follows: dppm = bis(diphenylphosphino)methane; dppe = bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane; dppp′ = 1,5-bis(diphenylphosphino)pentane; dpph = 1,6-bis(diphenylphosphino)hexane.

Preparation of $[(Ph_2P(CH_2)_nPPh_2)PdCl_2]_x$ (x = 1, n = 1–4; x = 2, n = 5, 6). The following procedure was used in preference to that developed by Verkade et al.[17] The syntheses may be carried out in open air. A solution of $Ph_2P(CH_2)_nPPh_2$ (n = 1–6) (2 mmol) in THF (20 mL) was added to a solution of Na_2PdCl_4 (0.59 g; 2 mmol) in ethanol (100 mL). $(Ph_2P(CH_2)_nPPh_2)PdCl_2$ formed as a yellow precipitate. After the solution was stirred for 2 h, solvent was removed by a rotary evaporator, and the yellow residue was washed with water (200 mL) and dried in an oven at 80 °C for 12 h. Yields of $(Ph_2P(CH_2)_nPPh_2)PdCl_2$: n = 1, 82%; n = 2, 75%; n = 3, 88%; n = 4, 88%. Yields of $[(Ph_2P(CH_2)_nPPh_2)PdCl_2]_2$: n = 5, 95%; n = 6, 61%. IR and ^{31}P NMR spectral characteristics of complexes with n = 1–5 were consistent with those given in the literature.[18-22] Mass spectral data for (dppm)$PdCl_2$ have been reported.[23] Other data are as follows. (dppe)$PdCl_2$: FAB-MS in 3-NBA matrix, m/z 574 (P^+). (dppp)$PdCl_2$: FAB-MS in 3-NBA matrix, m/z 553 ($P^+ - Cl$). (dppb)$PdCl_2$: FAB-MS in 3-NBA matrix, m/z 567 ($P^+ - Cl$). $[(dppp')PdCl_2]_2$: mol wt calcd 1234, found 1243; FAB-MS in 3-NBA matrix, m/z 1197 ($P^+ - Cl$). Anal. Calcd for $C_{58}H_{60}Cl_4P_4Pd_2$: C, 56.38; H, 4.86; P, 10.03. Found: C, 56.08; H, 4.75; P, 10.04. $[(dpph)PdCl_2]_2$: FAB-MS in 3-NBA matrix, m/z 1225 (P^+

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Table II. Crystal Data for $[(dpph)PdCl_2]_2$ (**6**)

formula	$C_{60}H_{64}Cl_4P_4Pd_2$	γ, deg	77.59 (2)
M_r	1263.59	V, Å^3	1774.9 (9)
cryst system	triclinic	Z	2
space group	$P\bar{1}$ (No. 2)	D(calcd), g cm^{-3}	2.364
a, Å	9.448 (2)	μ(Mo Kα), cm^{-1}	13.45
b, Å	11.772 (2)	T, K	286
c, Å	16.983 (3)	T_{max}/T_{min}	0.67/0.64
α, deg	74.18 (2)	$R(F)$, %	5.17
β, deg	87.14 (2)	$R(wF)$, %	5.44

– Cl). Anal. Calcd for $C_{60}H_{64}Cl_4P_4Pd_2$: C, 57.05; H, 5.07; P, 9.82. Found: C, 57.19; H, 5.20; P, 9.69.

Preparation of (dppm)PdB$_3$H$_7$ (1). In a typical reaction, $[Me_4N][B_3H_8]$ (0.12 g; 1.0 mmol) was added to a solution of (dppm)-PdCl$_2$ (0.56 g; 1.0 mmol) in MeCN (100 mL), thf (50 mL), toluene (25 mL), and Et$_3$N (2.5 mL). The mixture was stirred for 3 h and allowed to stand for 1 h as [Me$_4$N]Cl precipitated. The supernatent was removed by cannula, and solvent was removed in vacuo to give a dark brown crude residue. The product could only be partially separated by using column chromatography, being eluted with hexane as the first band (yield ≈ 2%).[24]

Preparation of (dppe)PdB$_3$H$_7$ (2). Crude **2** was prepared[10] on a 1.0-mmol scale by the same method described for **1**. The crude residue was washed with methanol and recrystallized from acetonitrile after the addition of 0.2 g of charcoal. Yield of **2**: ≈35%.[24]

Preparation of (dppp)PdB$_3$H$_7$ (3). Crude **3** was prepared on a 1.0-mmol scale by the same method described for **1**. The crude residue was washed with methanol and recrystallized from acetonitrile after the addition of 0.2 g of charcoal. Yield of **3**: ≈8%.[24]

Preparation of (dppb)PdB$_3$H$_7$ (4). Crude **4** was prepared on a 1.0-mmol scale by the same method described for **1**. The product was separated by using column chromatography and was eluted with hexane as the second band (yield ≈ 5%).[24]

Spectroscopic properties of compounds **1**–**4** are given in Table I.

Crystal Structure Determination. Crystallographic data for **6**, *trans*-$[(Ph_2P(CH_2)_6PPh_2)PdCl_2]_2$, are collected in Table II. A suitable crystal was obtained by recrystallization from CH_2Cl_2/hexane. The unit cell was obtained from the angular settings of 25 reflections (21° ≤ 2θ ≤ 30°); no symmetry higher than triclinic was found. The centrosymmetric alternative was initially assumed; this choice was verified by the chemically reasonable results of refinement. Corrections for absorption were applied by an empirical procedure. The structure was solved by heavy-atom methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. All phenyl rings were constrained to rigid, planar hexagons. Hydrogen atoms were treated as idealized, isotropic contributions.

All computations used SHELXTL (5.1) software (version 5.1).[25] Table III gives the atomic coordinates, and Table IV gives selected bond distances and angles.

Results and Discussion

Reaction of *cis*-$(Ph_2P(CH_2)_nPPh_2)PdCl_2$ (n = 1–4) with $[B_3H_8]^-$. It has previously been reported that the reaction of the octahydrotriborate(1–) anion with (dppe)PdCl$_2$ gives (dppe)-PdB$_3$H$_7$. The coordination mode of the triborane ligand in this compound has been inferred from infrared spectroscopic data and by a comparison with the molecular structure of the related compound $(Me_2PhP)_2PtB_3H_7$.[10] Here we compare the reactivity of $[B_3H_8]^-$ toward a series of palladium(II) chloro complexes containing bidentate phosphino ligands. For each of the complexes *cis*-$(Ph_2P(CH_2)_nPPh_2)PdCl_2$ (n = 1–4) a single palladaborane, $(Ph_2P(CH_2)_nPPh_2)PdB_3H_7$ is formed (compounds **1**–**4**, respectively). The yield of the metallaborane is dependent upon the length, n, of the organic chain in the phosphino ligand with the most effective reaction being that for n = 2. In each reaction, byproducts are $H_3B\cdot(Ph_2P(CH_2)_nPPh_2)\cdot BH_3$, $Et_3N\cdot B_3H_7$, and $Et_3N\cdot BH_3$,[24] the Et$_3$N originating from the solvent mixture.[10] Previously, we have characterized the complex (dppf)PdB$_3$H$_7$ (**5**) both spectroscopically and crystallographically.[13] Spectroscopic data for complexes **1**–**5** are listed in Table I, and the close similarity between the data suggest that the $\{P_2PdB_3H_7\}$ fragments in the five compounds are isostructural. ^{11}B NMR chemical shifts are extremely sensitive to environment, and for members of a related set of compounds such as **1**–**5**, a reproducible spectral pattern is good evidence for recurring structural characteristics for the borane ligand. The free and highly fluxional $[B_3H_8]^-$ ion is characterized by an ^{11}B NMR signal at δ –29.3. Complexes containing a bidentate $\{B_3H_8\}$ ligand bonded through B–H–M bridges to an octahedral metal atom exhibit ^{11}B NMR signals at δ –41 ± 3 (2 B) and δ –1 ± 6.[26] The ^{11}B NMR spectrum of the pseudooctahedral iridium(III) complex $(Ph_3P)_2(CO)HIrB_3H_7$ shows resonances at δ –15 (2 B) and +3 (1 B), while in the pseudo-square-planar palladium(II) complex (dppf)PdB$_3$H$_7$ (**5**) (Figure 1), the resonances are further downfield at δ +8.5 (2 B) and +20.1 (1 B). In $Fe_2(CO)_6B_3H_7$, in which the triborane fragment interacts with both iron atoms, the ^{11}B NMR resonances

Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for *trans*-$[(dpph)PdCl_2]_2$ (**6**)

	x	y	z	U
Pd	4707.0 (6)	163.4 (5)	7647.4 (4)	39.3 (2)
P(1)	4087 (2)	–1735 (2)	8037 (1)	43 (1)
P(2)	5137 (2)	2124 (2)	7325 (1)	45 (1)
Cl(1)	6097 (2)	–337 (2)	8826 (1)	57 (1)
Cl(2)	3240 (3)	691 (2)	6509 (1)	69 (1)
C(1)	3347 (1)	–2217 (7)	7225 (5)	59 (4)
C(2)	4505 (10)	–2509 (8)	6600 (5)	68 (4)
C(3)	3796 (11)	–2595 (10)	5845 (5)	89 (5)
C(4)	5165 (12)	2981 (10)	4787 (5)	93 (5)
C(5)	5767 (10)	2524 (8)	5645 (5)	70 (4)
C(6)	4758 (10)	3026 (7)	6271 (4)	60 (3)
C(11)	6991 (5)	–2932 (4)	8323 (3)	55 (3)
C(12)	8104	–3937	8612	76 (4)
C(13)	7774	–5037	9045	82 (5)
C(14)	6332	–5132	9189	72 (4)
C(15)	5220	–4127	8901	62 (4)
C(16)	5549	–3026	8468	44 (3)
C(21)	1299 (5)	–1901 (5)	8662 (3)	63 (4)
C(22)	212	–1824	9244	75 (5)
C(23)	493	–1573	9971	68 (4)
C(24)	1861	–1400	10116	63 (4)
C(25)	2948	–1477	9535	57 (3)
C(26)	2667	–1728	8808	42 (3)
C(31)	4036 (5)	2533 (4)	8802 (3)	59 (3)
C(32)	3114	3139	9292	71 (4)
C(33)	2135	4207	8934	61 (4)
C(34)	2078	4669	8085	62 (4)
C(35)	3000	4064	7594	54 (3)
C(36)	3979	2995	7953	43 (3)
C(41)	7326 (6)	3294 (4)	7558 (4)	74 (4)
C(42)	8765	3388	7606	103 (6)
C(43)	9887	2415	7573	104 (7)
C(44)	9570	1348	7491	98 (6)
C(45)	8132	1254	7443	73 (4)
C(46)	7010	2227	7477	50 (3)

Table IV. Selected Bond Distances and Angles for *trans*-$[(dpph)PdCl_2]_2$ (**6**) with Labeling Scheme Given in Figure 4

(a) Bond Distances (Å)

Pd–P(1)	2.344 (2)	Pd–P(2)	2.342 (2)
Pd–Cl(1)	2.316 (2)	Pd–Cl(2)	2.300 (2)
P(1)–C(1)	1.844 (10)	P(2)–C(6)	1.823 (7)
C(1)–C(2)	1.538 (12)	C(2)–C(3)	1.512 (14)
C(3)–C(4a)	1.515 (14)	C(4)–C(5)	1.503 (12)
C(5)–C(6)	1.544 (12)		

(b) Bond Angles (deg)

P(1)–Pd–P(2)	174.7 (1)	P(1)–Pd–Cl(2)	89.6 (1)
P(1)–Pd–Cl(1)	90.3 (1)	P(2)–Pd–Cl(2)	90.2 (1)
P(2)–Pd–Cl(1)	89.7 (1)	Cl(1)–Pd–Cl(2)	177.5 (1)

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(24) Other products of the reactions were identified by ^{11}B and ^{1}H NMR and mass spectroscopy as $Et_3N\cdot B_3H_7$, $Et_3N\cdot BH_3$, and [Et$_3$NH]Cl; the formation of $H_3B\cdot(Ph_2P(CH_2)_nPPh_2)\cdot BH_3$, n = 1–6, was also confirmed by comparing spectroscopy data with those of an authentic samples prepared independently by the reaction of $Ph_2P(CH_2)_nPPh_2$ with thf·BH$_3$: n = 1, ^{11}B NMR δ –37, ^{31}P NMR δ +6; n = 2, ^{11}B NMR δ –36, ^{31}P NMR δ +20; n = 3, ^{11}B NMR δ –38, ^{31}P NMR δ +11; n = 4, ^{11}B NMR δ –39, ^{31}P NMR δ +15; n = 5, ^{11}B NMR δ –39, ^{31}P NMR δ +16; n = 6, ^{11}B NMR δ –37, ^{31}P NMR δ +11.

(25) Sheldrick, G. Nicolet XRD, Madison, WI.

(26) Reference 12 and references therein.

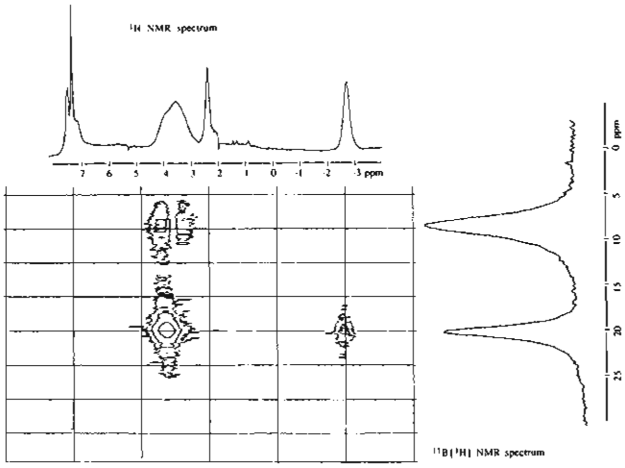


Figure 2. 400-MHz room-temperature $^{11}B-^{1}H$ NMR chemical shift correlation spectrum for (dppe)PdB$_3$H$_7$ (**2**) in CD$_2$Cl$_2$. BH resonances have been enhanced at the expense of resolution for the phenyl and methylene proton signals.

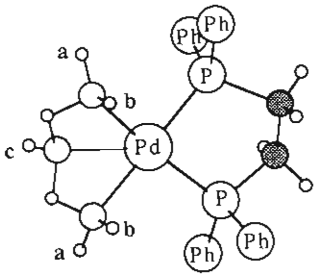


Figure 3. Proposed structure of (dppe)PdB$_3$H$_7$ (**2**) with atom-labeling scheme. The proposed structures of compounds **1**, **3**, and **4** are analogous with that of **2**.

are observed at δ +4.2 (2 B) and +12.4 (1 B).[5,27,28] In each of the reactions of L$_2$PdCl$_2$ (L$_2$ = dppe, dppp, dppb) with [B$_3$H$_8$]$^-$, the palladaborane product was characterized by two resonances at δ +8.3 ± 0.3 (2 B) and +19.6 ± 0.6 (1 B) in the ^{11}B NMR spectrum (e.g. as shown in Figure 2 for **2**). This spectral signature is the same as that observed for **5**. Compared to those for **2–4**, the ^{11}B NMR resonances of **1** are shifted slightly to higher field (Table I) but still imply a similar mode of bonding for the triborane. The ^{11}B NMR data are therefore consistent with each of the complexes **1–4** possessing a palladium(II) atom in a pseudo-square-planar environment and the {B$_3$H$_7$} ligand adopting an η^3-bonding mode (Figure 3) as in **5**[13] and (Me$_2$PhP)$_2$PtB$_3$H$_7$.[10]

The ^{1}H NMR data further support the above proposal. For each of compounds **1–4**, the room-temperature ^{1}H NMR spectrum exhibits one broad resonance at δ +3.2 ± 0.3 (5 H) assigned to terminal B–H and one signal at δ −2.8 or −2.9 (2 H) assigned to B–H–B (Figure 2). The spectrum may be resolved to some extent by thermal decoupling,[29] and at 203 K, two resonances are observed at δ +3.7 (3 H) and +3.2 (2 H), implying that the signal for the unique terminal hydrogen atom (BH$_t$(c) in Figure 3) is hidden under that of either BH$_t$(a) or BH$_t$(b), a situation that we also encountered in the ^{1}H NMR spectrum of compound **5**.[13] The observation that pairs of atoms BH$_t$(a) or BH$_t$(b) are not equivalent is evidence that the PdB$_3$ unit is nonplanar in agreement with the known structure of **5**.[13] Assignment of the terminal proton resonances is aided by use of the room-temperature $^{11}B-^{1}H$ NMR chemical shift correlation spectrum shown in Figure 2. Two cross peaks associated with the ^{11}B NMR signal at δ +8.6 arise since BH$_t$(a) and BH$_t$(b) are nonequivalent. The ^{11}B NMR resonance at δ +20.2 for the unique boron atom correlates with a proton resonance for BH$_t$(c) at δ +3.7; this correlation experiment therefore reveals the signal that is hidden in the ^{1}H NMR spectrum of **2** over the temperature range 298–203 K. Only one cross peak, rather than two, is observed for the bridging hydrogen atom, but this phenomenon is not unexpected.[30]

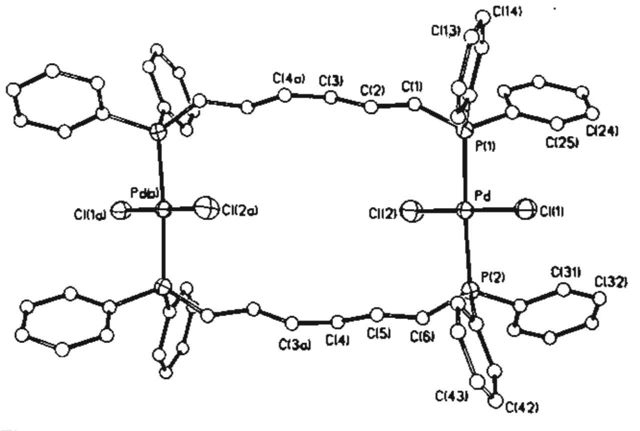
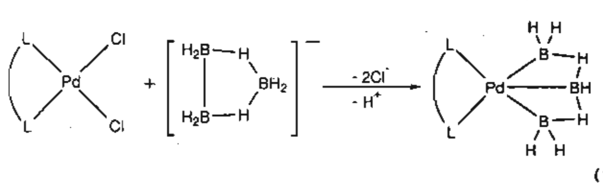


Figure 4. Molecular structure and atom-labeling scheme for *trans*-[(dpph)PdCl$_2$]$_2$ (**6**).

Recently, we described in detail the solution dynamics of compound **5**. The chelating dppf ligand is flexible, and two processes are accessed: at $T \geq 203$ K, mutual twisting of the cyclopentadienyl rings of the dppf moiety occurs, and at $T \geq 293$ K, the barrier to inversion at the phosphorus atoms is crossed. This latter process renders equivalent the terminal hydrogen atoms above and below the PdB$_3$ butterfly.[13] The observation that for each of **2–4** BH$_t$(a) and BH$_t$(b) are *non*equivalent in CD$_2$Cl$_2$ solution and at room temperature illustrates that a fluxional process involving inversion at the phosphorus atoms does not operate in these molecules. This is consistent with the fact that the chelate ring in complexes **2–4** is more constrained than that in **5**. Since the chelate ring in **1** is even smaller than in **2**, we would conclude that inversion at the phosphorus atoms does not occur in **1** either.

Attempted Reaction of [(Ph$_2$P(CH$_2$)$_n$PPh$_2$)PdCl$_2$]$_2$ (*n* = 5, 6) with [B$_3$H$_8$]$^-$. In an attempt to induce a structural change on the borane fragment by increasing the steric requirements of the bidentate phosphino ligand, we extended our investigations from dppb to 1,5-bis(diphenylphosphino)pentane (dppp′) and 1,6-bis(diphenylphosphino)hexane (dpph). However, in each case, the dichlorobis(phosphino)palladium(II) complex failed to react with the [B$_3$H$_8$]$^-$ anion. In general, the reaction of L$_2$PdCl$_2$ with [B$_3$H$_8$]$^-$ may presumably only give rise to L$_2$PdB$_3$H$_7$ when the chloro substituents of the precursor are mutually cis, as illustrated in eq 1. Thus, the observed lack of reactivity of (dpph)PdCl$_2$



(1)

with the octahydrotriborate(1−) anion is consistent with the results of McAuliffe and Hill et al. who have proposed that (dpph)PdCl$_2$ possesses a polymeric structure with a trans arrangement of chlorine atoms.[19] We now report that, in dichloromethane solution at least, the complex is dimeric in nature. The FAB mass spectrum of (bis(diphenylphosphino)hexane)palladium(II) dichloride gives the highest mass peak for (P$^+$ − Cl), where P$^+$ corresponds to the dimeric species, [(dpph)PdCl$_2$]$_2$ (**6**). No mass peaks corresponding to higher oligomers were observed. The complex is insoluble in benzene, and we were unable to determine a molecular weight cryoscopically.[31] However, we have been able to grow X-ray-

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[31] Hill and McAuliffe et al. similarly report an inability to determine the molecular weight of **7**.[19]

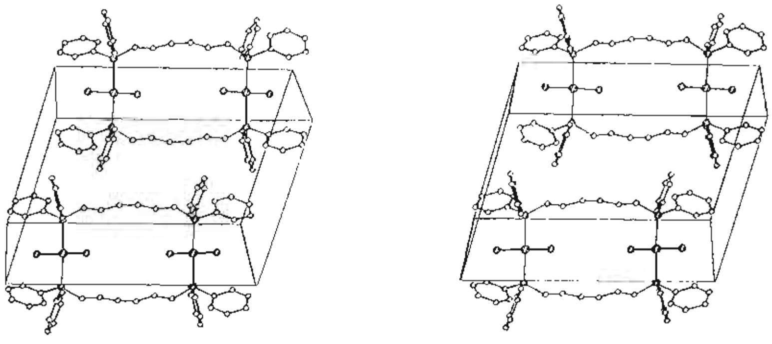

Figure 5. Stereoview of the unit cell packing diagram for *trans*-[(dpph)PdCl$_2$]$_2$ (**6**).

quality crystals of **6** from CH$_2$Cl$_2$ solution layered with hexane and have confirmed a dimeric structure for this complex and a formulation of *trans*-[(dpph)PdCl$_2$]$_2$ (see below).

The nonreaction of (bis(diphenylphosphino)pentane)palladium(II) dichloride with [B$_3$H$_8$]$^-$ implies that the chloro substituents in this precursor are also disposed in a trans manner. Like that in dpph, the backbone of the dppp′ ligand is too short to allow the formation of monomeric *trans*-(dppp′)PdCl$_2$, although with a smaller metal atom, a trans arrangement has been proposed in monomeric *trans*-(dppp′)NiCl$_2$.[32] The structural variation noted for complexes containing the dppp′ ligand with palladium(II) and platinum(II) is worth note. A polymeric structure has been crystallographically characterized for (dppp′)HgI$_2$,[33] and a dimeric structure has been confirmed by X-ray analysis for *trans*-[(^{t}Bu$_2$P(CH$_2$)$_5$P^{t}Bu$_2$)PdCl$_2$]$_2$.[21,34] In contrast, the crystal structure of *cis*-(dppp′)PtCl$_2$ has been reported and illustrates a monomeric complex;[35] this is discussed further below. For (dppp′)PdCl$_2$ itself, Shaw et al. have proposed a dimeric complex and have observed that in CDCl$_3$ solution [(dppp′)PdCl$_2$]$_2$ exhibits two ^{31}P NMR resonances (δ +26.6 and +16.5 in a ratio 1:3, respectively). These have been attributed to the presence of both cis and trans dimers.[21] Our present results, while confirming the dimeric nature of the complex through cryoscopic molecular weight determination and FAB mass spectrometry, illustrate that, in CD$_2$Cl$_2$ solution, [(dppp′)PdCl$_2$]$_2$ exhibits a single ^{31}P NMR resonance at δ +16.5. Since this complex does not react with [B$_3$H$_8$]$^-$, we assign the resonance to *trans*-[(dppp′)PdCl$_2$]$_2$ (**7**). Although square-planar palladium(II) complexes of the type L$_2$PdCl$_2$ (L = PPh$_n$Me$_{3-n}$) may undergo a cis–trans isomerization,[36] the presence of a bidentate bis(phosphino) ligand, L-L, will prevent this rearrangement unless the organic backbone of L-L is sufficiently long. Bulky terminal substituents in L-L also appear to favor the formation of a trans chelate.[19,37,38] The preference for a cis over a trans arrangement of donor atoms in a complex (L-L)PdX$_2$ in which L-L does indeed have a long backbone may be further influenced by the halo substituent X, as illustrated by the structural characterization of *cis*-(Ph$_2$P(CH$_2$)$_2$O(CH$_2$)$_2$O(CH$_2$)$_2$PPh$_2$)PdCl$_2$ and *trans*-(Ph$_2$P(CH$_2$)$_2$O(CH$_2$)$_2$O(CH$_2$)$_2$PPh$_2$)PdI$_2$.[37]

Molecular Structure of trans-[(dpph)PdCl$_2$]$_2$ (6). The molecular structure of **6** is shown in Figure 4, and selected bond lengths and angles are listed in Table IV. A packing diagram for **6** is shown in Figure 5. The complex is dimeric with each palladium atom in a regular square-planar environment with a trans arrangement of chlorine atoms; the deviations from strict planarity are less than 0.03 Å. The Pd–Cl distances in **6** of 2.300 (2) and 2.316 (2) Å are shorter than those found in monomeric *cis*-(dppm)PdCl$_2$ (2.362 (1) and 2.352 (1) Å), *cis*-(dppe)PdCl$_2$ (2.361 (2) and 2.357 (2) Å), and *cis*-(dppp)PdCl$_2$ (2.351 (1) and 2.358 (2) Å).[14] The Pd–P bonds in **6** of 2.344 (2) and 2.342 (2) Å are correspondingly longer than those in *cis*-(dppm)PdCl$_2$ (2.234 (1) and 2.250 (1) Å), *cis*-(dppe)PdCl$_2$ (2.233 (2) and 2.226 (2) Å), and *cis*-(dppp)PdCl$_2$ (2.244 (1) and 2.249 (2) Å).[14] These trends are readily interpreted in terms of the trans effect.

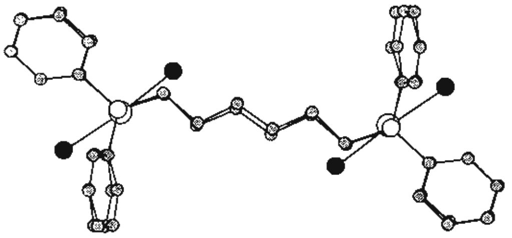

Figure 6. View of **6** through the plane containing the four phosphorus atoms. H atoms were omitted.

Table V. Torsional Angles (deg) for *trans*-[(dpph)PdCl$_2$]$_2$ (**6**) with Labeling Scheme Given in Figure 4

Pd(1)–P(1)–C(1)–C(2)	–65.6	C(3)–C(4a)–C(5a)–C(6a)	171.9
P(1)–C(1)–C(2)–C(3)	160.2	C(4a)–C(5a)–C(6a)–P(2a)	166.0
C(1)–C(2)–C(3)–C(4a)	162.6	C(5a)–C(6a)–P(2a)–Pd(a)	–70.2
C(2)–C(3)–C(4a)–C(5a)	152.7		

The dimetallic framework is supported by bridging dpph ligands, and the two Pd atoms are nonbonded with a separation of 9.089 (1) Å. There is a crystallographic inversion center midway between the two Pd atoms, and the molecule possesses an approximate mirror plane passing through the two Pd and the four Cl atoms (Figures 4 and 6). The alkane chain of each of the two ligands lies in an extended conformation (as previously noted for related complexes),[21,39] and the chains are eclipsed with respect to one another, as the view in Figure 6, taken through the plane containing the four phosphorus atoms, shows. Torsion angles describing the organic chain are listed in Table V, and their significance is discussed further below. Also evident from Figure 6 is the fact that the chlorine atoms are positioned so as to minimize their interactions with neighboring substituents. The chlorine–phenyl repulsions are dominant, and minimization of this interaction fixes, first, the configuration of the groups within the square plane of the palladium atom and, second, the orientation of this square plane with respect to the α-methylene groups. In **6**, the Cl(1)- -Cl(2) and Cl(1a)- -Cl(2a) vectors are necessarily parallel (imposed by the inversion center). This feature is only present if the alkane backbone of the bis(phosphino) ligand contains an *even* number of methylene groups and is thus also observed in *trans*-[(^{t}Bu$_2$P(CH$_2$)$_{10}$P^{t}Bu$_2$)PdCl$_2$]$_2$.[39] With an *odd* number of CH$_2$ groups as in *trans*-[(^{t}Bu$_2$P(CH$_2$)$_n$P^{t}Bu$_2$)PdCl$_2$]$_2$ (n = 5, 7)[21] there is no inversion center and one Cl–Pd–Cl group is forced to twist with respect to the other in order to minimize

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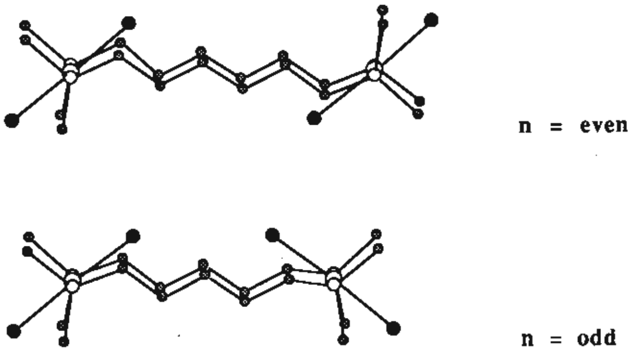
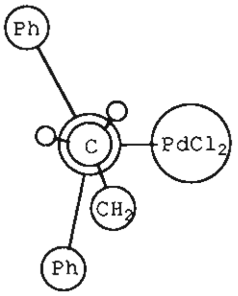


Figure 7. Schematic structures of **6** (determined) and **7** (proposed) that are representative of complexes of the type *trans*-[$(Ph_2P(CH_2)_nPPh_2)$-$PdCl_2]_2$ with even- and odd-membered carbon backbones. Only the ispo carbon of each Ph ring is shown, and H atoms are omitted.

interactions with the phosphorus-attached substituents (Figure 7). A projection along the $C_{\alpha\text{-}CH_2}$–P bond



reveals that the arrangement of substituents in **6** is the same as in *trans*-[$(^tBu_2P(CH_2)_nP^tBu_2)PdCl_2]_2$ (n = 5, 7),[21] indicating that the phenyl and *tert*-butyl groups exhibit similar steric requirements in these dimetallic ring systems.

Trends in torsion angles for the backbones of bis(phosphine) ligands supporting dipalladium(II) complexes deserve a comment. Shaw et al. have previously observed that in *trans*-[$(^tBu_2P(CH_2)_{10}P^tBu_2)PdCl_2]_2$ torsion angles for the two even-membered organic chains deviate significantly from 180°; twisting of the central part of each C_{10} chain is in accord with that in a regular long-chain alkane.[39] On the other hand, the odd-membered polymethylene chains of *trans*-[$(^tBu_2P(CH_2)_5P^tBu_2)PdCl_2]_2$ and *trans*-[$(^tBu_2P(CH_2)_7P^tBu_2)PdCl_2]_2$ are fully extended.[21] The present data illustrate an extended-chain conformation for an even-membered organic chain. We suggest that, whether containing an odd or even number of methylene groups, the organic backbone of the ligand will tend to adopt an extended conformation thus minimizing interactions that involve the L_2PdCl_2 groups. With "long" ($n \geq 10$)[39] polymethylene chains, a number of twisted conformations exhibiting *gauche*- rather than *anti*-C–C–C–C, but which retain minimal interactions involving the L_2PdCl_2 units, are possible. The conformation of each polymethylene chain in *trans*-[$(R_2P(CH_2)_nPR_2)PdCl_2$ (n = 8, 9; R = Ph, ^{t}Bu) remains to be crystallographically established.

We propose that **7** has a molecular structure analogous to that of **6**, but as detailed above, the molecule is expected to exhibit a crystallographic mirror plane rather than a center of inversion. This structural expectation contrasts with the monomeric nature of *cis*-(dppp′)$PtCl_2$.[35] It is difficult to rationalize this difference on steric grounds. In the latter complex, the Pt–P distances of 2.237 (3) and 2.256 (3) Å are very similar to those in *cis*-L_2PdCl_2 (L_2 = dppm, dppe, dppp), and similarly, Pt–Cl bond lengths in *cis*-(dppp′)$PtCl_2$ are close to those in the cis-palladium complexes.[14] Our own observations underline phenomena considered by Shaw[21] and by Hill and McAuliffe,[19] namely that the preference for the formation of a monomeric, dimeric, or higher oligomeric structure may be a marginal one for a complex containing a bis(diphenylphosphino)(n-alkane) ligand and especially for a molecule in which the ligand exhibits a backbone with either five or six carbon atoms.

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Supplementary Material Available: Tables S1–S5, containing complete crystallographic data, bond distances, bond angles, thermal parameters, and H atom coordinates (4 pages); Table S6, listing structure factors (22 pages). Ordering information is given on any current masthead page.

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Generalized Synthesis of *cis*- and *trans*-Dioxorhenium(V) (Bi)pyridyl Complexes

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Efficient new synthetic routes to *trans*-$(O)_2Re(py\text{-}X)_2(py\text{-}Y)_2^+$ and *cis*-$(O)_2Re(bpy\text{-}Y_2)(py\text{-}X)_2^+$ complexes have been devised (py = pyridine; bpy = 2,2′-bipyridine). The new routes make use of labile *cis*-$(O)_2Re(py\text{-}X)_2(I)$ species as preparative intermediates. The most useful new features of the synthetic chemistry are (1) the ability to prepare trans species containing electron-withdrawing substituents, (2) the ability to prepare mixed-ligand *trans*-dioxorhenium species, and (3) generalization of the *cis*-dioxorhenium preparation.

Introduction

trans-Tetrakis(pyridine)dioxorhenium(V) and related complexes have attracted considerable attention in the last 8 years on account of their redox catalytic activity,[1,2] persistent photophysical activity,[2,4] and multielectron electrochemical behavior.[1,5] We have been particularly interested in the last characteristic, especially as it relates to multielectron transfer *kinetics* at electrochemical interfaces. In kinetics studies, we have found it desirable to manipulate (or attempt to manipulate) reactivity by systematically varying the pyridyl ligand substituents. Brewer and Gray have expressed a similar interest in ligand tunability from the point of view of $(O)_2ReL_4^+$ photophysical studies.[6] Unfortunately, apart

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