ORGANOMETALLICS

Synthesis and study of the benzyl- and naphthylpalladium(IV) complexes PdBrMe2(CH2Ar)(L2) (L2 = bpy, phen) and .mu.-hydrocarbyl palladium(IV)-palladium(IV) and palladium(IV)-platinum(IV) complexes and the structure of fac-PdBrMe2(CH2-p-C6H4Br)(phen)

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and acetic acid (10 mL) was stirred at reflux temperature for 20 h. The mixture was cooled, and the black precipitate of tellurium was filtered off. The filtrate was worked up in the same manner as for the diacetoxylation of cyclohexene. Evaporation of the solvent left an oily residue, which was chromatographed on a short silica gel column (3.5 × 5 cm) with petroleum ether/ether (1:1) to give *cis*-1,2-diacetoxycyclohexane (**3**), yield 0.36 g, 1.8 mmol (90%). ^{13}C NMR spectroscopy showed the presence of only the cis isomer of **3**. When the reaction was carried out in the absence of LiOAc, ^{13}C NMR spectroscopy showed that the product was a mixture of cis and trans isomers of **3** in the ratio 77:23.

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Synthesis and Study of the Benzyl- and Naphthylpalladium(IV) Complexes $PdBrMe_2(CH_2Ar)(L_2)$ (L_2 = bpy, phen) and μ-Hydrocarbyl Palladium(IV)–Palladium(IV) and Palladium(IV)–Platinum(IV) Complexes and the Structure of *fac*-$PdBrMe_2(CH_2\text{-}p\text{-}C_6H_4Br)(phen)$

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Benzyl and naphthyl bromides react with dimethylpalladium(II) complexes $PdMe_2(L_2)$ (L_2 = bpy, phen) to form the palladium(IV) complexes $PdBrMe_2(CH_2Ar)(L_2)$ (Ar = p-C_6H_4X (X = H, Me, Br, NO_2), C_6F_5) and $PdBrMe_2(CH_2Ar)(bpy)$ (Ar = 1-$C_{10}H_7$, 2-$C_{10}H_7$). The 2,2′-bipyridyl complexes and $PdBrMe_2(CH_2C_6F_5)(phen)$ reductively eliminate ethane with formation of $PdBr(CH_2Ar)(bpy)$ and $PdBr(CH_2C_6F_5)(phen)$, respectively, on warming to ca. 40 °C in $(CD_3)_2CO$. The other 1,10-phenanthroline complexes undergo less selective reductive elimination, to form $PdBr(CH_2Ar)(phen)$ and $PdBrMe(phen)$ in a ca. 10:1 ratio (Ar = p-C_6H_4Me) and ca 3:1 ratio (Ar = p-C_6H_4X where X = H, Br, NO_2). α,α'-Dibromo-*m*-xylene reacts with $PdMe_2(bpy)$ to form $PdBrMe_2(CH_2\text{-}m\text{-}C_6H_4CH_2Br)(bpy)$, and this complex undergoes further oxidative addition with $MMe_2(bpy)$ (M = Pd, Pt) to form the binuclear complexes $(PdBrMe_2(bpy))_2(\mu\text{-}m\text{-}(CH_2)_2C_6H_4)$ and $(PdBrMe_2(bpy))(PtBrMe_2(bpy))(\mu\text{-}m\text{-}(CH_2)_2C_6H_4)$. The complex $PdBrMe_2(CH_2\text{-}p\text{-}C_6H_4Br)(phen)$ has a *fac*-PdC_3 configuration with the Pd–Br bond (2.636 (1) Å) trans to the benzyl group. The Pd–C(benzyl) bond (2.091 (6) Å) is ca. 0.06 Å longer than the Pd–CH_3 bonds. Crystals of $PdBrMe_2(CH_2\text{-}p\text{-}C_6H_4Br)(phen)$ are monoclinic, space group $P2_1/n$, with a = 8.465 (2) Å, b = 9.051 (2) Å, c = 26.364 (6) Å, β = 96.75 (2)°, and Z = 4.

Introduction

Although organoplatinum(IV) compounds have been known since 1907,[2] and (pentafluorophenyl)palladium(IV) complexes were isolated in 1975,[3] the first detailed studies implicating the formation of (hydrocarbyl)palladium(IV) species were reported by Stille and co-workers in 1976–1981[4-10] and by Baird and co-workers in 1982.[11] Gillie and Stille reported that *trans*-$PdMe_2$(TRANSPHOS) (TRANSPHOS = 2,11-bis((diphenylphosphino)methyl)benzo[*c*]phenanthrene) is stable toward reductive elimination at 100 °C in $(CD_3)_2SO$ but that addition of CD_3I to the complex results in the formation of CD_3CH_3 at ambient temperature.[7] These results suggest the occurrence of an oxidative-addition–reductive-elimination sequence, presumably via formation of the palladium(IV) cation $[PdMe_2(CD_3)(TRANSPHOS)]^+$, since the orientation of the diphosphine ligand prevents iodide coordination to form the octahedral geometry expected for d^6 palladium(IV).[7] Kinetic studies by Moravskiy and Stille are consistent with occurrence of the S_N2 mechanism for oxidative addition of methyl iodide to *cis*-dimethylpalladium(II) phosphine complexes to form palladium(IV) intermediates, e.g. "$PdIMe_3(PMePh_2)_2$", followed by rapid reductive elimination of ethane to form methyliodopalladium(II) products.[9] Related studies by Milstein and Stille also suggest the transient formation of similar benzylpalladium(IV) complexes,[5,6] e.g. formation of "$PdBrMe_2(CH_2Ph)(PPh_3)_2$" followed by reductive elimination to form ethylbenzene and *trans*-$PdBrMe(PPh_3)_2$, with inversion at carbon observed in the analogous reaction sequence by use of optically active α-deuteriobenzyl bromide.[5,10] In 1982 Weinberg, Hunter, and Baird reported that the reaction of iodomethane with $(PdCH_2CH(CO_2Et)_2CH_2NMe_2(\mu\text{-}Cl))_2$ in $CDCl_3$ gave a ^1H NMR spectrum exhibiting a singlet at 2.20 ppm, tentatively

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assigned to a $Pd^{IV}Me$ group, prior to further reaction(s) resulting in complex spectra, including a resonance for MeCl, perhaps formed by reductive elimination from a palladium(IV) intermediate.[11] These studies provided support for consideration of organopalladium(IV) species as intermediates in some catalytic reactions[6-8,12,13] and in some reactions of organopalladium(II) complexes,[13-15] including the reaction of benzyl bromide with $Pd(CH_2CMe_3)_2(bpy)$ to form $PhCH_2CH_2CMe_3$ and $PdBr(CH_2CMe_3)(bpy)$.[14]

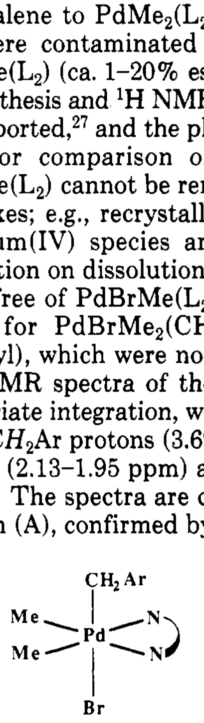
The possibility for development of a wider organometallic chemistry of palladium(IV) has been realized recently by the isolation of two classes of *fac*-trimethylpalladium(IV) complexes,[16-20] exemplified by structural studies of neutral $PdIMe_3$(2,2′-bipyridyl)[16,17] and cationic $[PdMe_3$(tris(pyrazol-1-yl)methane)]I.[17] A range of unstable complexes have now been detected spectroscopically in solution,[13,17-22] including the cations $[PdMe_3(bpy)(L)]^+$ (L = CD_3CN, $(CD_3)_2CO$ as solvent)[17,21] and similar tetramethylethylenediamine cations $[PdMe_3(tmeda)(L)]^+$.[19] Isolated neutral complexes related to Stille's initial studies are restricted to $PdIMe_3(L_2)$ (L_2 = bpy, phen),[16,17] phenacyl and η^1-allyl complexes $PdXMe_2R(L_2)$ (R = aryl-$COCH_2$, X = Br;[22] R = $CH_2CH{=}CHPh$, X = Br;[18] R = $CH_2CH{=}CH_2$, X = Br, I[18]), $PdXMe_3$(tmeda) (X = Br, I),[19] and $PdBrMe_2(CH_2Ph)$(tmeda).[20] Complexes of the type PdClMe(2,9-dimethyl-1,10-phenanthroline)(olefin) may be formally regarded as metallacyclic palladium(IV) complexes, but representation as palladium(II) complexes seems to be more appropriate; e.g., olefin coordination is reversible.[23]

We report here a study of the interaction of benzyl and related organo halides with $PdMe_2(L_2)$, resulting in the isolation of stable neutral palladium(IV) complexes $PdBrMe_2(CH_2Ar)(L_2)$, related to Milstein and Stille's early proposals for $Pd^{IV}Me_2$(benzyl) intermediates with phosphine donor ligands.[5,6] The first crystallographic study of an organopalladium(IV) complex that does not contain the simple *fac*-$PdMe_3$ group is presented, together with studies of the selectivity of reductive elimination of alkanes from the *fac*-$PdMe_2(CH_2Ar)$ complexes and syntheses of the first examples of (μ-hydrocarbyl)dipalladium(IV) and (μ-hydrocarbyl)palladium(IV)platinum(IV) complexes. Preliminary reports of part of this work have appeared;[12,24,25] related studies of the kinetics of formation of $PdBrMe_2(CH_2Ph)(L_2)$ and the reactivity of $PdBrMe_2(CH_2Ph)(L_2)$ toward alkyl halide transfer to dimethylplatinum(II) complexes have been reported separately.[26]

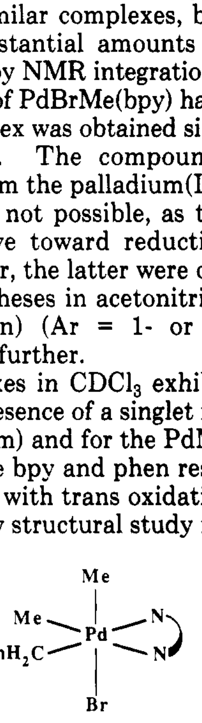
Results and Discussion

Synthesis of Palladium(IV) Complexes from Benzyl and Naphthyl Bromides. Addition of *p*-$XC_6H_4CH_2Br$ (X = H, Br, NO_2) to $PdMe_2(L_2)$ (L_2 = bpy, phen), or 2-(bromomethyl)naphthalene to $PdMe_2$(bpy), at 0 °C in acetone resulted in the formation of white to pale yellow solids in moderate yield (42–71%). ^1H NMR spectra and microanalyses of the complexes are readily interpretable in terms of the formulation "$PdBrMe_2(CH_2Ar)(L_2)$". Addition of *p*-$MeC_6H_4CH_2Br$, $C_6F_5CH_2Br$, 1-(bromomethyl)naphthalene, or 2-(bromomethyl)naphthalene to $PdMe_2(L_2)$ gave similar complexes, but they were contaminated with substantial amounts of $PdBrMe(L_2)$ (ca. 1–20% estimated by NMR integration). The synthesis and ^1H NMR spectra of PdBrMe(bpy) have been reported,[27] and the phen complex was obtained similarly for comparison of spectra. The compounds $PdBrMe(L_2)$ cannot be removed from the palladium(IV) complexes; e.g., recrystallization is not possible, as the palladium(IV) species are sensitive toward reductive elimination on dissolution. However, the latter were obtained free of $PdBrMe(L_2)$ by syntheses in acetonitrile, except for $PdBrMe_2(CH_2Ar)$(phen) (Ar = 1- or 2-naphthyl), which were not studied further.

^1H NMR spectra of the complexes in $CDCl_3$ exhibit appropriate integration, with the presence of a singlet for the $PdCH_2Ar$ protons (3.69–2.92 ppm) and for the PdMe protons (2.13–1.95 ppm) and simple bpy and phen resonances. The spectra are consistent with trans oxidative addition (A), confirmed by an X-ray structural study for $PdBrMe_2(CH_2$-*p*-$C_6H_4Br)$(phen) (Figure 1), in contrast with the cis oxidative addition of benzyl bromide to form the tetramethylethylenediamine complex B.[20] Complex B exhibits two PdMe singlets and two doublets ($^2J_{HH}$ = 6 Hz) for the $PdCH_2Ph$ protons at −20 °C, prior to facile reductive elimination to form ethane and $PdBr(CH_2Ph)$(tmeda).[20]



A ($L_2 = \widehat{N\,N}$ = bpy, phen)



B ($L_2 = \widehat{N\,N}$ = tmeda)

^1H NMR spectra of the palladium(IV) complexes, except for $PdBrMe_2(CH_2Ph)$(bpy), also show an additional low-intensity singlet for both the $PdCH_2Ar$ and PdMe protons, which are ca. 0.05 ppm upfield from the major resonances and retain a 2:3 intensity ratio. The upfield resonances may result from the presence of a minor conformer, e.g. that formed by rotation about the Pd–CH_2 bond, with the proportion of the minor conformer varying with both Ar and L_2 and covering the range ca. 1% (Ar = *p*-MeC_6H_4, L_2 = bpy) to ca. 20% (Ar = *p*-$NO_2C_6H_4$, L_2 = bpy). However, this interpretation would be expected to give additional resonances for the L_2 and Ar protons, although a conformational change along Pd–CH_2 may only affect the resonances of protons closest to the palladium center (CH_2, Me). The spectra are unaltered at lower tempera-

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Table I. Selected Bond Distances (Å) and Angles (deg) for $PdBrMe_2(CH_2$-*p*-$C_6H_4Br)(phen)$[a]

Bond Distances			
Pd-C(a)	2.033 (7)	Pd-N(a)	2.191 (4)
Pd-C(b)	2.033 (7)	Pd-N(b)	2.198 (5)
Pd-C(c)	2.091 (6)	Pd-Br	2.636 (1)
Bond Angles			
C(a)-Pd-C(b)	85.1 (3)	C(c)-Pd-Br	174.8 (2)
C(a)-Pd-C(c)	89.2 (3)	N(a)-Pd-N(b)	76.1 (2)
C(b)-Pd-C(c)	84.6 (3)	N(a)-Pd-Br	89.3 (1)
C(a)-Pd-N(a)	173.2 (3)	N(b)-Pd-Br	89.2 (1)
C(a)-Pd-N(b)	97.2 (3)	Pd-N(a)-C(a5)	113.3 (4)
C(a)-Pd-Br	91.9 (2)	Pd-N(a)-C(al)	127.0 (4)
C(b)-Pd-N(a)	101.6 (2)	Pd-N(b)-C(b5)	113.5 (4)
C(b)-Pd-N(b)	177.6 (2)	Pd-N(b)-C(b1)	128.9 (4)
C(b)-Pd-Br	90.4 (2)	Pd-C(c)-C(cl)	113.3 (4)
C(c)-Pd-N(a)	90.2 (2)	N(a)-C(a5)-C(b5)	119.2 (5)
C(c)-Pd-N(b)	95.8 (2)	N(b)-C(b5)-C(a5)	117.5 (5)

[a] The 1,10-phenanthroline ligand skeleton is substantially planar (χ^2 = 205), with deviations of Pd, C(a), and C(b) from the mean plane of 1,10-phenanthroline being 0.15, 0.30, and 0.26 Å, respectively.

Table II. Positional Parameters for $PdBrMe_2(CH_2$-*p*-$C_6H_4Br)(phen)$

atom	*x*	*y*	*z*
Pd	0.08048 (5)	0.22554 (5)	0.15497 (2)
Br	0.29573 (8)	0.14745 (8)	0.09551 (2)
C(a)	0.2506 (8)	0.2725 (10)	0.2138 (2)
C(b)	0.0843 (10)	0.0189 (8)	0.1853 (3)
N(a)	−0.1041 (5)	0.2033 (5)	0.0898 (2)
C(al)	−0.1826 (8)	0.0817 (8)	0.0745 (3)
C(a2)	−0.3023 (10)	0.0851 (13)	0.0317 (4)
C(a3)	−0.3378 (9)	0.2135 (7)	0.0074 (3)
C(a4)	−0.2577 (8)	0.3405 (11)	0.0227 (3)
C(a5)	−0.1367 (6)	0.3306 (7)	0.0645 (2)
C(a6)	−0.2870 (11)	0.4791 (17)	−0.0014 (4)
N(b)	0.0699 (5)	0.4456 (5)	0.1194 (2)
C(b1)	0.1577 (8)	0.5626 (9)	0.1321 (3)
C(b2)	0.1365 (14)	0.6991 (12)	0.1064 (6)
C(b3)	0.0204 (17)	0.7128 (13)	0.0702 (6)
C(b4)	−0.0766 (11)	0.5927 (10)	0.0536 (3)
C(b5)	−0.0470 (7)	0.4591 (7)	0.0799 (2)
C(b6)	−0.2032 (16)	0.5965 (14)	0.0121 (5)
C(c)	−0.0938 (7)	0.2670 (8)	0.2032 (2)
C(cl)	−0.1802 (7)	0.4038 (7)	0.1913 (2)
C(c2)	−0.3217 (7)	0.4046 (8)	0.1590 (2)
C(c3)	−0.4009 (7)	0.5344 (9)	0.1452 (2)
C(c4)	−0.3370 (7)	0.6653 (8)	0.1640 (2)
Br(c4)	−0.4428 (1)	0.8465 (1)	0.14472 (3)
C(c5)	−0.1986 (8)	0.6680 (7)	0.1978 (2)
C(c6)	−0.1225 (7)	0.5382 (8)	0.2108 (2)

ture, and no coalescence was observed on warming to 40 °C; rapid reductive elimination prevents observation of spectra of palladium(IV) species at higher temperatures (see below). Similar effects occur in the NMR spectra of μ-hydrocarbyl complexes (see below, Figure 2).

Structure of $PdBrMe_2(CH_2$-*p*-$C_6H_4Br)(phen)$. Organopalladium(IV) complexes are generally insufficiently stable for recrystallization, but crystals of $PdBrMe_2(CH_2$-*p*-$C_6H_4Br)(phen)$ obtained directly from its synthesis were suitable for crystallographic studies. Two projections of the structure are shown in Figure 1, and selected structural parameters are given in Table I. The benzyl group is trans to bromine, and the "$PdMe_2N_2$" group is planar, with C(a), C(b), N(a), and N(b) alternating above and below the PdC_2N_2 mean plane by 0.02 Å (C(a,b)) and 0.01 Å (N(a,b)). The planar phen group (maximum deviation from the ligand mean plane is 0.11 Å for C(b2)) forms an angle of 4.5° with the PdC_2N_2 mean plane, which in turn is tilted 25.8° relative to the benzyl ring plane. The palladium atom lies 0.15 Å from the phen mean plane toward the benzyl group. The Pd-CH_2 bond length is ca. 0.06 Å longer than the Pd-CH_3 bond lengths, and the Pd-CH_3 and Pd-N bond lengths are similar to those reported for $PdIMe_3(bpy)$ and $[PdMe_3((pz)_3CH)]I$.[17] The Pd-Br bond length (2.636 (1) Å) is longer than the values of 2.466 (3) and 2.470 (3) Å found for $[(CH_2NH_3)_2][PdBr_6]$, which appears to be the only previous report of Pd^{IV}-Br distances.[28]

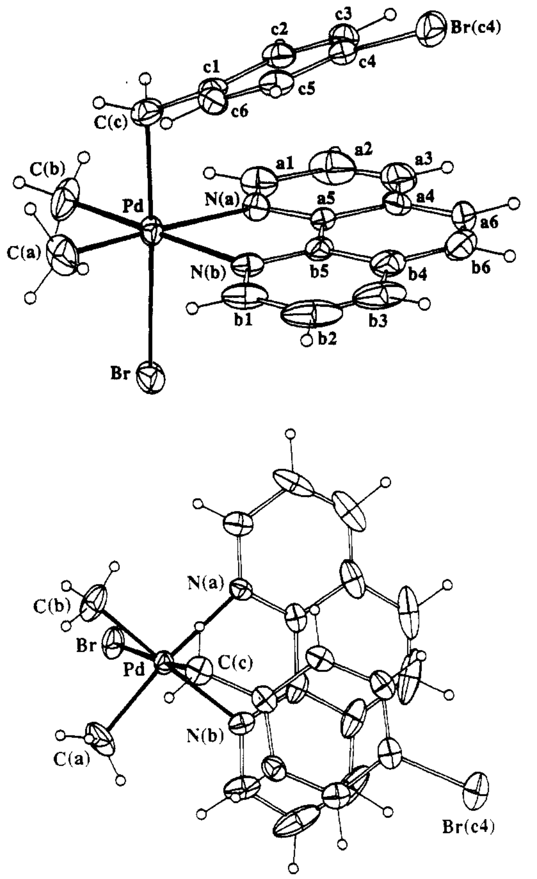

Figure 1. Two projections of $PdBrMe_2(CH_2$-*p*-$C_6H_4Br)(phen)$. The bottom projection is a view normal to the C_6H_4 plane; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms (constrained at estimated idealized positions) have been given an aribtrary radius of 0.1 Å.

Reductive Elimination from the Benzyl and Naphthyl Complexes. ^1H NMR spectra of $PdBrMe_2(CH_2Ar)(bpy)$ in $(CD_3)_2CO$ after slow warming to ca. 40 °C show that reductive elimination occurs with the formation of ethane and $PdBr(CH_2Ar)(bpy)$ (eq 1), together with a trace amount of $PdBrMe(bpy)$. Dissolved ethane gas is readily identified by a singlet at 0.84 ppm, which is eliminated by brief purging with nitrogen. The complexes $PdBr(CH_2Ar)(bpy)$ exhibit a characteristic $PdCH_2Ar$ sin-

$$PdBrMe_2(CH_2Ar)(bpy) \xrightarrow[(CD_3)_2CO]{\Delta} PdBr(CH_2Ar)(bpy) + Me\text{-}Me \quad (1)$$

$$PdBrMe_2(CH_2Ar)(phen) \xrightarrow[(CD_3)_2CO]{\Delta} a[PdBr(CH_2Ar)(phen) + Me\text{-}Me] + b[PdBrMe(phen) + ArCH_2\text{-}Me] \quad (2)$$

$$Ar = C_6F_5\text{: } a = 1, b = 0$$

$$Ar = p\text{-}C_6H_4Me\text{: } a \approx 0.9, b \approx 0.1$$

$$Ar = p\text{-}C_6H_4X \ (X = H, Br, NO_2)\text{: } a \approx 0.75, b \approx 0.25$$

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glet (4.01–3.41 ppm), similar to that reported for $PdBr(CH_2Ph)((pz)_3CH)$ (3.48 ppm)[29] and $PdBr(CH_2Ph)(tmeda)$ (3.03 ppm in $CDCl_3$).[20] Resonances of ethene (5.38 ppm in $(CD_3)_2CO$) and methane (0.17 ppm) are absent from the spectra.

The 1,10-phenanthroline analogues do not give exclusively $PdBr(CH_2Ar)(phen)$ and ethane in acetone, except for Ar = C_6F_5 (eq 2; a = 1, b = 0). Values of a and b are based on ^1H NMR integration for the $Pd^{II}CH_2Ar$ and $Pd^{II}Me$ protons in the products. For all except Ar = C_6F_5, the low solubility of the palladium(II) products prevented a satisfactory estimation of a and b; the complexes did not dissolve on addition of CD_3CN or $(CD_3)_2SO$. Both ethane and $ArCH_2$–Me (triplet at 1.37–1.24 ppm for the Me group) are also detected when $b > 0$, and the ethane resonance is dominant. Random loss of Me–Me and $ArCH_2$–Me would give $a = 0.33$ and $b = 0.66$, and thus for both the bpy and phen complexes there is a preference for ethane evolution. Mechanistic aspects of reductive elimination from palladium(IV) are discussed in detail elsewhere.[26,30] Reductive elimination from $PdIMe_3(bpy)$ occurs mainly via initial dissociation of iodide,[30] and elimination of ethane from solid $PdBrMe_2(CH_2Ph)(L_2)$ is far more exothermic than elimination of ethylbenzene.[26] Elimination from apical and equatorial groups in a five-coordinate intermediate is most likely,[26,30] and thus isomerization within the intermediate is assumed to occur for ethylbenzene elimination from $PdBrMe_2(CH_2Ar)(L_2)$. It has also been recently suggested that η^3 coordination of the benzyl group may occur during reductive elimination of ethane from $PdBrMe_2(CH_2Ph)(tmeda)$.[20]

Although both the bpy and phen complexes favor ethane evolution on reductive elimination in acetone, the different product distribution from the closely related complexes indicates that selectivity in reductive elimination is sensitive to both the neutral ligand and the CH_2Ar group. In this respect, it is of interest that in Milstein and Stille's studies of the reaction of benzyl bromide with *cis*-$PdMe_2(PPh_3)_2$, for which $PdBrMe_2(CH_2Ph)(PPh_3)_2$ was suggested as an intermediate, a preference for elimination of the benzyl group to form ethylbenzene and *trans*-$PdBrMe(PPh_3)_2$ elimination was found.[5] In a recent report it is noted that bibenzyl is also formed in this reaction.[20] Diversi, Fasce, and Santini found that benzyl bromide reacts with $Pd(CH_2CMe_3)_2(bpy)$ to form $PhCH_2CH_2CMe_3$ and $PdBr(CH_2CMe_3)(bpy)$, involving elimination of the benzyl group from a proposed palladium(IV) intermediate.[14]

Synthesis of Palladium(IV) Complexes from α,α'-Dibromo-*m*-xylene. Platinum(IV) nitrogen donor μ-hydrocarbyl complexes have attracted interest as models for proposed catalytic intermediates.[31–33] The ease of oxidative addition of benzyl and naphthyl bromides to $PdMe_2(L_2)$, allowing isolation of palladium(IV) complexes prior to reductive elimination, indicates that the reactivity of closely related α,α'-*m*-$(BrCH_2)_2C_6H_4$ may be sufficient to allow isolation of dipalladium(IV) complexes via successive oxidative-addition reactions. Initial studies indicated that $PdMe_2(bpy)$ is more suitable than the phen complex, as the binuclear complexes isolated have very low solubility and the bpy complexes are slightly more soluble and thus more amenable to studies of reactivity by ^1H NMR spectroscopy.

The mononuclear complex $PdBrMe_2(CH_2\text{-}m\text{-}C_6H_4CH_2Br)(bpy)$ was isolated on addition of $PdMe_2(bpy)$ to a 4-fold excess of the dibromo reagent in order to maintain a large organo halide:palladium ratio during the reaction and, thus, to minimize formation of the Pd(IV)–Pd(IV) complex. An initial precipitate was contaminated with the Pd(IV)–Pd(IV) complex and was rejected. The mononuclear complex exhibits a simple ^1H NMR spectrum, indicating trans oxidative addition, with chemical shift changes typical of those observed on formation of $Pd^{IV}Me_2(CH_2Ar)$ complexes: $\delta(Pd^{IV}Me)$ downfield from $\delta(Pd^{II}Me_2)$ and $\delta(CH_2Pd)$ upfield from $\delta(CH_2Br)$. Reaction of $PdMe_2(bpy)$ with *m*-$(BrCH_2)_2C_6H_4$ in a 2:1 mole ratio gave highly insoluble $(PdBrMe_2(bpy))_2(\mu\text{-}m\text{-}(CH_2)_2C_6H_4)$, and the Pd(IV)–Pd(IV) complex may also be obtained on reaction of $PdMe_2(bpy)$ with $PdBrMe_2(CH_2\text{-}m\text{-}C_6H_4CH_2Br)(bpy)$ (eq 3, M = Pd). The latter procedure

$$PdMe_2(bpy) \xrightarrow{m\text{-}(BrCH_2)_2C_6H_4} PdBrMe_2(CH_2\text{-}m\text{-}C_6H_4CH_2Br)(bpy) \xrightarrow{MMe_2(bpy)} (PdBrMe_2(bpy))(MBrMe_2(bpy))(\mu\text{-}m\text{-}(CH_2)_2C_6H_4) \quad (3)$$

$$M = Pd, Pt$$

is less satisfactory, since the mononuclear complex is not very soluble in acetone. However, the stepwise approach does allow isolation of a Pd(IV)–Pt(IV) complex (eq 3, M = Pt), and the insoluble binuclear complexes have satisfactory microanalyses and similar infrared spectra that differ from that of the mononuclear complex.

The binuclear complexes are insufficiently soluble for ^1H NMR spectroscopy, as found for the related diplatinum(IV) complex $(PtBrMe_2(phen))_2(\mu\text{-}o\text{-}(CH_2)_2C_6H_4)$.[31] However, monitoring of the syntheses conducted in NMR tubes clearly reveals resonances of the binuclear complexes during their crystallization, with resonances of the mononuclear complex decreasing in intensity as those of the binuclear complex increase (Figure 2). Resonances for the binuclear complexes are readily assigned on comparison with those of $PdBrMe_2(CH_2\text{-}m\text{-}C_6H_4CH_2Br)(bpy)$ and are consistent with trans oxidative addition, e.g. a downfield shift in $\delta(PtMe)$ and a decrease in $^2J(PtMe)$ from that for $PtMe_2(bpy)$, as tabulated earlier for oxidation of platinum(II) to platinum(IV).[34,35] The Pd(IV)–Pd(IV) and Pd(IV)–Pt(IV) complexes exhibit similar ^1H NMR spectra and, in view of the marked upfield shifts of the C_6H_4 protons on progressing from *m*-$(BrCH_2)_2C_6H_4$ (7.5–7.3 ppm) to the mononuclear (6.8–6.4 ppm) and to the binuclear complexes (5.9–4.9 ppm), they are shown with the central C_6H_4 ring adjacent to the 2,2′-bipyridyl groups in Figure 2. This proposed orientation of the organic group is similar to that established for $PdBrMe_2(CH_2\text{-}p\text{-}C_6H_4Br)(phen)$ by X-ray crystallography. As observed in spectra of the benzyl and naphthyl complexes, the spectra show additional low-intensity singlets for both the MCH_2Ar and MMe protons, indicated by asterisks in Figure 2.

Conclusions

The presence of the bidentate nitrogen donor ligands 2,2′-bipyridyl and 1,10-phenanthroline allows the isolation of the ambient-temperature-stable organopalladium(IV)

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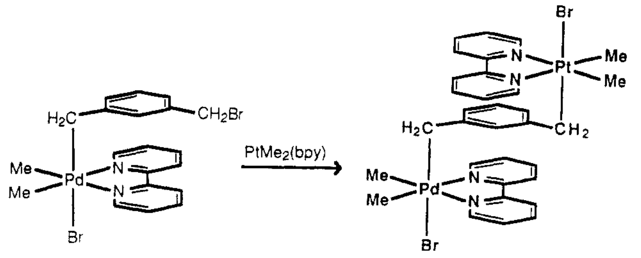

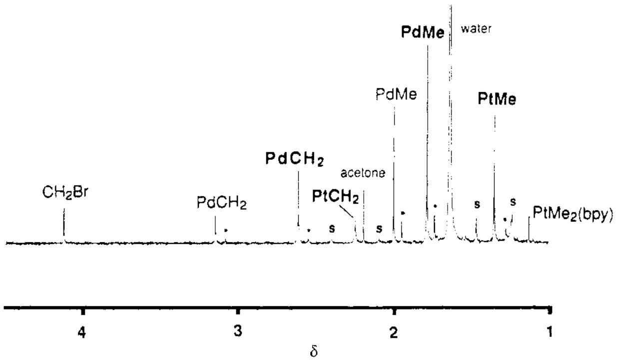

Figure 2. ^1H NMR spectrum in the upfield region obtained on oxidative addition of $PdBrMe_2(CH_2$-*m*-$C_6H_4CH_2Br)(bpy)$ to $PtMe_2(bpy)$ in $CDCl_3$ at 0 °C, 4 min after mixing and prior to completion of reaction, showing the assignments for $(PdBrMe_2(bpy))(PtBrMe_2(bpy))(\mu$-*m*-$(CH_2)_2C_6H_4)$ in boldface type (s indicates $^2J(^1H-^{195}Pt)$ satellites), together with unreacted reagents.

complexes *fac*-$PdBrMe_2(CH_2Ar)(L_2)$. The formation of the complexes by oxidative addition of $ArCH_2X$ to $PdMe_2(L_2)$ and the "clean" reductive elimination to the palladium(II) products $PdBrR(L_2)$ (R = Me, CH_2Ar) provide support for the early suggestion of Milstein and Stille[5] that undetected palladium(IV) complexes are formed in the reaction of benzyl bromides with dimethylpalladium(II) phosphine complexes. The complexes exhibit selectivity in reductive elimination, with the bpy complexes and $PdBrMe_2(CH_2C_6F_5)(phen)$ giving exclusively ethane, and the remaining phen complexes favoring ethane but also giving some $ArCH_2Me$. The presence of $Pd^{IV}BrMe_2(CH_2Ar)$ groups results in higher stability for palladium(IV) complexes compared with that of iodotrialkylpalladium(IV) complexes such as $PdIMe_3(bpy)$[17] and $PdIMe_2Et(bpy)$,[18] allowing synthesis of the first examples of binuclear Pd(IV)–Pd(IV) and Pd(IV)–Pt(IV) complexes by utilizing *m*-xylyl bridging groups.

Experimental Section

The reagents $[PdIMe(SMe_2)]_2$,[36] $PdMe_2(bpy)$, and $PdMe_2(phen)$ were prepared as described,[27] and the solvents were dried and distilled.[37] The organo halides were distilled or recrystallized, except for *p*-$MeC_6H_4CH_2Br$, which was sublimed. Microanalyses were by the Canadian Microanalytical Service, Vancouver, Canada, and ^1H NMR spectra were recorded with a Bruker AM 300 spectrometer, with chemical shifts given in ppm relative to Me_4Si. For the palladium(IV) complexes the minor conformers have $PdCH_2Ar$ and PdMe resonances ca. 0.05 ppm upfield from those of the major conformer; resonances for the major conformer are given below together with the ratio of conformers.

Synthesis of Complexes. PdBrMe(phen). A solution of $AgNO_3$ (0.187 g, 1.10 mmol) in acetonitrile (5 mL) was added to a stirred solution of $[PdIMe(SMe_2)]_2$ (0.30 g, 0.48 mmol) in acetonitrile (50 mL). After the mixture was stirred for 5 min, the precipitate of AgI was removed, and a solution of KBr (0.23 g, 1.93 mmol) in water (5 mL) was added to the filtrate. After filtration to remove some AgBr, a clear yellow solution was obtained. Gentle heating (ca. 40 °C) of the solution for ca. 20 min was followed by addition of 1,10-phenanthroline hydrate (0.192 g, 0.97 mmol). Rotary evaporation to a volume of ca. 10 mL gave a yellow powder, which was collected and recrystallized from acetone/ethanol/hexane to give a pale yellow powder (0.30 g, 81%). ^1H NMR ($CDCl_3$): δ 9.65 (dd, ^3J = 4.9, ^4J = 1.5 Hz, 1, H2,9 trans to PdMe), 9.02 (dd, b, 1, H2,9 trans to PdBr), 8.55 (dd, 1) and 8.45 (dd, 1, H4,7) (both with ^3J = 8.1, ^4J = 1.4 Hz), 7.97 (s, 1) and 7.96 (s, 1, H5,6), 7.88 (m, 2, H3,8), 1.21 (s, 3, PdMe). Anal. Calcd for $C_{13}H_{11}BrN_2Pd$: C, 40.9; H, 2.9; N, 7.3. Found: C, 40.5; H, 2.9; N, 7.2.

$PdBrMe_2(CH_2Ph)(bpy)$. Benzyl bromide (ca. 3 mmol) was added to a stirred, filtered solution of $PdMe_2(bpy)$ (ca. 1.5 mmol) in acetone at 0 °C (ca. 30 mL, warmed to dissolve if necessary). Rotary evaporation of the reaction solution at 0 °C to ca. 10 mL was followed by addition of hexane to assist precipitation of the product (yield 62%). The complex was washed with hexane and vacuum-dried. ^1H NMR ($CDCl_3$): δ 8.54 (m, ^3J = 5.2 Hz, 2, H6), 7.98 (d, ^3J = 8.1 Hz, 2, H3), 7.78 ("td", 2, H4), 7.36 (m, 2, H5), 6.72 (m, 1, H4(Ph)), 6.60 ("t", 2, H3,5 (Ph)), 6.40 (d, ^3J = 7.7 Hz, 3, H2,6 (Ph)), 3.17 (s, 2, $PdCH_2$), 1.98 (s, 6, PdMe). Anal. Calcd for $C_{19}H_{21}BrN_2Pd$: C, 49.2; H, 4.6; N, 6.0. Found: C, 49.4; H, 4.6; N, 6.0.

The following complexes were prepared by a similar procedure.

$PdBrMe_2(CH_2Ph)(phen)$: evaporation and hexane addition required, as above; yield 67%; ^1H NMR ($CDCl_3$) δ 8.91 (dd, ^3J = 4.9, ^4J = 1.4 Hz, 2, H2,9), 8.34 (dd, ^3J = 8.2, ^4J = 1.5 Hz, 2, H4,7), 7.85 (s, 2, H5,6), 7.70 (m, 2, H3,8), 6.50 (t, ^3J = 7.4 Hz, 1, Ph(4)), 6.30 ("t", 2, Ph(3,5)), 6.13 (d, ^3J = 7.8 Hz, 2, Ph(2,6)), 3.23 (s, 2, $PdCH_2$), 2.12 (s, 6, PdMe); conformer ratio ca. 95:5. Anal. Calcd for $C_{21}H_{21}BrN_2Pd$: C, 51.7; H, 4.3; N, 5.7. Found: C, 51.4; H, 4.7; N, 5.7.

$PdBrMe_2(CH_2$-*p*-$C_6H_4Br)(bpy)$: yield 52%; ^1H NMR ($CDCl_3$) δ 8.60 (d, 2, H6), 8.03 (d, 2, H3), 7.94 ("t", 2, H4), 7.46 ("t", 2, H5), 6.74 (d, 2, Ph(3,5)) and 6.30 (d, ^3J = 8.4 Hz, 2, Ph(2,6)), 3.09 (s, 2, $PdCH_2$), 1.98 (s, 6, PdMe); conformer ratio ca 85:15. Anal. Calcd for $C_{19}H_{20}Br_2N_2Pd$: C, 42.1; H, 3.7; N, 5.2. Found: C, 42.6; H, 3.7; N, 5.1.

$PdBrMe_2(CH_2$-*p*-$C_6H_4Br)(phen)$: yield 42%; ^1H NMR ($CDCl_3$) δ 8.93 (dd, ^3J = 4.9, ^4J = 1.4 Hz, 2, H2,9), 8.40 (dd, ^3J = 8.1, ^4J = 1.4 Hz, 2, H4,7), 7.91 (s, 2 H5,6), 7.77 (m, 2, H3,8), 6.36 (d, 2, Ph(3,5)) and 5.95 (d, ^3J = 8.3 Hz 2, Ph(2,6)), 3.13 (s, 2, $PdCH_2$), 2.13 (s, 6, PdMe); conformer ratio ca. 95:5. Anal. Calcd for $C_{21}H_{20}Br_2N_2Pd$: C, 44.5; H, 3.6; N, 4.9. Found: C, 44.6; H, 3.6; N, 5.0.

$PdBrMe_2(CH_2$-*p*-$C_6H_4NO_2)(bpy)$: yield 71%; ^1H NMR ($CDCl_3$) δ 8.59 (d (b), 2, H6), 8.06 (d, 2, H3), 7.96 ("t", (b), 2, H4), 7.50 (m (b), 4, H5 and Ph(3,5)), 6.54 (d (b), 2, Ph(2,6)), 3.16 (s, 2, $PdCH_2$), 2.07 (s, 6, PdMe); conformer ratio ca. 80:20. Anal. Calcd for $C_{19}H_{20}BrN_3O_2Pd$: C, 44.9; H, 4.0; N, 8.3. Found: C, 45.3; H, 4.2; N, 8.0.

$PdBrMe_2(CH_2$-*p*-$C_6H_4NO_2)(phen)$: yield 59%; ^1H NMR ($CDCl_3$) δ 8.94 (d, 2, H2,9), 8.40 (d, 2, H4,7), 7.93 (s, 2, H5,6), 7.79 (m, 2, H3,8), 7.17 (d, 2, Ph(3,5)) and 6.22 (d, ^3J = 8.6 Hz, 2, Ph(2,6)), 3.20 (s, 2, $PdCH_2$), 2.19 (s, 6, PdMe); conformer ratio ca. 95:5. Anal. Calcd for $C_{21}H_{20}BrN_3O_2Pd$: C, 47.4; H, 3.8; N, 7.9. Found: C, 47.4; H, 3.8; N, 7.8.

$PdBrMe_2(2$-$CH_2C_{10}H_7)(bpy)$: yield 75%; ^1H NMR ($CDCl_3$) δ 8.56 (d (b), 2, H6), 7.79 (d (b), 2, H3), 7.67 ("t" (b), 2, H4), 7.44 (m (b)) and 7.26 (m (b)) and 7.05 (d (b)) and 6.60 (m (b)) (H5 and $C_{10}H_7$), 3.33 (s, 2, $PdCH_2$), 2.03 (s, 6, PdMe); conformer ratio ca. 85:15. Anal. Calcd for $C_{23}H_{23}BrN_2Pd$: C, 53.8; H, 4.5; N, 5.5. Found: C, 53.9; H, 4.5; N, 5.5.

$PdBrMe_2(CH_2$-*p*-$C_6H_4Me)(bpy)$. *p*-$MeC_6H_4CH_2Br$ (ca. 3 mmol) was added to a stirred, filtered solution of $PdMe_2(bpy)$ (ca. 1.5 mmol) in acetonitrile (ca. 25 mL) at 0 °C. Rotary evaporation to ca. 10 mL was followed by addition of diethyl ether/hexane (2/3) to assist precipitation of the product (yield 67%). ^1H NMR ($CDCl_3$): δ 8.55 (d (b), 2, H6), 8.02 (d, 2, H3), 7.86 ("t", 2, H4), 7.40 ("t", 2, H5), 6.43 (d, 2, Ph) and 6.32 (d, 2, Ph) (both with ^3J = 7.8 Hz), 3.19 (s, 2, $PdCH_2$), 1.95 ("s", 6, Me and PdMe).

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Conformer ratio: ca. 99:1. Anal. Calcd for $C_{20}H_{23}BrN_2Pd$: C, 50.3; H, 4.9; N, 5.9. Found: C, 50.2; H, 4.9; N, 5.8.

The following complexes were prepared by a similar procedure.

PdBrMe$_2$(CH$_2$-*p*-C$_6$H$_4$Me)(phen): yield 59%; ^{1}H NMR (CDCl$_3$) δ 8.92 (d (b), 2, H2,9), 8.36 (d (b), 2, H4,7), 7.86 (s, 2, H5,6), 7.72 (dd, 2, H3,8), 6.08 (d, 2, Ph) and 5.99 (d, 2, Ph) (both with ^3J = 7.7 Hz), 3.23 (s, 2, PdCH$_2$), 2.20 (s, 3, Me), 2.09 (s, 3, PdMe); conformer ratio ca. 95:5. Anal. Calcd for $C_{22}H_{23}BrN_2Pd$: C, 52.7; H, 4.6; N, 5.6. Found: C, 51.7; H, 4.4; N, 5.9.

PdBrMe$_2$(CH$_2$C$_6$F$_5$)(bpy): yield 74%; ^{1}H NMR (CDCl$_3$) δ 8.62 (d (b), 2, H6), 8.0–8.1 (m, 4, H3,4), 7.60 (m, 2, H5), 2.92 (t (b), poorly resolved $^4J_{HF}$, 2, PdCH$_2$), 2.13 (s, 6, PdMe); conformer ratio ca. 95:5. Anal. Calcd for $C_{19}H_{16}BrF_5N_2Pd$: C, 41.2; H, 2.9; N, 5.1. Found: C, 40.7; H, 3.0; N, 5.2.

PdBrMe$_2$(CH$_2$C$_6$F$_5$)(phen): yield 53%; ^{1}H NMR (CDCl$_3$) δ 9.17 (d (b), 2, H2,9), 8.45 (dd, 2, H4,7), 7.92 (s, 2, H5,6), 7.88 (m, 2, H3,8), 2.93 (tb, poorly resolved $^4J_{HF}$, 2, PdCH$_2$), 2.27 (s, 6, PdMe); conformer ratio ca. 90:10. Anal. Calcd for $C_{21}H_{16}BrF_5N_2Pd$: C, 43.7; H, 2.8; N, 4.9. Found: C, 43.7; H, 3.0; N, 5.3.

PdBrMe$_2$(1-CH$_2$C$_{10}$H$_7$)(bpy): yield 73%; ^{1}H NMR (CDCl$_3$) δ 8.49 (d (b), 2, H6), 7.68 (ddd, 2, H4), 7.61 (d (b), 2, H3), 7.39 ("td", 2, H5), 7.21 (m (b), 4), 7.01 (m, 1), 6.84 ("t", 1), 6.68 (d, 1) (C$_{10}$H$_7$), 3.69 (s (b), 2, PdCH$_2$), 2.10 (s, 6, PdMe); conformer ratio ca. 95:5. Anal. Calcd for $C_{23}H_{23}BrN_2Pd$: C, 53.8; H, 4.5; N, 5.5. Found: C, 53.7; H, 4.5; N, 5.6.

PdBrMe$_2$(CH$_2$-*m*-C$_6$H$_4$CH$_2$Br)(bpy). A solution of PdMe$_2$(bpy) (0.20 g, 0.68 mmol) in acetone (20 mL) was added to a solution of *m*-(BrCH$_2$)$_2$C$_6$H$_4$ (0.70 g, 2.65 mmol) in acetone (20 mL) at 0 °C. A small amount of a white solid (0.045 g) was removed by filtration and identified by ^{1}H NMR spectroscpy as a mixture of the required complex and (PdBrMe$_2$(bpy))$_2$(μ-*m*-(CH$_2$)$_2$C$_6$H$_4$). Addition of hexane to the filtrate gave the product as a yellow solid (0.12 g), which was removed by filtration, and partial evaporation of the filtrate at 0 °C gave a further crop (0.06 g, total yield 47%). ^{1}H NMR (CDCl$_3$): δ 8.63 (dd, ^3J = 5.2 Hz), 2, H6), 8.06 (d, ^3J = 8.1 Hz, 2, H3), 7.92 ("td", 2, H4), 7.50 (m, 2, H5), 6.77 (d, ^3J = 7.5 Hz, 1, Ph), 6.62 ("t", 1, Ph(5)), 6.41 ("d") overlapping with 6.42 ("s") (2, Ph and Ph(2)), 4.13 (s, 2, CH$_2$Br), 3.16 (s, 2, PdCH$_2$), 2.03 (s, 6, PdMe). The spectrum is free of impurities, but the solid complex is insufficiently stable for postage for microanalysis, giving C, H, N values intermediate between the expected value and that for loss of ethane by reductive elimination.

(PdBrMe$_2$(bpy))$_2$(μ-*m*-(CH$_2$)$_2$C$_6$H$_4$). A solution of *m*-(BrCH$_2$)$_2$C$_6$H$_4$ (0.057 g, 0.22 mmol) in acetone (20 mL) was added to a solution of PdMe$_2$(bpy) (0.126 g, 0.43 mmol) in acetone (3 mL) at 0 °C with stirring. A pale yellow solid formed and was collected, washed with cold hexane, and vacuum-dried (64%). The complex may also be prepared as described below for the Pd(IV)–Pt(IV) complex, with addition of PdMe$_2$(bpy) to PdBr(CH$_2$-*m*-C$_6$H$_4$CH$_2$Br)Me$_2$(bpy), but this procedure is less satisfactory since chloroform is required to dissolve the latter reagent and PdMe$_2$(bpy) is sensitive to chloroform. ^{1}H NMR (CDCl$_3$; obtained during precipitation): δ 8.42 (d, ^3J = 4.5 Hz, 2, H6), 7.91 (m, H3 overlapping with H4 of the mononuclear complex), 7.88 ("t", 2, H4), 7.32 ("t", 2, H5), 5.90 (b, 3, Ph(4–6)), 5.10 (b, 1, Ph(2)), 2.60 (2, PdCH$_2$), 1.79 (s, 12, PdMe). Anal. Calcd for $C_{32}H_{36}Br_2N_4Pd_2$: C, 45.3; H, 4.3; N, 6.6. Found: C, 45.1; H, 4.2; N, 6.5.

(PdBrMe$_2$(bpy))(PtBrMe$_2$(bpy))(μ-*m*-(CH$_2$)$_2$C$_6$H$_4$). Chloroform (5 mL) was added to a suspension of PdBr(CH$_2$-*m*-C$_6$H$_4$CH$_2$Br)Me$_2$(bpy) (0.029 g, 0.10 mmol) in acetone (5 mL) at 0 °C, and a solution of PtMe$_2$(bpy) (0.02 g, 0.05 mmol) in acetone (5 mL) was added with stirring, to give a pale yellow solid that was collected and washed with petroleum ether and vacuum-dried (32%). ^{1}H NMR (CDCl$_3$; obtained during precipitation): δ 8.53 (d (b), with poorly resolved $^3J_{HPt}$, 2, H6 (Pt)), 8.41 (d (b), 2, H6 (Pd)), 7.83 (m (b), H3,4), 7.32 (m (b), H5), 5.90 (b, 2, Ph), 5.65 (b, 1, Ph), 4.90 (b, 1, Ph(2)), 2.62 (s, 2, PdCH$_2$), 2.25 ("t", J_{HPt} = 93 Hz, 2, PtCH$_2$), 1.79 (s, 6, PdMe), 1.36 ("t", J_{HPt} = 70 Hz, 6, PtMe). Anal. Calcd for $C_{32}H_{36}Br_2N_4PdPt$: C, 41.0; H, 3.9; N, 6.0. Found: C, 40.8; H, 4.1; N, 6.3.

X-ray Structure Determination. A unique data set was measured to $2\theta_{max} = 50°$ with a Syntex P2$_1$ four-circle diffractometer fitted with a monochromatic Mo Kα radiation (λ = 0.710 6$_9$ Å) source and operating in the conventional $2\theta-\theta$ scan mode. A total of 3479 independent reflections were obtained, 2399 with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after analytical absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were constrained at estimated values. Residuals R and R_w on $|F|$ at convergence were 0.034 and 0.036; statistical weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0002\sigma^4(I_{diff})$ were employed. Neutral-atom complex scattering factors were used;[38] computation used the XTAL program system implemented by S. R. Hall on a Perkin-Elmer 3241 computer.[39] Crystal data: PdBrMe$_2$(CH$_2$-*p*-C$_6$H$_4$Br)(phen), $C_{21}H_{20}Br_2N_2Pd$, M_r = 566.6, monoclinic, space group $P2_1/n$ (C_{2h}^5), a = 8.465 (2) Å, b = 9.051 (2) Å, c = 26.364 (6) Å, β = 96.75 (2)°, Z = 4.

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Supplementary Material Available: Listings of thermal parameters, hydrogen atom parameters, ligand and benzyl geometries, and mean plane data (5 pages); a listing of observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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[38] Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

[39] Hall, S. R., Stewart, J. M., Eds. *XTAL User's Manual-Version 2.4*; Universities of Western Australia and Maryland, 1988.