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Synthesis, Reactivity, and Structural Studies in Trimethylpalladium(IV) Chemistry, Including $PdIMe_3(bpy)$ and $[MMe_3((pz)_3CH)]^+$ (M = Pd, Pt)

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The first synthetic, spectroscopic, and structural studies in (hydrocarbyl)palladium(IV) chemistry are reported. The *fac*-$Pd^{IV}Me_3$ complexes $PdIMe_3(L_2)$ and $[PdMe_3(L_3)]I$ are formed on oxidative addition of iodomethane to $PdMe_2(L_2)$ (L_2 = 2,2′-bipyridyl, 1,10-phenanthroline, other planar bidentates with pyridin-2-yl (py) and 1-methylimidazol-2-yl (mim) groups) and $PdMe_2(L_3)$ (L_3 = tripodal nitrogen donors containing pyrazol-1-yl (pz), py, and mim groups). The complexes $PdIMe_3(L_2)$ (L_2 = bpy, phen) are stable on storage at ca. −20 °C, but in solution reductive elimination of ethane occurs with formation of $PdIMe(L_2)$. Palladium(IV) complexes with the other bidentate ligands could be detected in situ by ^1H NMR spectroscopy but could not be isolated. ^1H NMR studies in CD_3CN show that the bidentate ligand complexes form an equilibrium between $PdIMe_3(L_2)$ and $[PdMe_3(L_2)(CD_3CN)]^+$, and oxidative addition of CD_3I or MeI to $PdMe_2(bpy)$ in $(CD_3)_2CO$ at low temperature indicates that a cation is formed prior to formation of $PdIMe_2R(bpy)$. The complex $PdIMe_3(bpy)$ has octahedral geometry, with Pd–I = 2.834 (1) Å, Pd–N = 2.188 (5), 2.173 (5) Å, and Pd–C = 2.034 (7)–2.046 (7) Å. The isolated complexes of the tripod ligands, $[PdMe_3(L_3)]I$, are stable at ambient temperature. In solution, the complexes containing pyridine and 1-methylimidazole donor rings as part of the tripod ligand, e.g. $[PdMe_3((py)(mim)_2CH)]I$, are more stable than $[PdMe_3((pz)_3CH)]I$, although the tetrafluoroborate derivative $[PdMe_3((pz)_3CH)]BF_4$ appears to be indefinitely stable. The isostructural complexes $[MMe_3((pz)_3CH)]I$ have essentially identical M–C bond distances, but the Pd–N distances are ca. 0.04 Å longer than Pt–N. Crystals of $PdIMe_3(bpy)$ are monoclinic, space group $P2_1/c$, with a = 7.917 (4) Å, b = 9.528 (4) Å, c = 20.207 (8) Å, β = 104.28 (4)°, and Z = 4. The complexes $[MMe_3((pz)_3CH)]I$ (M = Pd, Pt) are monoclinic, space group $C2/c$, with Z = 8. Palladium [platinum] complex cells have a = 21.254 (8) [21.253 (8)] Å, b = 9.213 (5) [9.099 (4)] Å, c = 19.144 (8) [19.284 (8)] Å, and β = 105.65 (3)° [105.63 (3)°].

Introduction

Organoplatinum(IV) chemistry has developed steadily[2] following the initial report of $[PtIMe_3]_4$ and related complexes in 1907,[3] but the synthesis of organopalladium(IV) complexes is limited to several mono- and bis(pentafluorophenyl) derivatives,[4-6] e.g. the 2,2′-bipyridyl complexes $PdCl_3(C_6F_5)(bpy)$ and $PdCl_2(C_6F_5)_2(bpy)$, formed by oxidative addition of chlorine to $PdCl(C_6F_5)(bpy)$ and $Pd(C_6F_5)_2(bpy)$, respectively.[5,6] Organopalladium(IV) species have often been suggested, or considered as possible intermediates in organic synthesis and catalytic reactions,[7-9] and proposed to explain aspects of the reactivity of organopalladium(II) complexes,[8,10,12-14] but the intermediates have not been detected, although ^1H NMR data indicate that an organopalladium(IV) intermediate may be formed in the reaction of MeI with $[Me_2\overline{NCH_2CH(C(CO_2Et)_2)CH_2Pd}(\mu\text{-}Cl)]_2$.[13] The "inorganic chemistry" of palladium(IV) is also limited in comparison with that of platinum(IV).[15]

In studying the reactivity of $Pd^{II}Me_2$ derivatives of nitrogen donor ligands toward iodomethane, initially as a route to $Pd^{II}Me$ complexes and as model reactions for the role of palladium catalysts in coupling reactions,[16] we have obtained several stable trimethylpalladium(IV) complexes. We report here the first synthetic, spectroscopic, and X-ray structural studies in alkylpalladium(IV) chemistry, including isostructural Pd^{IV} and Pt^{IV} complexes. Initial studies with 2,2′-bipyridyl and tris(pyrazol-1-yl)methane

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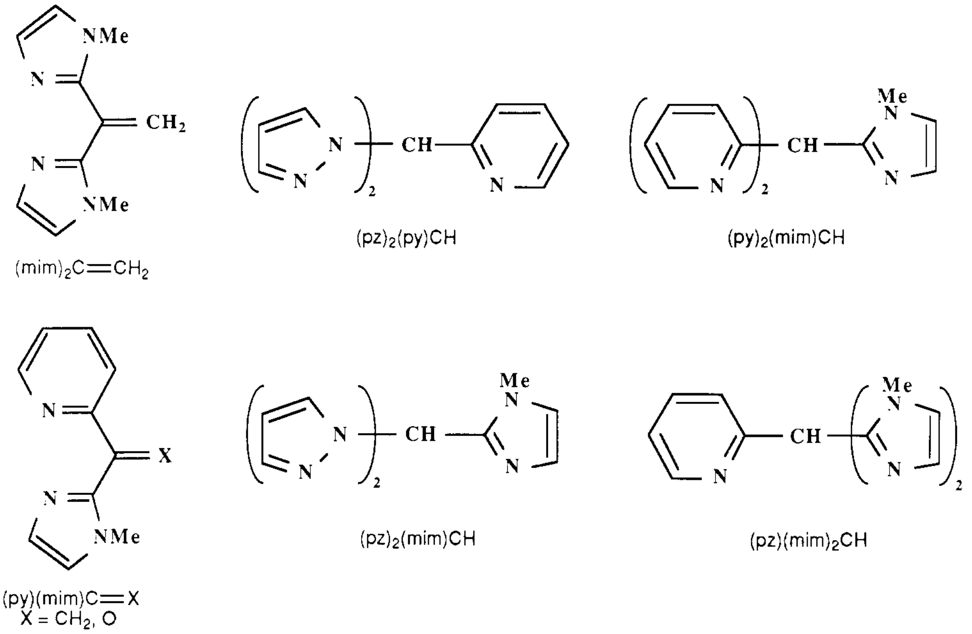
Chart I



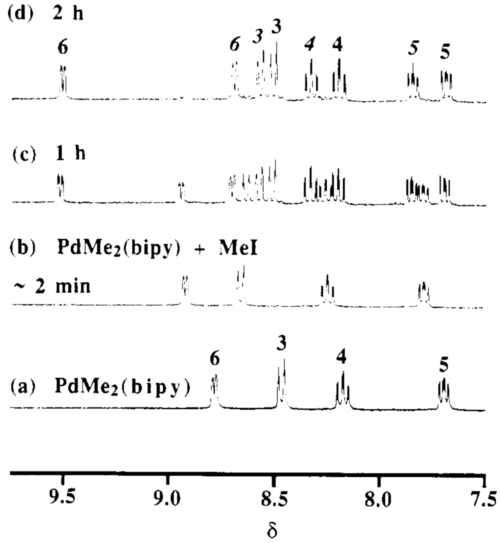


Figure 1. ^{1}H NMR spectra at ambient temperature in the 2,2′-bipyridyl region: (a) spectrum for PdMe$_2$(bpy); (b) spectrum immediately after addition of MeI to form PdIMe$_3$(bpy); (c) spectrum 1 h after addition; (d) spectrum 2 h after addition showing the presence of PdIMe(bpy)(singlets for the PdMe group and ethane at 0.83 and 0.84 ppm, respectively). Assignments for PdMe$_2$(bpy) and PdIMe(bpy) are from ref 22, and for PdIMe(bpy) the assignments in *italics* are for the ring trans to iodine.

((pz)$_3$CH) as ligands have been extended to include 1,10-phenanthroline (phen), tris(pyridin-2-yl)methane ((py)$_3$CH), and the related N-donor ligands illustrated in Chart I, containing pz, py, and 1-methylimidazol-1-yl (mim) donor groups. Preliminary reports of part of this work have been given,[17,18] and reports of related but unstable Pd^{IV} complexes detected at low temperature by NMR spectroscopy have since appeared.[9,19,20]

Table I. δ(PdMe) for ^{1}H NMR Spectra of Trimethylpalladium(IV) Complexes

complex	δ(PdMe)[a]	
Complexes Detected in (CD$_3$)$_2$CO[b]		
PdIMe$_3$((mim)$_2$C=CH$_2$)[c]	1.60 (6 H, mim)	1.29 (3 H, I)
PdIMe$_3$((py)(mim)C=CH$_2$)	1.83 (3 H, py) 1.55 (3 H, mim)	1.35 (3 H, I)
PdIMe$_3$((py)(mim)C=O)	1.82 (3 H, py) 1.57 (3 H, mim)	1.46 (3 H, I)
[PdMe$_3$(bpy)((CD$_3$)$_2$CO)]$^{+}$[d]	1.61 (6 H, bpy)	0.82 (3 H, (CD$_3$)$_2$CO)
Isolated Complexes in (CD$_3$)$_2$CO[e]		
PdIMe$_3$(bpy)	1.85 (6 H, bpy)	1.14 (3 H, I)
PdIMe$_3$(phen)	1.96 (6 H, phen)	1.20 (3 H, I)
Isolated Complexes in CDCl$_3$[e]		
[PdMe$_3$((pz)$_3$CH)]I	1.58 (9 H, pz)	
[PdMe$_3$((pz)$_3$CH)]BF$_4$	1.58 (9 H, pz)	
[PdMe$_3$((pz)$_2$(py)CH)]I	1.53 (6 H, pz)	1.59 (3 H, py)
[PdMe$_3$((pz)$_2$(mim)CH)]I	1.56 (6 H, pz)	1.38 (3 H, mim)
[PdMe$_3$((py)$_3$CH)]I	1.50 (9 H, py)	
[PdMe$_3$((py)$_2$(mim)CH)]I	1.53 (6 H, py)	1.28 (3 H, mim)
[PdMe$_3$((py)(mim)$_2$CH)]I	1.55 (3 H, py)	1.33 (6 H, mim)

[a] Relative intensity and trans group in parentheses. [b] At −10 °C. [c] PdMe$_2$((mim)$_2$C=O) is too insoluble for NMR studies.[22] [d] At −50 °C; PdIMe$_3$(bpy) has δ(PdMe) 1.77 (6 H) and 1.11 (3 H) ppm at this temperature. [e] At 20 °C.

Results and Discussion

Complexes of Bidentate Ligands. Addition of excess iodomethane to PdMe$_2$(L$_2$) (L$_2$ = bpy, phen, (py)(mim)-C=O) in (CD$_3$)$_2$CO at ambient temperature immediately gives ^{1}H NMR spectra attributable to PdIMe$_3$(L$_2$), followed by slow reductive elimination to form PdIMe(L$_2$) and ethane (eq 1, Figure 1). Similar behavior was observed for complexes of (mim)$_2$C=CH$_2$ and (py)(mim)-C=CH$_2$, except that the lower stability of the Pd^{IV} complexes required studies at −10 °C to obtain good spectra for the intermediates.[21] Trimethylpalladium(IV) complexes of bpy, phen, and (mim)$_2$C=CH$_2$ exhibit two PdMe resonances in a 2:1 ratio, and complexes of (py)(mim)C=

$$\mathrm{PdMe_2(L_2) + MeI \rightarrow PdIMe_3(L_2) \rightarrow PdIMe(L_2) + MeMe} \qquad (1)$$

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Table II. δ(PdMe) for $PdIMe_3(L_2)$ and $[PdMe_3(L_2)(CD_3CN)]^+$ in CD_3CN at -35 °C

ligand	neutral complex: cation ratio	δ(PdMe)[a] neutral complex	δ(PdMe)[a] cation
bpy[b]	ca. 3:1	1.79 (bpy) 1.20 (I)	1.61 (bpy) 1.06 (CD_3CN)
phen	ca. 5:2	1.93 (phen) 1.26 (I)	1.73 (phen) 1.13 (CD_3CN)
$(mim)_2C{=}CH_2$	ca. 3:4	1.60 (mim) 1.37 (I)	1.35 (mim) 1.29 (CD_3CN)
$(py)(mim)C{=}CH_2$	ca. 4:3	1.80 (py) 1.53 (mim) 1.39 (I)	1.56 (py) 1.28 (mim) ?
$(py)(mim)C{=}O$	ca. 5:1	1.82 (py) 1.59 (mim) 1.56 (I)	1.37 1.36 ?

[a] Trans group in parentheses. Ligand resonances for each species are also present, with relative intensities in agreement with the ratio neutral complex:cation. [b] From ref 23.

CH_2 and $(py)(mim)C{=}O$ exhibit three resonances in a 1:1:1 ratio, consistent with "*fac*-$PdMe_3$" geometry (Table I). Ligand resonances are readily assigned, with the donor ring protons exhibiting expected multiplets and with assignments assisted by the use of shift correlation spectroscopy (COSY) and comparison with the reported spectra of $PdMe_2(L_2)$ and $PdIMe(L_2)$.[22] The $Pd^{IV}Me_3$ resonances occur ca. 1.6–1.9 ppm (Me trans to L_2) and ca. 1.3–1.5 ppm (Me trans to I) downfield from the value(s) for the corresponding $PdMe_2(L_2)$ complexes.

The complexes $PdIMe_3(L_2)$ (L_2 = bpy, phen) were subsequently isolated, by addition either of MeI to $PdMe_2(L_2)$ or of the ligand to $[PdMe_2(pyridazine)]_n$ followed by addition of MeI, but complexes of the other bidentate ligands could not be isolated. The two isolated complexes exhibit spectra identical with those of the appropriate intermediates discussed above, and although they reductively eliminate ethane at ambient temperature in both the solid state and solution, the solid complexes may be satisfactorily stored at ca. -20 °C.

Kinetic studies have recently established that oxidative-addition reactions to form the bpy and phen complexes $MIMe_3(L_2)$ (M = Pd, Pt) proceed by an S_N2 mechanism,[23,24] but spectroscopic detection of cationic intermediates in organometallic S_N2 reactions from 16-electron substrates appears to be limited to dimethylplatinum(II) systems.[25,26] In particular, reaction of CD_3I with $PtMe_2(bpy)$ in CD_3CN at -40 °C gives a ^1H NMR spectrum showing both [*trans*-$PtMe_2(CD_3)(bpy)(CD_3CN)]^+$ and *trans*-$PtIMe_2(CD_3)(bpy)$, with PtMe resonances of the cation upfield from those of the neutral complex. On further reaction the cation decays irreversibly to the neutral complex, and scrambling of the Me and CD_3 groups occurs with the scrambling occurring faster for the cation.[26]

Addition of MeI to $PdMe_2(L_2)$ in CD_3CN at -40 °C gives two species, $[PdMe_3(L_2)(CD_3CN)]^+$ and $PdIMe_3(L_2)$, for all of the bidentate ligands. The PdMe resonances for the cations occur upfield from resonances of the neutral analogues, as found for $[PtMe_3(bpy)(CD_3CN)]^+$ and $PtIMe_3(bpy)$,[26] and the readily assigned H6 resonance for the pyridin-2-yl groups (L_2 = bpy, $(py)(mim)C{=}CH_2$, $(py)(mim)C{=}O$) occurs ca. 0.1–0.5 ppm upfield from that for the neutral analogues. However, unlike the case for $[PtMe_3(bpy)(CD_3CN)]^+$, the Pd^{IV} cations do not convert irreversibly to the neutral complex on warming. When the compounds are warmed, the PdMe resonances for the cations broaden and coalesce, followed by broadening of the PdMe resonances for the neutral complexes and coalescence of ligand resonances (Figure 2). The spectra are reversed on cooling and are consistent with the presence of an equilibrium (eq 2), with exchange of methyl group

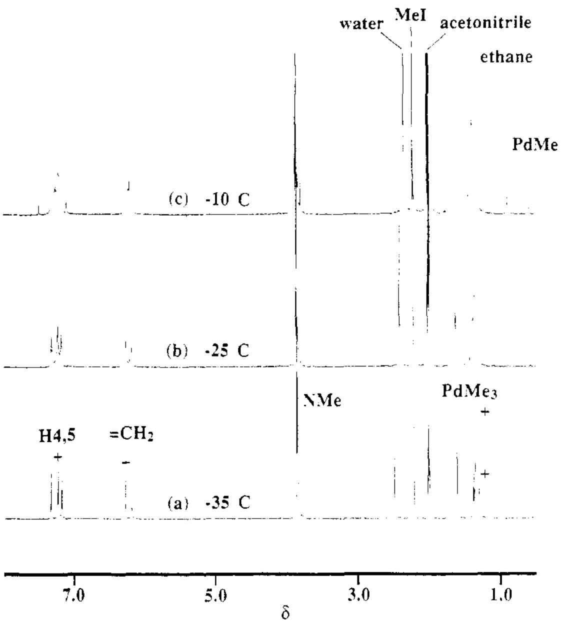

Figure 2. ^1H NMR spectra obtained on addition of MeI to $PdMe_2((mim)_2C{=}CH_2)$ in CD_3CN at low temperature, followed by warming to -10 °C, showing, at low temperature, two 1-Me, two $=CH_2$, and two mim environments, with $Pd^{IV}Me_3$ resonances in a 2:1 ratio (trans to mim and iodine) for both $PdIMe_3((mim)_2C{=}CH_2)$ and $[PdMe_3((mim)_2C{=}CH_2)(CD_3CN)]^+$. The cation is indicated with a plus sign, and on warming resonances of $PdIMe((mim)_2C{=}CH_2)$ and ethane are present.

$$[PdMe_3(L_2)(CD_3CN)]^+I^- \rightleftharpoons PdIMe_3(L_2) + CD_3CN \quad (2)$$

environments within each species most likely occurring via a labile five-coordinate cation. For bpy and phen as ligands, identical variable-temperature spectra are obtained on addition of the isolated $Pd^{IV}Me_3$ complexes to CD_3CN.

Spectra obtained in similar experiments involving addition of CD_3I to $PdMe_2(L_2)$ in $(CD_3)_2CO$ at -50 °C indicate formation of a cation for the substrate $PdMe_2(bpy)$ only, with PdMe and H6(py) resonances upfield from those for the neutral complex, although initial experiments with the bpy complex did not reveal cations.[23] The Me and CD_3 groups are scrambled in both the cation and neutral complex at -50 °C, with the ratio of complexes cation:neutral ca. 1:(4–5) for spectra measured soom after mixing of reagents. Complete and irreversible conversion to the neutral complex occurs on warming to ca. 0 °C, and thus, as for the platinum analogue,[26] formation of the neutral complex via a cation is assumed (eq 3).

$$PdMe_2(bpy) + CD_3I \xrightarrow{(CD_3)_2CO} [PdMe_2(CD_3)(bpy)((CD_3)_2CO)]^+I^- \rightarrow PdIMe_2(CD_3)(bpy) + (CD_3)_2CO \quad (3)$$

Kinetic studies of the reaction of iodomethane with $Pd^{II}Me_2$ phosphine complexes, giving $Pd^{II}IMe$ complexes and ethane, are consistent with the occurrence of oxidative addition, with rapid elimination of ethane precluding spectroscopic detection of $Pd^{IV}Me_3$ intermediates.[8d] Iso-

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lation of stable bpy and phen complexes appears to result from several interrelated factors, including the enhanced stability expected for complexes of bidentate ligands and of higher oxidation states in the presence of nitrogen donor ligands.[27,28] Oxidative addition of MeI to the nitrogen donor complexes occurs readily at −50 °C, and reductive elimination is slow below ca. −10 °C, allowing formation of $Pd^{IV}Me_3$ complexes under conditions mild enough to allow isolation of complexes before reductive elimination occurs.

Complexes of Tridentate Ligands. Complexes of the tripod ligands illustrated, together with $(pz)_3CH$ and $(py)_3CH$, were readily obtained by the procedures developed for synthesis of the bpy and phen complexes. The cations $[PdMe_3(L_3)]^+$ exhibit simple ^1H NMR spectra in $CDCl_3$, and the spectra are readily assigned on comparison with the spectra[29] for $PdMe_2(L_3)$ and $PdIMe(L_3)$. Complexes of the symmetrical ligands ($(pz)_3CH$, $(py)_3CH$) show one PdMe resonance and one ligand ring environment, and the remaining complexes show two PdMe resonances in a 2:1 ratio (Table I). The ligand methine proton for the complexes of $(pz)_3CH$, $(pz)_2(py)CH$, and $(pz)_2(mim)CH$ exchanges with the deuterium of $CDCl_3$, over several hours, and the exchange may be reversed on addition of $CHCl_3$ to the solid obtained on removal of $CDCl_3$–$CHCl_3$.

The order of donor ability of the groups is expected to be mim > py > pz,[30] and the tripod ligands with the stronger donor groups form the most stable complexes. Thus, although all of the solid complexes $[PdMe_3(L_3)]I$ are stable at ambient temperature, in $CDCl_3$ the $(pz)_3CH$ complex shows traces of ethane and $PdIMe((pz)_3CH)$ after 2–4 h at ambient temperature and the complexes $[PdMe_3((py)_2(mim)CH)]I$ and $[PdMe_3((py)(mim)_2CH)]I$ may be heated for ca. 1 h at 60 °C in $CDCl_3$ without a trace of reductive elimination.

The complex $[PdMe_3((pz)_3CH)]BF_4$, prepared from $[PdMe_3((pz)_3CH)]I$ and $AgBF_4$, is more stable than the iodide salt; e.g., after 3 days in $CDCl_3$ at ambient temperature the iodide had completely decomposed to $PdIMe((pz)_3CH)$ and ethane but the tetrafluoroborate salt was unchanged. Kinetic studies indicate that the reductive elimination of ethane from $PdIMe_3(bpy)$ is concerted, occurring mainly after ionization of the iodo group, but with a minor proportion of the complex undergoing reductive elimination directly from $PdIMe_3(bpy)$.[23] Kinetic parameters obtained under conditions of a large excess of iodide indicate a polar intermediate or transition state for the latter path, probably involving at least partial ionization of iodide, $[Me_3(bpy)Pd^{\delta+}\cdots I^{\delta-}]$, before reductive elimination of ethane.[23] The higher stability of $[PdMe_3((pz)_3CH)]BF_4$ compared to that of $[PdMe_3((pz)_3CH)]I$ indicates that reductive elimination from the complexes $[PdMe_3(L_3)]I$ may proceed by a similar path, with formation of an intermediate with bidentate L_3, $[Me_3(L_3\text{-}N,N')Pd^{\delta+}\cdots I^{\delta-}]$. A "model complex" for this intermediate is the stable Pt^{IV} complex $PtIMePh_2((pz)_3CH\text{-}N,N')$, formed on oxidative addition of iodomethane to $PtPh_2((pz)_3CH)$.[31] These results indicate that the enhanced stability of $[PdMe_3(L_3)]I$ compared to that of $PdIMe_3(L_2)I$ at least partly results from the requirement for dissociation of one donor group of the tripod ligand, since the complexes of bidentate ligands may reductively eliminate directly via either ionization or partial ionization of the iodo group.

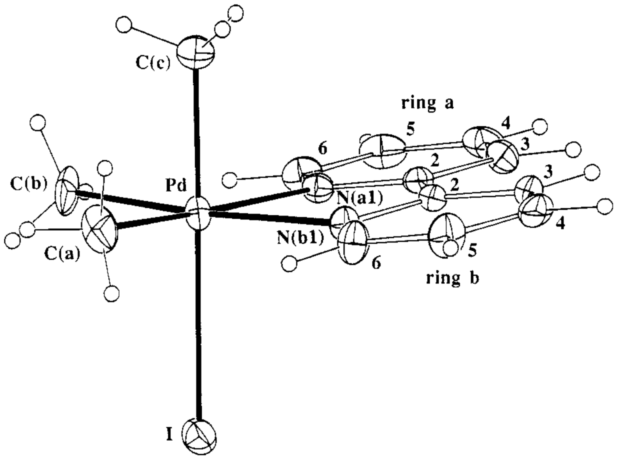

Figure 3. Molecular projection for *fac*-$PdIMe_3(bpy)$ showing the atom numbering. Thermal ellipsoids (20%) are shown for the non-hydrogen atoms, and hydrogen atoms (constrained at estimated positions) have been given an arbitrary radius of 0.1 Å.

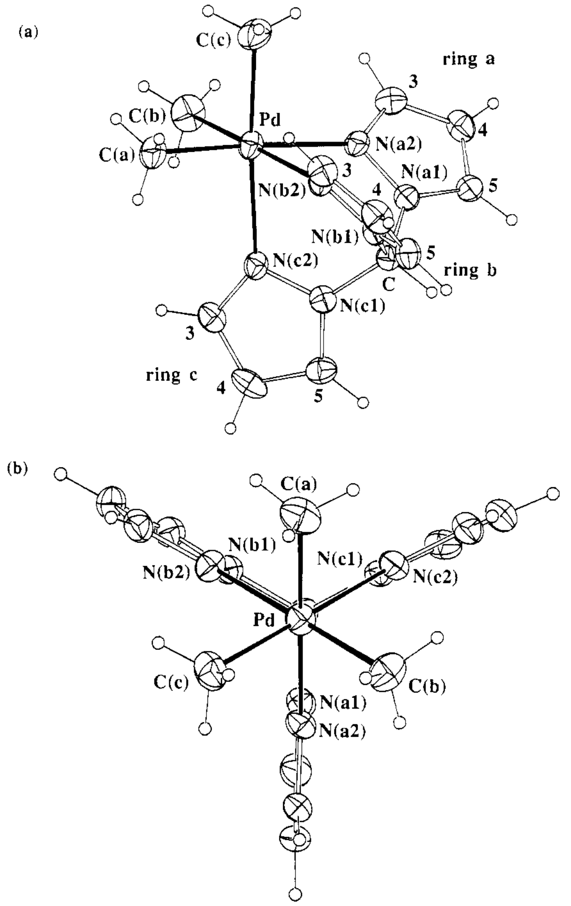

Figure 4. Two projections of the cation $[PdMe_3((pz)_3CH)]^+$. Projection b is a view directly along the (noncrystallographic) 3-fold axis.

X-ray Structural Studies. Crystals of $PdIMe_3(bpy)$ and $[PdMe_3((pz)_3CH)]I$ obtained from their preparations were suitable for crystallographic studies, and in view of the simple donor set arrangement for the latter, "*fac*-PdC_3N_3", the platinum(IV) analogue was synthesized for comparison. "Oxidative addition" of MeI to $PtMe_2((pz)_3CH)$ does not give the expected $[PtMe_3((pz)_3CH)]I$ but instead gives a complex with cyclometalated $(pz)_3CH$, $PtIMe_2((pz)_2(C_3H_2N_2)CH\text{-}N,N',C''^5)$,[17b,31] and thus

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Table III. Selected Bond Distances (Å) and Angles (deg) for $PdIMe_3(bpy)$[a]

	Bond Distances		
Pd–C(a)	2.046 (7)	Pd–N(a1)	2.188 (5)
Pd–C(b)	2.034 (7)	Pd–N(b1)	2.173 (5)
Pd–C(c)	2.040 (6)	Pd–I	2.834 (1)
	Bond Angles		
C(a)–Pd–C(b)	86.6 (3)	C(c)–Pd–N(b1)	89.3 (3)
C(a)–Pd–C(c)	87.0 (3)	C(c)–Pd–I	178.1 (2)
C(b)–Pd–C(c)	86.8 (3)	N(a1)–Pd–N(b1)	75.6 (2)
C(a)–Pd–N(a1)	172.3 (3)	N(a1)–Pd–I	89.8 (1)
C(a)–Pd–N(b1)	97.4 (3)	N(b1)–Pd–I	92.1 (1)
C(a)–Pd–I	93.9 (2)	Pd–N(a1)–C(a2)	115.5 (4)
C(b)–Pd–N(a1)	100.1 (3)	Pd–N(a1)–C(a6)	126.3 (4)
C(b)–Pd–N(b1)	174.2 (3)	Pd–N(b1)–C(b2)	116.1 (4)
C(b)–Pd–I	91.7 (2)	Pd–N(b1)–C(b6)	125.3 (4)
C(c)–Pd–N(a1)	89.5 (2)	N(a1)–C(a2)–C(b2)	116.4 (5)
		N(b1)–C(b2)–C(a2)	115.6 (6)

[a] The 2,2′-bipyridyl ligand skeleton is substantially planar ($\chi^2 = 70$), with an interplanar angle of 2.1° between rings a and b and with deviations of Pd, C(a), and C(b) from the mean plane of 2,2′-bipyridyl being 0.218, 0.496, and 0.556 Å, respectively.

$[PtMe_3((pz)_3CH)]I$ was obtained by the reaction of $(pz)_3CH$ with $Pt^{IV}Me_3$ species[25,32] formed in situ by reaction of MeI with $[PtMe_2(SEt_2)]_2$. Crystals of the platinum complex were obtained by slow vapor diffusion of diethyl ether into an acetone solution of the complex at ca. −20 °C.

Projections of the structures are shown in Figures 3 and 4, selected structural parameters are given in Tables III and IV, and crystallographic details and positional parameters are given in Tables V–VII. The metal atom environments are basically "octahedral" but with considerable distortion resulting from the "bite" of bpy and $(pz)_3CH$, giving N–Pd–N angles of 75.6 (2)° for the bpy complex and 81.7 (3)–83.2 (3)° for the $(pz)_3CH$ complex. The *fac*-$PdMe_3$ moieties in the complex also have C–Pd–C < 90°, ranging from 86.6 (3) to 88.0 (4)°. The py and pz rings are planar, with the Pd atom 0.151 and 0.239 Å (bpy) and 0.084, 0.170, and 0.119 Å ($(pz)_3CH$) from the mean planes of the individual rings.

Iodopalladium(IV) complexes are rare, and Pd^{IV}–I bond distances have not been reported.[33] The value obtained for the bpy complex, 2.834 (1) Å, is similar to that for the most directly comparable Pt^{IV} complex, *fac*-$PtIMe_3((3,5\text{-}Me_2pz)_2CH_2)$ (2.843 (1) Å),[34] which has a similar "MIC_3N_2" donor set with the iodo ligand trans to a methyl group, but Pd^{IV}–I is ~0.06 Å longer than the Pt^{IV}–I bond in *fac*-$PtIMe_3(PhMeAsCH_2CH_2AsPhMe)$ (2.771 (2) Å), which also has the iodo ligand trans to a methyl group.[35]

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[MMe_3((pz)_3CH)]I$[a]

	M = Pd	M = Pt
	Bond Distances	
M–C(a)	2.036 (11)	2.031 (8)
M–C(b)	2.060 (9)	2.056 (7)
M–C(c)	2.049 (10)	2.056 (7)
M–N(a2)	2.191 (8)	2.156 (6)
M–N(b2)	2.207 (7)	2.156 (5)
M–N(c2)	2.225 (7)	2.189 (5)
	Bond Angles	
C(a)–M–C(b)	86.6 (4)	87.9 (3)
C(a)–M–C(c)	88.0 (4)	89.2 (3)
C(b)–M–C(c)	87.4 (4)	88.4 (3)
N(a2)–M–N(b2)	83.2 (3)	84.1 (2)
N(a2)–M–N(c2)	81.7 (3)	83.0 (2)
N(b2)–M–N(c2)	82.4 (2)	83.7 (2)
C(a)–M–N(a2)	176.8 (3)	177.3 (2)
C(a)–M–N(b2)	95.1 (3)	94.4 (2)
C(a)–M–N(c2)	95.4 (3)	94.6 (2)
C(b)–M–N(a2)	95.0 (3)	93.5 (3)
C(b)–M–N(b2)	177.8 (3)	176.9 (3)
C(b)–M–N(c2)	96.1 (3)	94.0 (2)
C(c)–M–N(a2)	94.8 (3)	93.2 (3)
C(c)–M–N(b2)	94.1 (3)	93.8 (2)
C(c)–M–N(c2)	175.3 (3)	175.6 (3)
M–N(a2)–N(a1)	118.4 (5)	117.1 (4)
M–N(a2)–C(a3)	137.8 (6)	136.3 (5)
M–N(b2)–N(b1)	117.8 (5)	117.9 (3)
M–N(b2)–N(b3)	137.1 (7)	137.0 (5)
M–N(c2)–N(c1)	117.2 (5)	116.3 (3)
M–N(c2)–N(c3)	138.2 (6)	138.3 (5)

[a] The pyrazol-1-yl rings are planar (χ^2 range 0.3–2.3), with the Pd atom 0.084, 0.170, and 0.119 Å from the mean planes of rings a, b, and c, respectively, and the Pt atom 0.036, 0.159, and 0.078 Å from the corresponding planes.

The Pd^{IV}–N bond lengths, 2.173 (5) and 2.188 (5) Å in the bpy complex and 2.191 (8)–2.225 (8) Å in the $(pz)_3CH$ complex, are longer than those recorded for other Pd^{IV} complexes, 2.037 (4) and 2.044 (4) Å in $PdCl_4(bpy)$[28] and 2.058 (1)–2.066 (2) Å in *trans*-$[PdCl_2L]^+$, where L is the macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane.[36] The Pd^{IV}–N bond lengths in the bpy complex are also longer than Pt^{IV}–N in the related complex *fac*-$PtIMe_3((3,5\text{-}Me_2pz)_2CH_2)$ (2.236 (4) Å).[34] The Pd^{IV}–C bond lengths, 2.034 (7)–2.046 (7) Å in the bpy complex and 2.036 (11)–2.060 (9) Å in the $(pz)_3CH$ complex, are similar to the Pt^{IV}–C bond lengths in *fac*-$PtMe_3((3,5\text{-}Me_2pz)_2CH_2)I$ (2.04–2.05 Å)[34] and are comparable with the values in the seven previously reported structural studies of $Pd^{II}Me$ complexes, *trans*-$PdMe(HCO_3\text{-}O)(PEt_3)_2$ (2.05 (2) Å),[37] *cis*-$PdMe_2(PPh_3)_2$ (2.089 (3), 2.090 (3) Å),[38] $[Pd(\mu\text{-}Cl)Me(SMe_2)]_2$ (2.016 (4) Å),[39] $[PdMe(bpy)(\gamma\text{-picoline})]BF_4$ (2.036 (6) Å),[18] $PdMe_2((NMe_2CH_2)_2)$ (2.026 (3), 2.029 (3) Å),[19] $PdBrMe(2\text{-}(Ph_2P)C_6H_4CH_2NMe_2)$ (2.142 (8) Å, methyl trans to nitrogen),[14] and $[PdMe(N(CH_2CH_2PPh_2)_3)]I$ (2.10 (3) Å, methyl trans to nitrogen).[40] The A-frame complex $[Pd_2I(\mu\text{-}I)Me(Ph_2PCH_2PPh_2)_2]BF_4\cdot{}^1/_2H_2O$ also has a $Pd^{II}Me$ bond, but the value determined, 2.28 (4) Å, reflects the presence of disordering of Pd–Me and Pd–I environments.[41]

A better comparison between Pd^{IV} and Pt^{IV} is afforded by the cations, which are isostructural and thus the effects of crystal packing are constant. However, the absence of crystallographic C_{3v} symmetry for the cations implies that packing effects at individual Me groups and pz rings may be different, perhaps partly accounting for the minor but significant variation in M–C and M–N distances in the complexes. The M^{IV}–C bond lengths are essentially identical, ~2.04–2.05 Å, but the Pd^{IV}–N distance is ~0.04 Å longer than Pt^{IV}–N; a similar difference for M^{II}–P and M^0–P bond lengths has been reported for the complexes *cis*-$MMe_2(PMePh_2)_2$[38] and $M(PBu^t{}_2Ph)_2$,[42] respectively.

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Table V. Specific Crystallographic Details

complex	PdIMe$_3$(bpy)	[PdMe$_3$((pz)$_3$CH)]I	[PtMe$_3$((pz)$_3$CH)]I
formula	$C_{13}H_{17}IN_2Pd$	$C_{13}H_{19}IN_6Pd$	$C_{13}H_{19}IN_6Pt$
formula mass, au	434.6	492.6	581.3
cryst syst	monoclinic	monoclinic	monoclinic
space group	C_{2h}^5-$P2_1/c$	C_{2h}^6-$C2/c$	C_{2h}^6-$C2/c$
a, Å	7.917 (4)	21.254 (8)	21.253 (8)
b, Å	9.528 (4)	9.213 (5)	9.099 (4)
c, Å	20.207 (8)	19.144 (8)	19.284 (8)
β, deg	104.28 (4)	105.65 (3)	105.63 (3)
V, Å^3	1477 (1)	3624 (3)	3585 (3)
Z	4	8	8
ρ_{calcd}, g cm^{-3}	1.95	1.81	2.15
cryst dimens, mm	0.10 × 0.25 × 0.08	0.11 × 0.14 × 0.32	0.24 × 0.15 × 0.28
$F(000)$	832	1904	2160
μ(Mo Kα), cm^{-1}	31	25	91
abs factor; min, max	1.25, 1.36	1.31, 1.90	2.7, 4.6
$2\theta_{max}$, deg	50	50	60
N	2619	3215	4624
N_o	1822	2030	3284
R	0.032	0.040	0.031
R_w	0.027	0.041	0.029
hkl range	+9,+11,±23	+25,+10,±21	+21,+12,±26

Table VI. Positional Parameters for PdIMe$_3$(bpy)

atom	x	y	z
Pd	0.29078 (7)	0.21660 (5)	0.14310 (3)
I	−0.05938 (6)	0.12305 (5)	0.10211 (3)
C(a)	0.3928 (10)	0.0225 (7)	0.1337 (4)
C(b)	0.3066 (10)	0.1647 (8)	0.2421 (4)
C(c)	0.5415 (8)	0.2859 (8)	0.1756 (4)
N(a1)	0.1992 (6)	0.4333 (5)	0.1426 (3)
C(a2)	0.2015 (7)	0.5084 (7)	0.0860 (3)
C(a3)	0.1594 (9)	0.6498 (7)	0.0805 (4)
C(a4)	0.1108 (9)	0.7158 (8)	0.1342 (4)
C(a5)	0.1067 (9)	0.6392 (8)	0.1910 (4)
C(a6)	0.1507 (9)	0.4989 (8)	0.1937 (4)
N(b1)	0.2850 (6)	0.2925 (6)	0.0411 (2)
C(b2)	0.2524 (8)	0.4314 (7)	0.0300 (3)
C(b3)	0.2631 (8)	0.4941 (7)	−0.0299 (3)
C(b4)	0.3085 (9)	0.4143 (9)	−0.0796 (3)
C(b5)	0.3439 (10)	0.2738 (9)	−0.0683 (4)
C(b6)	0.3277 (9)	0.2179 (7)	−0.0076 (4)

Variations in M–C and M–N distances in the bpy and (pz)$_3$CH complexes suggest that a detailed comparison of bond lengths for Pd^{IV} and Pt^{IV}, as given for M^{II} and M^0,[38] is not warranted.

Experimental Section

The reagents [PdMe$_2$(pyridazine)]$_n$ and PdMe$_2$(L$_2$),[22] PdMe$_2$(L$_3$),[29] and [PtMe$_2$(SEt$_2$)]$_2$[32] were prepared as described, and solvents were purified as described.[22,29] Microanalyses were performed by the Australian Microanalytical Service, Melbourne, Australia, and the Canadian Microanalytical Service, Vancouver, Canada. ^{1}H NMR spectra were recorded with a Bruker AM 300 spectrometer, with chemical shifts given in ppm relative to Me$_4$Si.

Synthesis of Complexes. PdIMe$_3$(bpy). Iodomethane (0.5 mL, 8.0 mmol) was added to a stirred, filtered solution of PdMe$_2$(bpy) (0.40 g, 1.37 mmol) in acetone (ca. 60 mL, warm to dissolve if necessary) at 0 °C. A clear, slightly yellow solution formed immediately, hexane (ca. 5 mL) was added, and the solution was reduced to ca. half the volume by rotary evaporation at 0 °C (ca. 15 min). The solid was collected by vacuum filtration on a sinter, washed with two portions of cold hexane (10 mL), and dried immediately under high vacuum at ambient temperature. The complex (0.35 g, 60%) did not require recrystallization and was stored at ca. −20 °C. ^{1}H NMR ((CD$_3$)$_2$CO): δ 8.95 (ddd, J_{56} = 5.3, J_{46} = 1.7, J_{36} = 0.8 Hz, 2, H6), 8.65 (m, J_{34} = 8.1, J_{35} ≈ 1 Hz, 2, H3), 8.25 (ddd, J_{34} = 8.1, J_{45} = 7.6, J_{46} = 1.7 Hz, 2, H4), 7.80 (ddd, J_{45} = 7.6, J_{56} = 5.3, J_{35} = 1.2 Hz, 2, H5), 1.85 (s, 6, PdMe), 1.14 (s, 3, PdMe). Anal. Calcd for $C_{13}H_{17}N_2IPd$: C, 35.9; H, 3.9; N, 6.5. Found: C, 36.0; H, 4.1; N, 6.5.

All of the trimethylpalladium(IV) complexes may be prepared by this method, but a more convenient procedure is that described in detail for the 1,10-phenanthroline complex.

PdIMe$_3$(phen). 1,10-Phenanthroline hydrate (0.25 g, 1.39 mmol) was added to a suspension of dimethyl(pyridazine)palladium(II) (0.30 g, 1.39 mmol) in acetone (30 mL) at 0 °C. The mixture was stirred for 1–2 min and filtered into a precooled round-bottomed flask. Addition of iodomethane (0.5 mL, 8.0 mmol), followed by rotary evaporation to half the volume at 0 °C, addition of cold hexane (10 mL), and further evaporation, gave the complex. The white solid was collected, washed with two portions of cold diethyl ether (10 mL), and dried immediately under high vacuum (0.33 g, 52%). ^{1}H NMR ((CD$_3$)$_2$CO): δ 9.31 (dd, J_{23} = 4.9, J_{24} = 1.5 Hz, 2, H2,9), 8.84 (dd, J_{34} = 8.2, J_{24} = 1.5 Hz, 2, H4,7), 8.27 (s, 2, H5,6), 8.12 (dd, J_{34} = 8.2, J_{23} = 4.9 Hz, 2, H3,8), 1.96 (s, 6, PdMe), 1.20 (s, 3, PdMe). Anal. Calcd for $C_{15}H_{17}N_2IPd$: C, 39.3; H, 3.7; N, 6.1. Found: C, 39.7; H, 3.9; N, 6.4.

[PdMe$_3$((pz)$_3$CH)]I. Yield: 45%. ^{1}H NMR (CDCl$_3$): δ 12.02 (s, 1, CH), 8.99 (dd, J_{45} = 2.7, J_{35} = 0.6 Hz, 3, H5), 7.70 (d, J_{34} ≈ 1.8 Hz, 3, H3), 6.47 (dd, J_{45} = 2.7, J_{34} ≈ 2 Hz, 3, H4), 1.58 (s, 9, PdMe). Anal. Calcd for $C_{13}H_{19}N_6IPd$: C, 31.7; H, 3.9; N, 17.1. Found: C, 31.9; H, 4.3; N, 17.4.

[PdMe$_3$((pz)$_2$(py)CH)]I. Yield: 65%. ^{1}H NMR (CDCl$_3$; incorrectly reported in preliminary communication[17b]): δ 10.73 (s, 1, CH), 9.01 (d, J_{45} = 2.7 Hz, 2, H5(pz)), 8.87 (d, J_{34} = 7.8 Hz, 1, H3(py)), 8.56 (d, J_{56} = 5.4 Hz, 1, H6(py)), 8.06 (ddd, J_{45} ≈ J_{34} ≈ 7.8, J_{46} = 1.8 Hz, H4(py)), ~7.6 (m, 3, H3(pz) and H5(py)), 6.43 (dd, J_{45} = 2.6, J_{34} ≈ 1.9 Hz, 2, H4(pz)), 1.59 (s, 3, PdMe), 1.53 (s, 6, PdMe). Anal. Calcd for $C_{15}H_{20}N_5IPd$: C, 35.6; H, 4.0; N, 13.8. Found: C, 35.9; H, 4.0; N, 14.0.

[PdMe$_3$((pz)$_2$(mim)CH)]I. Yield: 54%. ^{1}H NMR (CDCl$_3$): δ 10.60 (s, 1, CH), 9.24 (dd, J_{45} = 2.7, J_{35} = 0.6 Hz, 2, H5(pz)), 7.62 (d, J_{34} = 1.8 Hz, 2, H3(pz)), 7.15 (d, 1) and 7.00 (d, J_{45} = 1.5 Hz, 1, H4,5(mim)), 6.39 (dd, J_{45} = 2.7, J_{34} = 1.7 Hz, 2, H4(pz)), 4.36 (s, 3, NMe), 1.56 (s, 6, PdMe), 1.38 (s, 3, PdMe). Anal. Calcd for $C_{14}H_{21}N_6IPd$: C, 33.2; H, 4.2; N, 16.6. Found: C, 33.3; H, 4.2; N, 16.6.

[PdMe$_3$((py)$_3$CH)]I. Yield: 56%. ^{1}H NMR (CDCl$_3$; incorrectly reported in preliminary communication[17b]): δ 8.93 (d, J_{34} = 7.7 Hz, 3, H3), 8.47 (dd, J_{56} = 5.6, J_{46} = 1.7 Hz, 3, H6), 8.27 (s, 1, CH), 7.96 (ddd, J_{34} ≈ J_{45} ≈ 7.7, J_{46} = 1.7 Hz, 3, H4), 7.45 (ddd, 3, J_{45} = 7.7, J_{56} = 5.6, J_{35} = 1.3 Hz, 3, H5), 1.50 (s, 9, PdMe). Anal. Calcd for $C_{19}H_{25}N_3IPd$: C, 43.4; H, 4.2; N, 8.0. Found: C, 43.0; H, 4.3; N, 7.8.

[PdMe$_3$((py)$_2$(mim)CH)]I. Yield: 54%. ^{1}H NMR (CDCl$_3$): δ 9.12 (m, J_{34} = 7.9 Hz, 2, H3(py)), 8.47 (m, J_{56} = 5.5 Hz, 2, H6(py)), 7.95 (ddd, J_{45} ≈ J_{34} ≈ 7.7, J_{46} = 1.7 Hz, 2, H4(py)), 7.87 (s, 1, CH), 7.44 (ddd, J_{45} = 7.6, J_{56} = 5.3, J_{35} = 1.2 Hz, 2, H5(py)), 7.03 (d, 1) and 6.92 (d, J_{45} = 1.5 Hz, 1, H4,5(mim)), 4.30 (s, 3, NMe), 1.53 (s, 6, PdMe), 1.28 (s, 3, PdMe). Anal. Calcd for $C_{18}H_{25}N_4IPd$: C, 40.9; H, 4.4; N, 10.6. Found: C, 41.0; H, 4.4; N, 10.4.

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Table VII. Positional Parameters for [MMe$_3$((pz)$_3$CH)I]

	M = Pd			M = Pt		
atom	*x*	*y*	*z*	*x*	*y*	*z*
M	0.16992 (3)	0.60239 (8)	0.29807 (3)	0.16999 (1)	0.60141 (3)	0.30052 (1)
C(a)	0.2347 (5)	0.5803 (10)	0.2374 (5)	0.2348 (3)	0.5808 (8)	0.2406 (4)
C(b)	0.1091 (5)	0.4676 (12)	0.2238 (6)	0.1077 (4)	0.4676 (9)	0.2271 (4)
C(c)	0.2096 (5)	0.4193 (11)	0.3535 (5)	0.2091 (4)	0.4162 (8)	0.3569 (4)
C	0.1332 (4)	0.8921 (10)	0.3707 (4)	0.1327 (3)	0.8910 (7)	0.3691 (4)
N(a1)	0.0960 (3)	0.7736 (8)	0.3886 (3)	0.0963 (2)	0.7719 (6)	0.3880 (3)
N(a2)	0.1002 (3)	0.6393 (8)	0.3623 (4)	0.1012 (2)	0.6345 (6)	0.3632 (3)
C(a3)	0.0588 (4)	0.5630 (10)	0.3872 (5)	0.0605 (3)	0.5526 (7)	0.3864 (3)
C(a4)	0.0291 (4)	0.6443 (12)	0.4291 (5)	0.0287 (3)	0.6372 (8)	0.4278 (4)
C(a5)	0.0536 (4)	0.7799 (10)	0.4292 (4)	0.0518 (3)	0.7755 (8)	0.4276 (2)
N(b1)	0.2030 (3)	0.8691 (8)	0.3977 (3)	0.2023 (2)	0.8699 (6)	0.3970 (2)
N(b2)	0.2317 (2)	0.7519 (8)	0.3778 (3)	0.2308 (2)	0.7493 (6)	0.3775 (3)
C(b3)	0.2942 (5)	0.7660 (12)	0.4113 (5)	0.2945 (3)	0.7642 (9)	0.4105 (3)
C(b4)	0.3049 (5)	0.8960 (13)	0.4512 (5)	0.3051 (3)	0.8936 (10)	0.4500 (3)
C(b5)	0.2462 (6)	0.9564 (11)	0.4412 (5)	0.2469 (4)	0.9571 (8)	0.4407 (3)
N(c1)	0.1158 (3)	0.9146 (8)	0.2912 (4)	0.1151 (2)	0.9129 (6)	0.2923 (2)
N(c2)	0.1270 (3)	0.8093 (8)	0.2467 (3)	0.1267 (2)	0.8047 (6)	0.2480 (3)
C(c3)	0.1050 (4)	0.8637 (10)	0.1811 (5)	0.1049 (3)	0.8574 (9)	0.1821 (3)
C(c4)	0.0798 (5)	1.0002 (13)	0.1832 (5)	0.0790 (3)	0.9995 (9)	0.1843 (4)
C(c5)	0.0860 (4)	1.0303 (11)	0.2547 (5)	0.0863 (3)	1.0304 (8)	0.2546 (4)
I	0.09451 (4)	0.19203 (8)	0.47435 (4)	0.09280 (3)	0.18611 (6)	0.47776 (3)

[PdMe$_3$((py)(mim)$_2$CH)]I. Yield: 49%. ^{1}H NMR (CDCl$_3$): δ 9.38 (m, J_{34} = 7.9 Hz, 1, H3(py)), 8.50 (dd, J_{56} = 5.2, J_{46} = 1.5 Hz, 1, H6(py)), 7.95 (ddd, $J_{34} \approx J_{45} \approx 7.7$, J_{46} = 1.7 Hz, 1, H4(py)), 7.43 (ddd, J_{45} = 7.6, J_{56} = 5.2, J_{35} = 1.2 Hz, 1, H5(py)), 7.24 (s, 1, CH), 7.03 (d, 2) and 6.89 (d, J_{45} = 1.4 Hz, H4,5(mim)), 4.32 (s, 6, NMe), 1.55 (s, 3, PdMe), 1.33 (s, 3, PdMe). Anal. Calcd for $C_{17}H_{25}N_5IPd$: C, 38.4; H, 4.5; N, 13.2. Found: C, 38.6; H, 4.5; N, 13.0.

[PdMe$_3$((pz)$_3$CH)]BF$_4$. Silver tetrafluoroborate (0.51 mmol) in acetone (4.2 mL) was added to a stirred suspension of [PdMe$_3$((pz)$_3$CH)]I (0.25 g, 0.50 mmol) in acetone (40 mL) at 0 °C. After filtration, addition of hexane (20 mL), and rotary evaporation at 0 °C, white crystals of the product were collected and dried under vacuum at ambient temperature (yield 64%). ^{1}H NMR (CDCl$_3$): δ 9.89 (s, 1, CH), 8.54 (d, J_{45} = 2.6 Hz, 3, H5), 7.72 (d, J_{34} = 2.0 Hz, 3, H3), 6.48 ("t", $J_{43} \approx J_{45} \approx 2.4$ Hz, 3, H4), 1.58 (s, 9, PdMe). Anal. Calcd for $C_{13}H_{19}N_6BF_4Pd$: C, 34.5; H, 4.2; N, 18.6. Found: C, 34.3; H, 4.2; N, 18.3.

[PtMe$_3$((pz)$_3$CH)]I. To a solution of [PtMe$_2$(SEt$_2$)]$_2$ (0.16 mmol) and (pz)$_3$CH (0.32 mmol) in acetone (10 mL), which do not react at ambient temperature was added iodomethane (0.16 mmol). The solution was stirred for 10 min and briefly rotary evaporated to remove excess MeI and hexane added until cloudiness developed. The white solid formed in 92% yield. ^{1}H NMR (CDCl$_3$): δ 12.24 (s, 1, CH), 9.08 (dd, J_{45} = 2.7, J_{35} = 0.6 Hz, 3, H5), 7.73 (d, J_{34} = 2.1 Hz, 3, H3), 6.54 (dd, J_{45} = 2.7, J_{34} = 2.1 Hz, 3, H4), 1.14 ("t", J_{HPt} = 72 Hz, 9, PtMe). The spectrum is similar to that reported for the hexafluorophosphate salt,[34] and the complex was also characterized by X-ray crystallography.

Studies of Reactivity with ^{1}H NMR Spectroscopy. Solutions of dimethylpalladium(II) complexes were cooled in the variable-temperature probe of the spectrometer, prior to addition of excess iodomethane (or CD$_3$I) in the same solvent, and spectra were recorded as soon as possible after addition. Additions were generally performed at −50 °C, with warming in 5 °C increments until oxidative addition commenced and a stable intermediate was produced. Further warming allows the subsequent reactivity to be observed—conversion of cationic to neutral species (bpy complex in (CD$_3$)$_2$CO), equilibria between cationic and neutral species (in CD$_3$CN), and reductive elimination (all experiments, except most tridentate ligand complexes). The presence of ethane as a product, e.g. as shown in Figure 2, was confirmed by loss of the resonance of ethane on purging the solution with nitrogen gas and the obtainment of spectra of solutions of ethane gas bubbled into (CD$_3$)$_2$CO and CD$_3$CN.

X-ray Structure Determinations. Unique data sets were measured to the specified $2\theta_{\max}$ limits at 295 K with use of a Syntex P2$_1$ four-circle diffractometer fitted with a monochromatic Mo Kα radiation (λ = 0.7106$_9$ Å) source, operating in the conventional 2θ–θ scan mode. Cell dimensions for the isostructural complexes were determined on the same machine on the same day. N independent reflections were obtained, N_o 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, and U_{iso} for H atoms were constrained at estimated values. Conventional R and R_w values on $|F|$ at convergence are given in Table V. Statistical weights, derived from $\sigma^2(I) = \sigma^2(I_{\mathrm{diff}}) + 0.0002\sigma^4(I_{\mathrm{diff}})$, were employed. Although a couple of very intense reflections suggested extinction effects in the Pt structure, meaningful refinement was not supported by the body of data. No abnormal features were observed in final difference maps. Neutral atom complex scattering factors were used;[43] computation used the XTAL program system implemented by S. R. Hall on a Perkin-Elmer 3241 computer.[44]

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Registry No. phen, 66-71-7; PdMe$_2$(bpy), 95841-49-9; *fac*-PdIMe$_3$(bpy), 110182-93-9; PdMe$_2$(pyridazine), 119661-33-5; *fac*-PdIMe$_3$(phen), 119661-45-9; [PdMe$_3$((pz)$_3$CH)]I, 114867-35-5; [PdMe$_3$((pz)$_2$(py)CH)]I, 114867-36-6; [PdMe$_3$((pz)$_2$(mim)CH)]I, 114867-37-7; [PdMe$_3$((py)$_3$CH)]I, 114867-38-8; [PdMe$_3$((py)$_2$(mim)CH)]I, 124920-31-6; [PdMe$_3$((py)(mim)$_2$CH)]I, 124920-32-7; [PdMe$_3$((pz)$_3$CH)]BF$_4$, 124920-34-9; [PtMe$_3$((pz)$_3$CH)]I, 114867-42-4; (pz)$_3$CH, 80510-03-8; (pz)$_2$(py)CH, 115030-91-6; (pz)$_2$(mim)CH, 115030-92-7; (py)$_3$CH, 77429-58-4; (py)$_2$(mim)CH, 124920-30-5; (py)(mim)$_2$CH, 120302-91-2; [PtMe$_2$(SEt$_2$)]$_2$, 62343-09-3; *fac*-PdIMe$_3$((mim)$_2$C=CH$_2$), 124942-46-7; *fac*-PdIMe$_3$((py)(mim)C=CH$_2$), 124920-35-0; *fac*-PdIMe$_3$((py)(mim)C=O), 124920-36-1; *fac*-[PdMe$_3$(bpy)((CD$_3$)$_2$C=O)]$^+$, 124920-37-2; *fac*-[PdMe$_3$(phen)(CD$_3$CN)]$^+$, 124920-38-3; *fac*-[PdMe$_3$((mim)$_2$C=CH$_2$)(CD$_3$CN)]$^+$, 124920-39-4; *fac*-[PdMe$_3$((py)(mim)C=CH$_2$)(CD$_3$CN)]$^+$, 124920-40-7; *fac*-[PdMe$_3$((py)(mim)C=O)(CD$_3$CN)]$^+$, 124942-47-8.

Supplementary Material Available: Listings of non-hydrogen atom thermal parameters, hydrogen atom parameters, and ligand geometry for the complexes (7 pages); listings of observed and calculated structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

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