Synthetic routes to methylpalladium(II) and dimethylpalladium(II) chemistry and the synthesis of new nitrogen donor ligand systems

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Reaction of 2b with PhCHO. A solution of **2b** (1 mmol) in THF was added dropwise to a solution of PhCHO (0.15 g, 1.4 mmol) in ether (1 mL) at -20 °C, and the reaction was monitored by ^{1}H NMR spectroscopy. The mixture was stirred for 30 min at -20 °C and then hydrolyzed, extracted, dried, and concentrated in vacuo. The residue was treated with pentane (2 mL) at -20 °C. After decantation and drying in vacuo, the resulting white powder was identified as pure **14b**: yield 0.26 g (62%); mp 78-80 °C; ^{1}H NMR (C_6D_6) δ 2.10 (s, 6 H, *p*-CH_3), 2.23 and 2.25 (s, 12 H, *o*-CH_3), 5.20 (d, 1 H, CH), 5.30 (d, 1 H, GeH), J(HC-GeH) = 3 Hz, 6.60 and 6.63 (s, 4 H, C_6H_2), 6.95 (s, 5 H, C_6H_5); IR (Nujol, KBr) 2060 (Ge-H), 3300 cm^{-1} (OH); mass spectrum m/z 420 ($M^{\bullet+}$). Anal. Calcd for $C_{25}H_{30}GeO$: C, 71.69; H, 7.16. Found: C, 71.76; H, 7.58.

The thermal decomposition of **14b** was monitored by ^{1}H NMR spectroscopy with use of a solution of **14b** in C_6D_6 that had been heated in a sealed tube for 4 h at 160 °C. The presence of **1b** (25%), PhCHO (25%), and **14b** (73%) was thereby confirmed.

A solution of **14b** (0.21 g, 0.5 mmol) in C_6H_6 (2 mL), Mes_3SiCl (0.06 g, 0.55 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.10 g, excess) was stirred for 15 h at 20 °C. After removal of DBU·HCl by filtration, the solution was concentrated in vacuo. **15** was then recovered by distillation: yield 0.11 g (44%); bp 95 °C (4×10^{-2} mmHg); ^{1}H NMR (C_6D_6) δ 0.05 (s, 9 H, $SiMe_3$), 2.05 (s, 6 H, *p*-CH_3), 2.30 (s, 12 H, *o*-CH_3), 5.50 (s, 2 H, GeH, CH),[28] 6.65 (s, 4 H, C_6H_2), 6.90-7.15 (m, 5 H, C_6H_5); IR (pure, KBr) 2050 cm^{-1} (Ge-H). Anal. Calcd for $C_{28}H_{38}OSiGe$: C, 68.50; H, 7.74. Found: C, 67.83; H, 7.96.

(28) Using $CDCl_3$ as solvent, we observed the expected δ(CH) and δ(GeH) signals and their coupling: δ 5.20 (d, 1 H, CH) and 5.35 (d, 1 H, GeH), J(HC-GeH) = 3 Hz.

Synthetic Routes to Methylpalladium(II) and Dimethylpalladium(II) Chemistry and the Synthesis of New Nitrogen Donor Ligand Systems

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Convenient and widely applicable synthetic routes to methylhalogenopalladium(II), $PdXMe(L_2)$, and dimethylpalladium(II) complexes, $PdMe_2(L_2)$, have been developed, including complexes of triphenylphosphine and a wide range of bidentate nitrogen donor ligands. These routes involve either the generation of $Pd^{II}Me_n$ species at low temperature from methyllithium reagents and *trans*-$PdCl_2(SMe_2)_2$ followed by addition of ligand, PdIMe(2,2′-bipyridyl) being synthesized through the oxidative-addition reactivity of $Pd_2(dba)_3(CHCl_3)$, or the facile synthesis of complexes with the reagents $[PdIMe(SMe_2)]_2$ and $[PdMe_2(pyridazine)]_n$ in organic solvents at ambient temperature. These reagents are particularly suitable for ligands sensitive to MeLi reagents, and $[PdIMe(SMe_2)]_2$ is also a suitable substrate for the synthesis of chloro and bromo complexes, $PdXMe(L_2)$, including PPh_3 complexes. Several new nitrogen donor bidentate ligands are described, containing 1-methylimidazol-2-yl (mim) and pyridin-2-yl (py) groups in $(mim)_2C{=}CH_2$ and $(py)(mim)C{=}CH_2$ as relatives of planar ligands such as 2,2′-bipyridyl and mim, py, and pyrazol-1-yl (pz) groups in $(py)(mim)CH_2$, $(py)(mim)CHMe$, $(mim)_2CH_2$, $(mim)_2CHMe$, and $(pz)(mim)CH_2$ as relatives of ligands such as $(py)_2CH_2$ and $(pz)_2CH_2$. Methylpalladium(II) complexes of unsymmetrical bidentate ligands exhibit isomerism; e.g., isomers of $PdIMe\{(py)(mim)C{=}O\}$ occur in the ratio 9:1, where the dominant isomer has the pyridine ring trans to methyl. The ligands with methane bridges, e.g. $(pz)(py)CH_2$, ethane bridges, e.g. $(pz)_2CHMe$, and propane bridges, e.g. $(py)_2CMe_2$, form complexes $PdMe_2(L_2)$ and $PdIMe(L_2)$ that exhibit variable-temperature NMR spectra indicating boat-to-boat inversion of the chelate ring, but complexes of $(mim)_2CHMe$ and $(py)(mim)CHMe$ appear to adopt only the conformation with the methyl group axial and adjacent to palladium.

Introduction

Palladium and its compounds are widely used in catalysis and organic synthesis,[1-5] and the organometallic chemistry of palladium involving Pd-C σ bonds has been focused primarily on the divalent oxidation state with phosphine-based ligands.[1,6-8] Nitrogen donor complexes involve predominantly studies of cyclometalation and intramolecular coordination systems,[5,9] which also have applications for organic synthesis.[5,10] The intramolecular coordination systems usually involve Pd^{II}-C(sp^2) bonds,[5,9] although some Pd-C(sp^3) systems are known, e.g. four- and five-membered palladacycle rings in $[Pd(CHMeCHMeNMe_2)(NHMe_2)_2]^+$[11] and $[Pd(CH_2(C(CO_2Et)_2)CHCH_2NMe_2)(\mu\text{-}Cl)]_2$,[12] respectively. Palladacyclopentadiene complexes, e.g. $Pd[C(CO_2Me)]_5(bpy)$,[13] 2,2′-biphenyldiyl complexes, e.g. $PdC_{12}H_8(bpy)$,[14] and some

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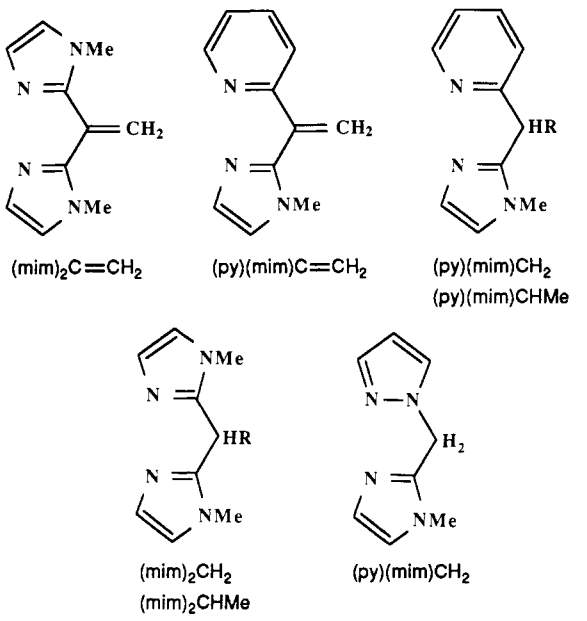
butadienyl complexes, e.g. $Pd(CBu^tCl{=}CMeCMe{=}CBu^t)(bpy)Cl$,[15] are also known, but *simple* alkylpalladium(II) nitrogen donor ligand complexes are restricted to $PdR_2(bpy)$ (R = Me,[16,17] Et,[18] CH_2CMe_3[19]), the tetramethylethylenediamine complex $PdMe_2(tmeda)$,[17] PdXMe(bpy) (X = Cl,[20] I (doubtful)[21]), $PdBr(CH_2CMe_3)(bpy)$,[19] PdXMe(tmeda) (X = Br, Cl),[17] $PdBr(CH_2Ph)(tmeda)$,[17] PdMeCl(2,9-dimethyl-1,10-phenanthroline),[22] and the closely related palladacyclopentane complexes $Pd[CH_2CH(R)CH(R)CH_2](L)$ (R = H, L = bpy;[23,24] R = H, L = tmeda[25]). This is surprising in view of the extensively developed nitrogen donor chemistry of alkylplatinum(II) and -platinum(IV),[7,26] the potential of nitrogen donor alkylpalladium(II) complexes for comparison with widely studied phosphine complexes as model systems for catalytic reactions and the potential for catalytic activity,[27] and also the potential for development of higher oxidation state organopalladium chemistry, which prior to the commencement of this work has been limited to several $Pd^{IV}(C_6F_5)$ and $Pd^{IV}(C_6F_5)_2$ complexes with nitrogen donor ligands.[28]

In this paper we report the development of new and general synthetic routes to $Pd^{II}Me_2$ and $Pd^{II}Me$ complexes of nitrogen, phosphorus, and sulfur donor ligands that are more facile, convenient, and widely applicable than previous routes and the synthesis of a range of new ligands that are expected to be of general interest in coordination and organometallic chemistry. The application of some of these developments for the synthesis and study of the first hydrocarbylpalladium(IV) complexes has been reported.[29-31] Preliminary reports of part of this work have been given,[29,30,32] and a subsequent report of the syntheses of several of the simple $Pd^{II}Me$ and $Pd^{II}Me_2$ complexes listed above has appeared recently.[17]

Chart I



Results and Discussion

Choice and Synthesis of Ligands. In addition to the classical ligands 2,2′-bipyridyl (bpy) and 1,10-phenanthroline (phen), a range of related bidentates containing pyridin-2-yl (py), pyrazol-1-yl (pz), and 1-methylimidazol-2-yl (mim) rings were chosen as ligands. The ligands include bidentate 1-methyl-2-(pyridin-2-yl)-imidazole (py(mim)), (py)(mim)C=O, $(mim)_2C{=}O$, $(py)_2CRR'$ (R = R′ = H, Me; R = H, R′ = Me), $(pz)_2CRR'$ (R = R′ = H, Me; R = H, R′ = Me), and $(py)(pz)CH_2$, together with the new ligands shown in Chart I, illustrating the connectivity and nomenclature of the ligands.

These ligands were chosen in order to vary the donor ability of the rings (mim > py > pz),[33] to vary the chelate ring geometry (five- and six-membered heterocycles and chelate rings, planar and puckered chelate rings), to vary the flexibility of the polydentates (least for phen, greatest for CH_2-bridged ligands), and to probe the steric effects of substitution at bridgehead carbons, e.g. R and R′ in $(mim)_2CRR'$. The ketones (py)(mim)C=O and $(mim)_2C{=}O$, and the analogous alkenes, were obtained as intermediates in syntheses of methane- and ethane-bridged ligands and were included in the synthesis of complexes, as they have potential in coordination chemistry as relatives of planar 2,2′-bipyridyl, except that they form NMN angles closer to 90°; e.g., the complex $Cu\{(mim)_2C{=}O\}(SO_4)(H_2O)_2$ has NCuN = 90.25 (5)°.[34] The wide range of ligands was also chosen to firmly establish the synthetic routes to complexes, with a view to the subsequent development of alkylpalladium(IV) chemistry following our initial report of the first hydrocarbylpalladium(IV) complex, *fac*-$PdIMe_3(bipy)$.[29]

Ligand Synthesis. An improved procedure for the reported[35] synthesis of (py)(mim)C=O has been developed and a new method for the synthesis of $(mim)_2C{=}O$, involving the reaction of CO_2 with 2-lithio-1-methylimidazole

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(eq 1), found to be more convenient than the reported methods.[36,37] The ligands (py)(mim)CH_2 and $(mim)_2CH_2$ are formed on reduction of the ketones (L)(mim)C=O (L = py, mim; eq 2), in the same manner as reported for reduction of $(py)_2C{=}O$ to $(py)_2CH_2$,[38] and the ligands (L)(mim)C=CH_2 and (L)(mim)CHMe (L = py, mim) were obtained as shown in eq 3–6. The ligand (pz)(mim)CH_2 may be obtained on reaction of (mim)CH_2Cl with potassium pyrazolide (eq 7).

$$2\text{Li(mim)} \xrightarrow[\text{slow addition}]{CO_2} (\text{mim})_2C{=}O \quad (1)$$

$$(\text{L})(\text{mim})C{=}O \xrightarrow{N_2H_4{\cdot}H_2O/KOH} (\text{L})(\text{mim})CH_2 \quad (2)$$
L = py, mim

$$\text{Me(py)}C{=}O \xrightarrow{\text{Li(mim)}} (\text{py})(\text{mim})C(OH)\text{Me} \quad (3)$$

$$\text{Me(EtO)}C{=}O \xrightarrow{\text{2Li(mim)}} (\text{mim})_2C(OH)\text{Me} \quad (4)$$

$$(\text{L})(\text{mim})C(OH)\text{Me} \xrightarrow{H_2SO_4/\Delta} (\text{L})(\text{mim})C{=}CH_2 \quad (5)$$
L = py, mim

$$(\text{L})(\text{mim})C{=}CH_2 \xrightarrow{H_2/Pd} (\text{L})(\text{mim})CH\text{Me} \quad (6)$$
L = py, mim

$$(\text{mim})CH_2Cl \xrightarrow{\text{Kpz}} (\text{pz})(\text{mim})CH_2 \quad (7)$$

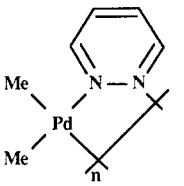
Synthesis of Dimethylpalladium(II) Complexes. Nitrogen donor dialkylpalladium(II) complexes are generally synthesized by the reaction of dihalogeno complexes with alkylithium reagents,[16,17,19,23,25] although $PdEt_2(bpy)$ has been obtained from the reaction of $AlEt_2(OEt)$ with $Pd(acac)_2$ and bpy,[18] and both $\overline{PdCH_2CH(R)CH(R)CH_2}$-(bpy)[23-25] and, more recently, $PdMe_2(bpy)$[17] have been obtained by displacement of tmeda from its complexes. The alkyllithium route has only been reported for bpy complexes, $PdR_2(bpy)$ (R = Me,[16] CH_2CMe_3[19]), and the tmeda complexes $\overline{PdCH_2CH(R)CH(R)CH_2}(tmeda)$[23-25] and $PdMe_2(tmeda)$.[17] As a general route for synthesis this method requires prior isolation and characterization of dihalogeno complexes and appropriate reactivity of the dihalogeno complex toward alkylating agents and is restricted to complexes containing ligands insensitive to alkylating agents. Two improved general methods are reported here, one involving generation of $PdMe_2(SMe_2)_n$ with dimethyl sulfide as a weak donor ligand at low temperature followed by direct addition of ligand to give complexes stable at ambient temperature and a related method in which the weak donor pyridazine (pyd) forms a solid, $[PdMe_2(pyd)]_n$, which reacts readily with a range of ligands under mild conditions.

Reaction of methyllithium with the *cis*-dichloropalladium(II) complex of 1,2-bis(methylthio)ethane at ca. 0 °C gave $PdMe_2(MeSCH_2CH_2SMe)$,[16] but analogous reactions of *trans*-$PdCl_2(SEt_2)_2$ with LiMe[16] or $MgMe_2$[39] did not give an organopalladium(II) product. However, we have found that the reaction of *trans*-$PdCl_2(SMe_2)_2$ with LiMe at ca. −60 °C gives a colorless solution, and on addition of a range of nitrogen donor ligands at ca. −60 °C followed by slow warming to ca. −15 °C and hydrolysis, complexes may be readily obtained (eq 8), e.g. with py-

$$\textit{trans}\text{-}PdCl_2(SMe_2)_2 \xrightarrow[\text{(ii) } L_2]{\text{(i) 2–3LiMe (halide free)}} PdMe_2(L_2) \quad (8)$$

ridazine and a selection of ligands listed as method A in Table I. For these syntheses LiMe must be "methyl halide free", i.e. either a commercial product that has low halide content and is free of MeI or a sample prepared in the laboratory from chloromethane, since syntheses with LiMe prepared from MeI give methylpalladium(II) complexes (see below).

The pyridazine complex is unstable at ambient temperature but may be satisfactorily stored for several weeks at ca. −20 °C. It gives a simple ^1H NMR spectrum, indicating the stoichiometry "$PdMe_2(pyd)$", but on recrystallization gives a highly insoluble product. The insoluble form may be $[PdMe_2(pyd)]_n$ ($n > 2$), and the initial product may be $[PdMe_2(pyd)]_2$, but since the value of n could not be determined, the initial product is formulated as $[PdMe_2(pyd)]_n$.



$[PdMe_2(pyd)]_n$

The initial product is an excellent substrate for the synthesis of complexes under mild conditions, presumably owing to the very low basicity of pyridazine, and the reagent is particularly useful for ligands sensitive to LiMe, e.g. (py)(mim)C=O, for ligands commonly available as hydrates, e.g. phen·H_2O, for ligands sensitive to water (hydrolysis following eq 8), and for ligands insoluble at ca. −30 °C (decomposition occurs above ca. −30 °C in the absence of added ligand) in the diethyl ether solvent used in the alternative synthetic method (eq 8). The pyridazine route (denoted method B) is most suitable for strong donor ligands, the weaker pyrazole-based complexes, for example, being better prepared by the alternative method, and appears to have wide application, providing a facile route to *cis*-$PdMe_2(PPh_3)_2$, for example, and thus should be applicable for the synthesis of a wider range of phosphine complexes than is currently accessible via the reaction of $PdX_2(phosphine)_2$ substrates with alkylating agents.

The complexes $PdMe_2(L_2)$ (L_2 = bpy, phen) are stable at ambient temperature and may be recrystallized from boiling acetone, although decomposition occurs under these conditions after 15–30 min. The other complexes are best stored at ca. −20 °C and are only stable in solution at ambient temperature for 15–30 min, with complexes of weaker donor ligands being the least stable.

Synthesis of Methylhalogenopalladium(II) Complexes PdXMe(L). General synthetic routes for alkylpalladium(II) complexes of nitrogen donor ligands have not been reported, and only a few complexes have been isolated. The synthesis of $PdBr(CH_2CMe_3)(bpy)$ requires the prior preparation of $Pd(CH_2CMe_3)_2(bpy)$ and subsequent reaction with benzyl bromide,[19] $PdMe_2(tmeda)$ reacts similarly with RX to form PdXMe(tmeda) (RX = MeBr, MeI) and $PdBr(CH_2Ph)(tmeda)$,[17] PdClMe(bpy) has been reported but the synthetic method omitted,[20] and a solid obtained as a byproduct on reaction of $PdMe_2(bpy)$ with $C_3F_7{}^nI$ and thought[21] to possibly be PdIMe(bpy) does not appear to have the same properties as an authentic sample. Attempted syntheses of $PdCl(CH_2CMe_3)(bpy)$ by reaction of the stoichiometric quantity of neopentyllithium with $PdCl_2(bpy)$ gave the dineopentyl complex, possibly

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Table I. Yield and Characterization Data for Complexes Isolated

ligand	method[a]	yield, %	anal. found (calcd), % C	H	N	δ(MePd)[b]
			$Me_2Pd(L_2)$			
pyd[c]	A	75				0.06
phen	B(a)	82	53.0 (53.1)	4.4 (4.5)	9.2 (8.9)	0.38
bpy[d]	A, B(a)	82	48.5 (49.2)	4.8 (4.8)	9.3 (9.6)	0.24
py(mim)	B(a)	46	44.4 (44.7)	5.0 (5.1)	14.0 (14.2)	0.24, 0.05
(py)(mim)C=O	B(a)	46	44.1 (44.5)	4.6 (4.7)	12.8 (13.0)	0.08, −0.06
$(mim)_2C=O$	B(a)	78	39.5 (40.4)	5.0 (4.9)	17.7 (17.2)	0.10
(py)(mim)C=CH_2	B(a)	52	48.5 (48.5)	5.3 (5.3)	12.6 (13.1)	0.08, −0.10
$(mim)_2C=CH_2$	B(a)	61	44.3 (44.4)	5.5 (5.6)	17.1 (17.2)	−0.03
$(py)_2CH_2$	B(b)	71	50.5 (50.9)	5.2 (5.3)	9.2 (9.1)	0.12
$(py)_2CHMe$	B(b)	65	52.7 (52.4)	5.5 (5.7)	8.7 (8.7)	0.12
$(py)_2CMe_2$	B(b)	62	53.8 (53.8)	5.9 (6.0)	8.6 (8.4)	0.14
$(pz)_2CH_2$[c]	A	56				0.11
$(pz)_2CHMe$	A	61	40.7 (40.2)	5.6 (5.4)	18.9 (18.8)	0.11
$(pz)_2CMe_2$	A	75	42.2 (42.2)	5.9 (5.8)	17.3 (18.0)	0.09
$(mim)_2CH_2$	B(a)	79	42.8 (42.3)	5.9 (5.8)	16.2 (17.9)	−0.09
$(mim)_2CHMe$	B(a)	49	43.7 (44.1)	6.1 (6.2)	17.0 (17.1)	−0.02
$(py)(pz)CH_2$	B(b)	54	44.6 (44.7)	5.0 (5.1)	14.1 (14.2)	0.14, 0.08
$(pz)(mim)CH_2$	B(a)	54	40.2 (40.2)	5.4 (5.3)	18.8 (18.5)	0.09, −0.01
$(py)(mim)CH_2$	B(a)	69	46.2 (46.5)	5.4 (5.5)	13.4 (13.6)	0.07, −0.07
(py)(mim)CHMe	B(a)	59	47.9 (48.2)	5.8 (5.9)	12.7 (13.0)	0.11, −0.03
$(CH_2SMe)_2$[d]	A	65				0.12
2 PPh_3[e]	B(a)	55				0.20
			$PdXMe(L_2)$[k]			
phen	D(a)	78	36.5 (36.4)	2.6 (2.6)	6.6 (6.5)	1.00
bpy	C, D(a), F	79[f]	33.4 (32.7)	2.7 (2.7)	7.2 (6.9)	0.83
bpy, Br	E	75	35.7 (37.0)	3.0 (3.1)	7.7 (7.8)	0.86
bpy, Cl[g]	E	73	41.4 (42.2)	3.5 (3.5)	8.6 (8.9)	0.86
py(mim)	D(a)	81	29.7 (29.5)	2.9 (3.0)	10.3 (10.3)	0.91
(py)(mim)C=O	D(a)	68	30.5 (30.3)	2.8 (2.8)	9.7 (9.7)	0.82
$(mim)_2C=O$	D(a)	88	27.9 (27.4)	3.0 (3.0)	12.9 (12.7)	insol
(py)(mim)C=CH_2	D(a)	66	33.1 (33.2)	3.4 (3.3)	9.6 (9.7)	0.77
$(mim)_2C=CH_2$	D(a)	82	30.7 (30.3)	3.5 (3.5)	12.6 (12.8)	0.60
$(py)_2CH_2$	C,[h] D(b)	76	34.3 (34.4)	3.1 (3.1)	6.6 (6.7)	0.77
$(py)_2CHMe$	D(b)	71	36.2 (36.1)	3.5 (3.5)	6.5 (6.5)	0.77, 0.78
$(py)_2CMe_2$	D(b)	62	37.3 (37.6)	3.9 (3.8)	6.3 (6.3)	0.79
$(pz)_2CH_2$	C,[h] D(a), F	51[i]	24.2 (24.2)	2.6 (2.8)	14.1 (14.1)	0.83
$(pz)_2CHMe$	D(a), F	69[i]	26.1 (26.3)	3.0 (3.2)	13.9 (13.7)	0.84
$(pz)_2CMe_2$	D(a), F	73[i]	28.3 (28.3)	3.5 (3.6)	13.2 (13.2)	0.83
$(pz)_2CMe_2$, Br	E	66	31.5 (31.8)	3.9 (4.0)	14.5 (14.8)	0.84
$(pz)_2CMe_2$, Cl	E	57	36.0 (36.1)	4.5 (4.5)	16.5 (16.8)	0.85
$(mim)_2CH_2$	D(a)	89	28.2 (28.3)	3.6 (3.6)	13.1 (13.2)	0.60
$(mim)_2CHMe$	D(a)	73	30.5 (30.1)	4.0 (3.9)	12.6 (12.8)	0.62
$(py)(pz)CH_2$	D(a)	57	29.6 (29.5)	3.0 (3.0)	10.2 (10.3)	0.87, 0.75
$(pz)(mim)CH_2$	D(b)	58	26.9 (26.3)	3.5 (3.2)	13.8 (13.7)	0.76, 0.66
$(py)(mim)CH_2$	D(a)	76	31.7 (31.3)	3.4 (3.4)	10.0 (10.0)	0.80
(py)(mim)CHMe	D(a)	76	34.6 (33.1)	3.8 (3.7)	10.0 (9.7)	0.80
$(CH_2SMe)_2$	F	69	16.6 (16.2)	3.5 (3.5)		0.83
2 PPh_3[e]	D(a)	82				0.23
2 PPh_3, Br[j]	E	79				0.08
2 PPh_3, Cl[j]	E	75				−0.03

[a] Legend: A, addition of L_2 to $PdCl_2(SMe_2)$/LiMe; B, addition of L_2 to $[PdMe_2(pyd)]_n$ in acetone (a) or benzene (b); C, reaction of $Pd_2(dba)_3(CHCl_3)$ with MeI, followed by addition of L_2; D, addition of L_2 to $[PdIMe(SMe_2)]_2$ in acetone (a) or benzene (b); E replacement of halide in $PdIMe(L_2)$; F, addition of L_2 to $PdCl_2(SMe_2)_2$/LiMe (from Li + MeI). [b] In $(CD_3)_2CO$ at ambient temperature, except for $PdMe_2\{(mim)_2CH_2\}$, recorded in $(CD_3)_2SO$, and the PPh_3 complexes and PdXMe(bpy) (X = Cl, Br), recorded in $CDCl_3$. [c] Insufficiently stable at ambient temperature for postage for microanalysis. [d] Previously reported;[16] yield is for method A. [e] Previously reported.[59] [f] Yield is for methods C and D(a). [g] Previously reported.[20] [h] Low yield with $Pd_2(dba)_3(CHCl_3)$ as reagent for these two complexes, but good yield for PdIMe(bpy) (79%). [i] Yield is for method F. [j] Previously reported.[60] [k] X = I unless indicated otherwise.

due to the very low solubility of $PdCl_2(bpy)$;[19] we found in preliminary studies that $PdCl_2\{(pz)_2CH_2\}$ does not give organometallic products on reaction with LiMe prepared from MeI, and thus this potential route has not been further explored.

In initial studies we found that oxidative addition of iodomethane to the dibenzylideneacetone complex $Pd_2(dba)_3(CHCl_3)$ in the presence of a ligand appeared to be a promising approach (method C in Table I), providing a convenient route to PdIMe(bpy) in 79% yield, but following low yields for similar reactions with the representative ligands $(py)_2CH_2$ and $(pz)_2CH_2$ this synthetic method was abandoned.

However, a procedure similar to that above for synthesis of $PdMe_2(L_2)$, but with the weaker methylating agent MgIMe, or LiMe prepared from Li and MeI, gave the complexes $PdIMe(L_2)$ (eq 9 and method F in Table I).

$$\textit{trans}\text{-}PdCl_2(SMe_2)_2 \xrightarrow[\text{or (i) LiMe/LiI/MeI, (ii) } L_2]{\text{(i) 2MgIMe, (ii) } L_2} PdIMe(L_2) \quad (9)$$

The Grignard route was only attempted for the synthesis of $PdIMe(L_2)$ (L = bpy, $(pz)_2CH_2$, $(pz)_2CHMe$, $(pz)_2CMe_2$), and although the method was satisfactory, the yields were lower and the products usually required recrystallization, so the method was abandoned following the successful

development of the methyllithium route.

As for the synthesis of $PdMe_2(L_2)$ with use of LiMe (method A, eq 8), solubility of the ligand in diethyl ether at low temperature is required. For syntheses of $PdIMe(L_2)$ involving methyllithium, it is assumed that residual iodomethane results in an oxidative-addition–reductive elimination (of ethane) sequence to generate $Pd^{II}IMe$ species prior to and/or after addition of L_2. For platinum, which forms alkylplatinum(IV) thioether complexes that do not readily undergo reductive-elimination reactions, a similar reactivity has been observed to give Pt^{IV} complexes that may be analogues of intermediates formed in eq 9; e.g., $[PtMe_2(\mu\text{-}SEt_2)]_2$ reacts with MeI to form isolable $[PtIMe_3(\mu\text{-}SEt_2)]_2$,[40] *cis*-$PtCl_2(SMe_2)_2$ reacts with LiMe to form isolable $[PtMe_2(\mu\text{-}SMe_2)]_2$ but with LiMe prepared from MeI to form isolable $[PtMe_4(\mu\text{-}SMe_2)]_2$,[41] and *cis*-$PtMe_2(SMe_2)_2$ reacts with a stoichiometric amount of MeI in acetone to form *fac*-$[PtIMe_3(SMe_2)_2]$, which could not be isolated due to loss of SMe_2.[42]

The reaction of *trans*-$PdCl_2(SMe_2)_2$ with 1 mol equiv of halide-free LiMe, i.e. in the *absence* of MeI, allows isolation of $[PdMe(SMe_2)(\mu\text{-}Cl)]_2$ in 45% yield,[43] but with 2 mol equiv of LiMe and subsequent addition of MeBr or MeI the complexes $[PdMe(SMe_2)(\mu\text{-}X)]_2$ (X = Br (41%), I (91%)) are formed.[43] Platinum(II) analogues of these dimers have not been isolated, although $[PtMe(SMe_2)(\mu\text{-}I)]_2$ has been detected spectroscopically.[44]

We have found that $[PdIMe(SMe_2)]_2$ is an excellent precursor for the synthesis of all of the $Pd^{II}IMe$ complexes, and since we initiated this study De Renzi et al. have also recognized the potential of $[PdClMe(SMe_2)]_2$[43] for the synthesis of the 2,9-dimethyl-1,10-phenanthroline complex $PdClMe(2,9\text{-}Me_2phen)$.[22] Neutral phosphine complexes are readily obtained, exemplified by the isolation of *trans*-$PdIMe(PPh_3)_2$ in 82% yield from acetone, and complexes of bidentate nitrogen donor ligands sensitive to LiMe are similarly obtained (eq 10, method D in Table I).

$$\tfrac{1}{2}[PdIMe(SMe_2)]_2 + L_2 \rightarrow PdIMe(L_2) + SMe_2 \qquad (10)$$

The complex is also a suitable precursor for the synthesis of bromo and chloro complexes (eq 11, method E in Table I). Thus, treatment of an acetonitrile solution with 2.4

$$\tfrac{1}{2}[PdIMe(SMe_2)]_2 \xrightarrow{\text{(i) } Ag^+\text{, filter; (ii) } X^-\text{, filter; (ii) } L_2} PdXMe(L_2) \qquad (11)$$

mol equiv of $AgNO_3$, followed by filtration to remove AgI, addition of 4.0 mol equiv of KBr in a small volume of acetone/water with subsequent removal of the remaining Ag^+ as AgBr, and addition of ligand, gave $PdBrMe(L_2)$. A similar procedure, but with the addition of ligand preceded by the addition of water and additional KCl with stirring for 15 min, gave the chloro analogues.

Method E has only been explored for bpy, $(pz)_2CMe_2$, and PPh_3 but is assumed to be applicable for the other ligands since bpy and $(pz)_2CMe_2$ are representative of the strong and weak donor ligands, respectively.

^{1}H NMR Characterization and Structure of the Complexes. ^{1}H NMR spectra of the $Pd^{II}Me_2$ complexes are generally readily assigned, with $\delta(PdMe_2)$ +0.38 to −0.1 ppm and with the donor rings exhibiting expected multiplets,[45] confirmation of assignments being obtained by shift correlation spectroscopy (COSY). Ligand resonances generally occur ca. 0.2–0.3 ppm downfield from free ligand values, in the absence of unusual effects (see below), with PdMe groups trans to pyridine and pyrazole groups at similar chemical shifts and ca. 0.15 ppm downfield from PdMe trans to 1-methylimidazole donors. For the $Pd^{II}X$-Me complexes δ(PdMe) occurs in the range 1.0–0.6 ppm, and donor rings cis to the halogen are discerned by the marked downfield shifts for the ligand proton nearest to the halogen; e.g., the H(6) proton adjacent to X in PdXMe(bpy) occurs at 9.13 (Cl), 9.31 (Br), and 9.53 ppm (I) compared with 8.70–8.73 ppm for the proton adjacent to PdMe (Figure 1), and the H(3) proton adjacent to X in $PdXMe\{(pz)_2CMe_2\}$ occurs at 7.90 (Cl), 8.00 (Br), and 8.11 (I) compared with 7.81–7.78 ppm for the proton adjacnt to MePd.

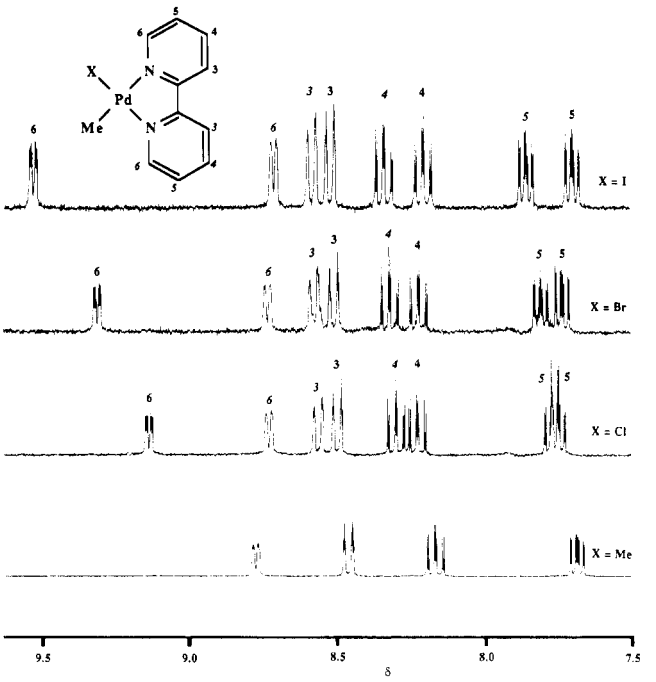

Figure 1. ^{1}H NMR spectra of PdXMe(bpy) in $(CD_3)_2CO$ in the region showing 2,2′-bipyridyl resonances, illustrating the effect of halide substitution on the chemical shift of *H(6)* adjacent to the halide.

For the $Pd^{II}IMe$ complexes of unsymmetrical ligands, mixtures of isomers are obtained, with the dominant isomers illustrated in Chart II. There is a marked preference for the pyridine donor to occur trans to the methyl group and for the pyrazole donor to occur trans to methyl in the $(pz)(mim)CH_2$ complex. Assignment of the structure follows directly from a comparison of spectra of related complexes, COSY spectra, and the expected downfield shifts for protons adjacent to the iodo ligand; e.g., for the isomers of $PdIMe\{(pz)(mim)CH_2\}$ shown in Figure 2 the dominant isomer has H(3)(pz ring) downfield from *H(3)* for the minor isomer and the minor isomer has *H(4′)*(mim ring) downfield from H(4′) for the major isomer.

The $Pd^{II}Me_2$ and $Pd^{II}Me$ complexes exhibit ^{1}H NMR spectra indicating the presence of fluxional and confor-

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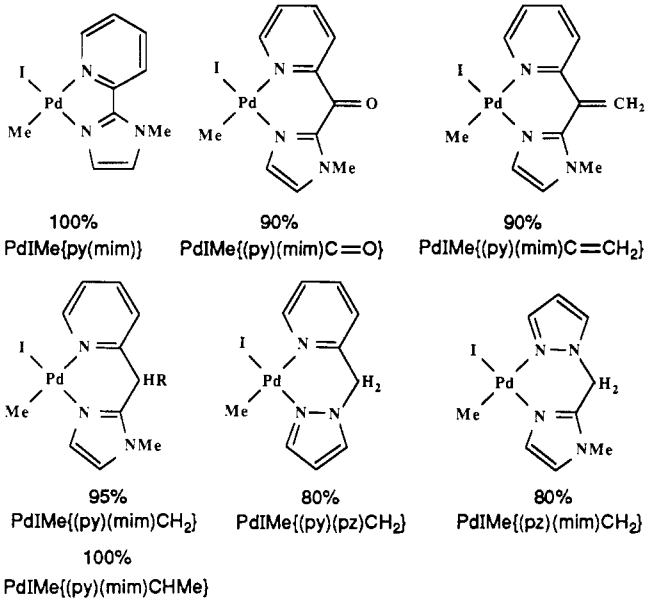
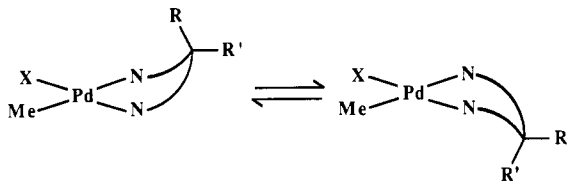
(45) The assignment of pyridine resonances is straightforward, and well-established criteria for the assignment of pyrazole resonances were used, in particular $J_{45} > J_{34}$ and broadening of the H3 signal by the nuclear quadrupole relaxation effect of N2: Elguero, J. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds. Pergamon Press: Oxford, U.K., 1984; Vol. 5, p 167. Esterulas, M. A.; Oro, L. A.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H.; Claramunt, R. M.; Lopez, C.; Elguero, J.; Begtrup, M. *J. Organomet. Chem.* **1988**, *344*, 93.

Chart II



mational behavior. The methane- and propane-bridged complexes undergo boat-to-boat inversion for the chelate ring, as reported for the dichloropalladium(II) complex $PdCl_2\{(pz)_2CMe_2\}$,[46] with a broad CH_2 (or CMe_2) resonance giving rise to two doublets (CH_2) or two singlets (CMe_2) at low temperature, except for the complexes of $(mim)_2CH_2$, $(py)(mim)CH_2$, and $(pz)(mim)CH_2$, which give a singlet for the methylene protons down to −70 °C consistent with more rapid inversion, and $PdIMe\{(py)_2CMe_2\}$, which has coalescence at >50 °C.

Except for the 1-methylimidazole-containing ligands (see below), the presence of one methyl group in the bridgehead position, together with the inversion process, results in equilibria between conformers:



X = Me or I: L = $(py)_2CH_2$, $(pz)_2CH_2$, $(py)(pz)CH_2$, $(mim)_2CH_2$, $(py)(mim)CH_2$, $(pz)(mim)CH_2$, $(pz)_2CHMe$, $(pz)_2CMe_2$
X = Me: L = $(py)_2CHMe$, $(py)_2CMe_2$
X = I: L = $(py)_2CHMe$, $(py)_2CMe_2$, with T_c > 50 °C

Thus, $PdMe_2\{(py)_2CHMe\}$ gives broad CH and CMe resonances at 50 °C, resolved into two quartets and two doublets at −10 °C with the conformers in a 1:1 ratio as shown in Figure 3. The downfield CH and CMe resonances are assigned to isomers A and B, respectively, as they occur ca. 0.5 ppm downfield from values for the other isomer and they are further downfield from the free ligand, with marked downfield shifts in other complexes associated with proximity to palladium.[47] Similar behavior is observed for $PdMe_2\{(pz)_2CHMe\}$ (2:1 ratio) and $PdIMe\{(pz)_2CHMe\}$ (3:2 ratio), but for $PdIMe\{(py)_2CHMe\}$ spectra showing conformers in a 9:11 ratio remain resolved up to 50 °C. Spectra for the isomers of $PdIMe\{(py)_2CHMe\}$ can

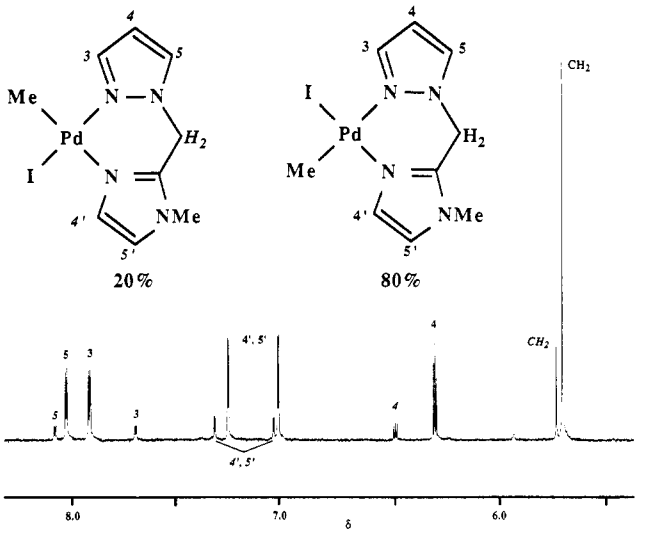
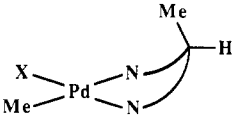


Figure 2. ^1H NMR spectrum of $PdIMe\{(pz)(mim)CH_2\}$ in $(CD_3)_2CO$ in the region of (1-methylimidazol-2-yl)(pyrazol-1-yl)methane resonances, showing the presence of isomers, with assignments based on COSY spectra, comparison with spectra of related complexes, and the expected downfield shift for ligand protons adjacent to the iodo ligand.

be assigned in the same manner as for the $Pd^{II}Me_2$ complex (downfield shifts with proximity to Pd), but similar assignments for the complexes of $(pz)_2CHMe$ are not straightforward since the CH and CMe chemical shifts are separated by only 0.07–0.22 ppm. The smaller chemical shift differences between axial and equatorial groups in the $(pz)_2CHMe$ complexes are assumed to reflect mainly the expected longer Pd···H and Pd···Me interactions compared with that in the $(py)_2CHMe$ complex, giving a smaller effect of palladium on the chemical shift of axial groups. Molecular models indicate that the presence of two five-membered rings in $(pz)_2CHMe$ results in less puckering for the boat conformation of the chelate ring, giving longer Pd···axial interactions than for ligands with two six-membered rings, and crystal structures of related complexes exhibit longer interactions for pyrazole-based ligands than pyridine-based ligands. Thus, although other factors are present, the complex $PdCl_2\{(pz)_2CMe_2\}$ has Pd···Me = 3.296 (3) Å[46] but $PdCl_2\{(py)_2C(OH)_2\}$ has Pd···OH = 2.824 (6) Å.[48]

For $Pd^{II}Me_2$ and $Pd^{II}Me$ complexes of $(mim)_2CHMe$ and $(py)(mim)CHMe$, spectra showing a single species or rapid equilibrium are observed down to −60 °C, with a single species favored, since molecular models indicate an unfavorable steric interaction would occur between the bridgehead methyl group and the 1-Me group(s) of the ring(s) in the conformer with the methyl group equatorial.



X = Me or I: L = $(mim)_2CHMe$, $(py)(mim)CHMe$

Experimental Section

Halide-free methyllithium was prepared from lithium shot (1% Na) and methyl chloride as described,[49] with the reaction vessel

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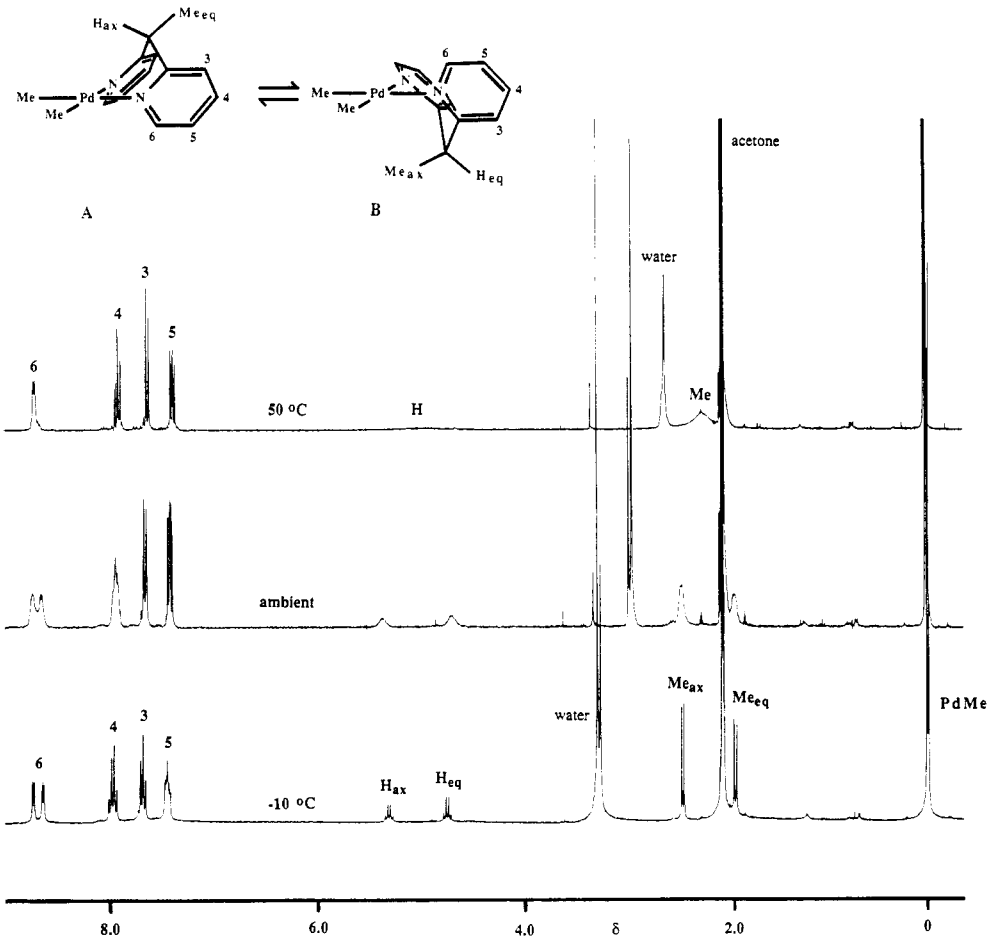

Figure 3. ^1H NMR spectra of $PdMe_2\{(py)_2CHMe\}$ at 50, 25, and −10 °C, illustrating exchange between conformers. At −10 °C the $Pd^{II}Me_2$ resonances are resolved into singlets at 0.09 and 0.11 ppm.

cooled in an ice bath to maintain reaction temperatures of ca. 25 °C and reaction times of ca. 1.5 h. Methyllithium (from Li and MeI), *n*-butyllithium, and phenyllithium were prepared by standard procedures. Both of the LiMe reagents and $LiBu^n$ were standardized before use, with 1,3-diphenyl-2-propanone tosylhydrazone (in tetrahydrofuran at 0 °C),[50] but LiPh was consistently formed in 95–100% yield and titration was found to be unneccesary. The reagents $Pd_2(dba)_3(CHCl_3)$[51] and $[PdIMe(SMe_2)]_2$[43] were prepared as reported, and *trans*-$PdCl_2(SMe_2)_2$ was prepared from *trans*-$PdCl_2(NCPh)_2$ and dimethyl sulfide in benzene with recrystallization effected by dissolution, filtration, and addition of petroleum ether. Solvents and reagents were purified as follows: acetone was treated with $KMnO_4$ at acetone reflux until the violet color persisted, followed by drying over $CaSO_4$ and distillation; benzene was washed with concentrated H_2SO_4, water, and 2 M NaOH and then refluxed and distilled from P_2O_5 and stored over sodium; bromobenzene was predried over $CaCl_2$, refluxed and distilled from Ca turnings, and stored over 4-Å molecular sieves; chloroform was washed with water, predried over $CaCl_2$, and then refluxed and distilled from P_2O_5 and stored in the dark; diethyl ether was predried over $CaCl_2$, passed through a column of sieves, refluxed and distilled from Na/benzophenone and stored over Na; iodomethane was distilled in the dark and stored at −20 °C over sieves; 1-methylimidazole was predried over K_2CO_3 for 24 h, distilled, and stored over sieves; tetrahydrofuran was predried over KOH, refluxed and distilled from Na/benzophenone, and stored over sodium.

Microanalyses were performed by the Australian Microanalytical Service, Melbourne, Australia, and the Canadian Microanalytical Service, Vancouver, Canada. Melting points were determined with a Reichart Thermo apparatus and stereomicroscope and are uncorrected. Infrared spectra were recorded on a Hitachi 270-30 infrared spectrophotometer as neat liquids or as Nujol mulls, and ^1H NMR spectra were recorded on a Bruker AM 300 spectrometer, with chemical shifts given in ppm relative to Me_4Si (acetone at 2.06 ppm for spectra in $(CD_3)_2CO$). Mass spectra were obtained with a Vacuum General Micromass 7070F spectrometer.

Dimethyl(pyridazine)palladium(II), $[PdMe_2(pyd)]_n$. Halide-free LiMe (11.9 mL, 10.3 mmol) was added to a suspension of *trans*-$PdCl_2(SMe_2)_2$ (1.5 g, 5.0 mmol) in diethyl ether (130 mL) at −60 °C under nitrogen. The resulting mixture was stirred with slow warming to −30 °C, giving a clear colorless solution with no unreacted palladium reagent; pyridiazine (0.38 mL, 5.2 mmol) in diethyl ether (10 mL) was added, followed by hydrolysis (ca. 2–5 mL) at ca. −15 °C and rapid filtration. The yellow-orange solid was washed well with water and several portions of dry diethyl ether, dried immediately under high vacuum at ambient temperature, and stored at −20 °C until required (0.75–0.85 g, 70–80%); mp 80 °C dec. ^1H NMR ($(CD_3)_2CO$): δ 9.23 (m, 2, H3,6), 7.98 (m, 2, H4,5), 0.06 (s, 2, PdMe).

Synthesis of Ligands. The ligands $(pz)_2CH_2$,[52] $(pz)_2CHMe$,[53] $(pz)_2CMe_2$,[53] py(mim),[54] $(py)_2CH_2$,[38] and $(py)_2CMe_2$[54] were prepared as reported, and pyridazine was distilled and stored at −20 °C; $(py)_2CHMe$ was prepared as reported,[55] and although a synthesis of $(py)(pz)CH_2$ has recently been reported,[56] an alter-

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native synthesis is described below. The only new ligands that formed as crystalline solids, $(mim)_2CH_2$ and $(mim)_2CHMe$, were subjected to microanalysis, but the remaining ligands formed as oils and were characterized by NMR and IR spectroscopy, mass spectra, and the formation of $Pd^{II}Me$ and $Pd^{II}Me_2$ derivatives.

(Pyridin-2-yl)(pyrazol-1-yl)methane, (py)(pz)CH_2. Pyrazole (4.9 g, 72.2 mmol) was added to a stirred suspension of potassium (2.8 g, 72.2 mmol) in tetrahydrofuran (150 mL) under nitrogen. After the initial rapid evolution of hydrogen the mixture was heated at reflux with stirring until beads of molten potassium were no longer evident. The thick white suspension was cooled, and 2-(chloromethyl)pyridine (4.6 g, 36.1 mmol, a *severe irritant*, prepared as reported[57]) was added in one portion, the mixture refluxed for 5 h, cooled, and filtered, and the solvent removed on a rotary evaporator. The product was obtained by vacuum distillation, giving (py)CH_2Cl followed by (py)(pz)CH_2 at 76–78 °C and 0.1 mmHg (10.2 g, 90%) as a colorless viscous oil, which solidifies on standing at ca. −20 °C. ^1H NMR ($(CD_3)_2CO$): δ 8.54 (d, J_{56} = 4.4 Hz, 1, H6), 7.78 (d, J_{45} = 2.2 Hz, 1, H5(pz)), 7.72 (ddd, $J_{45} \approx J_{34} \approx 7.7$ Hz, J_{46} = 1.8 Hz, 1, H4), 7.49 (d, J_{34} = 1.5 Hz, 1 H3(pz)), 7.28 (m, 1, H5), 6.98 (d, J_{34} = 7.7 Hz, 1 H3), 6.30 ("t", $J_{34} \approx J_{45}$ = 2.0 Hz, 1, H4(pz)), 5.36 (s, 2, CH_2). MS: m/e 159 (M, 100%), 81 (54%), 65 (46%).

(Pyrazol-1-yl)(1-methylimidazol-2-yl)methane, (pz)(mim)CH_2. Anhydrous ammonia gas was bubbled through a suspension of 2-(chloromethyl)-1-methylimidazole hydrochloride (5 g, 30 mmol, prepared as reported[58]) in anhydrous benzene for 10 min. The suspension was purged of excess ammonia by bubbling nitrogen through for 15 min with gentle warming to ca. 40 °C. Filtration under nitrogen, through a filter agent (Celite), gave a clear colorless solution of (mim)CH_2Cl, a *severe irritant*. Potassium pyrazolide (60 mmol, prepared as above) was added, the mixture refluxed for 5 h, cooled, and filtered, and the solvent removed by rotary evaporation. The product was obtained as a white solid on zone sublimation (3.44 g, 71%); mp 77–79 °C. ^1H NMR ($(CD_3)_2CO$): δ 7.59 (d, J_{45} = 2.1 Hz, 1 H5), 7.42 (d, $J_{34} \approx$ 1.3 Hz, 1, H3), 7.02 (d, 1, H4 or H5 (mim)) and 6.85 (d, J_{45} = 1.1 Hz, 1, H5 or H4 (mim)), 6.24 ("t", $J_{34} \approx J_{45}$ = 2.0 Hz, 1, H4), 5.40 (s, 2, CH_2), 3.72 (s, 3, NMe). IR: ν_{max} 1500, 1274, 1092, 1052, 938, 762, 676, 652, 628, 616 cm^{-1}. MS: m/e 162 (M, 30%), 161 (30%), 95 (100%), 94 (45%). Anal. Calcd for $C_8H_{10}N_4$: C, 59.2; H, 6.2; N, 34.5. Found: C, 59.1; H, 5.9; N, 34.2. An easier synthesis, requiring double the quantity of potassium pyrazolide, however, uses Kpz to neutralize (mim)CH_2Cl·HCl.

Bis(1-methylimidazol-2-yl)methanone, $(mim)_2C{=}O$, and Bis(1-methylimidazol-2-yl)methane, $(mim)_2CH_2$. Phenyllithium (from 2.64 g of lithium and 20 mL of bromobenzene) was added slowly to a suspension of 1-methylimidazole (15 mL) in diethyl ether (150 mL) at −60 °C under a nitrogen atmosphere, to give a light tan suspension that upon gradual warming to ca. −10 °C gave a purple solution. With the solution stirred efficiently and cooled by an ice/salt bath, carbon dioxide (dried by passage through P_2O_5) was passed over the solution surface at the slow rate of 130 mL min^{-1} for 1.5 h to give a thick white gelatinous suspension. Hydrolysis and careful addition of 4 M HCl until the aqueous phase was acidic gave a white emulsion, with passage through filter agent allowing separation of the organic and aqueous phases. Extraction of the organic phase with 4 M HCl (5 × 10 mL) and neutralization of the combined aqueous phases with Na_2CO_3, followed by filtration and continuous extraction of the filtrate with chloroform for 16 h, gave a brown oil on evaporation of chloroform. The oil was redissolved in chloroform, and the solution was dried over $MgSO_4$ and passed through a short silica column (vacuum). On evaporation of chloroform and dissolution in the minimum volume of dichloromethane, followed by addition of hexane and slow removal of dichloromethane under a vacuum at ambient temperature, $(mim)_2C{=}O$ formed as white crystals, which were collected, washed with hexane, and dried under high vacuum (8.7 g, 48%); mp 145–148 °C (lit.[36] mp 151 °C); ν(CO) as reported earlier.[35] ^1H NMR ($(CD_3)_2CO$): δ 7.38 (s, 2, H4 or H5), 7.12 (s, 2, H5 or H4), 3.98 (s, 6, 1-Me).

A Wolff–Kishner reduction of $(mim)_2C{=}O$ to $(mim)_2CH_2$ was achieved by a method analogous to that given by Newkome et al.[38] for the preparation of $(py)_2CH_2$, except that the reaction was performed for 4 h at 140 °C. When they were cooled, the contents of the bomb were extracted for 12 h with chloroform and the extracts dried over $MgSO_4$, filtered, and evaporated; dissolution of the brown solid in dichloromethane, and passage through a short silica column (vacuum) followed by addition of hexane and slow removal of dichloromethane under a vacuum at ambient temperature, gave $(mim)_2CH_2$ as cream-colored needles, which were collected, washed with hexane, and dried under high vacuum (65%); mp 143–148 °C. ^1H NMR ($(CD_3)_2CO$): δ 6.92 (d, 2, H4 or H5) and 6.77 (d, J_{45} = 1.1 Hz, 2, H5 or H4), 4.15 (s, 2, CH_2), 3.69 (s, 6, 1-Me). IR: ν_{max} 1528, 1412, 1192, 1170, 1146, 1096, 934, 788, 692 cm^{-1}. MS: m/e 176 (M, 100%), 175 (25%), 161 (20%), 96 (45%), 95 (75%). Anal. Calcd for $C_9H_{12}N_4$: C, 61.3; H, 6.9; N, 31.8. Found: C, 61.2; H, 6.9; N, 31.5.

(Pyridin-2-yl)(1-methylimidazol-2-yl)methanone, (py)(mim)C=O, and (Pyridin-2-yl)(1-methylimidazol-2-yl)methane, (py)(mim)CH_2. One mole equivalent of 2-lithio-1-methylimidazole, cooled to −50 °C by a jacketed dropping funnel, was added to a solution of ethyl pyridine-2-carboxylate in diethyl ether at −60 °C. The white suspension formed was worked up as described[35] to give yields of (py)(mim)C=O in the range 60–70%, with characterization data as reported.[35] ^1H NMR ($(CD_3)_2CO$): δ 8.70 (ddd, J_{56} = 4.7 Hz, J_{46} = 1.5 Hz, J_{36} = 0.9 Hz, 1, H6), 8.08 (m, J_{34} = 7.8 Hz, 1, H3), 7.95 (ddd, $J_{45} \approx J_{34} \approx 7.6$ Hz, J_{46} = 1.7 Hz, 1, H4), 7.55 (ddd, J_{45} = 7.5 Hz, J_{56} = 4.7 Hz, J_{35} = 1.3 Hz, 1 H5), 7.48 (s, 1, H4 or H5 (mim)), 7.15 (s, 1 H5 or H4 (mim)), 4.11 (s, 3, 1-Me).

Reduction of (py)(mim)C=O to (py)(mim)CH_2 was accomplished as described above for $(mim)_2C{=}O$, except that the bomb was heated for 3 h at 140 °C followed by 1 h at 160 °C. When they were cooled, the contents of the bomb were extracted for ca. 6 with chloroform and the extracts dried over $MgSO_4$, filtered, and evaporated to give a brown oil. Distillation at 100–110 °C and 0.22 mmHg gave (py)(mim)CH_2 as a clear, slightly yellow oil (81%) mp ca. 20 °C. ^1H NMR ($(CD_3)_2CO$): δ 8.47 (ddd, J_{56} = 4.8 Hz, J_{46} = 1.6 Hz, J_{36} = 1.0 Hz, 1, H6), 7.68 (ddd, $J_{45} \approx J_{34} \approx J_{46} \approx 1.9$ Hz, 1, H4), ca. 7.20 (m, 2, H3 and H5), 6.97 (d, 1 H4 or H5 (mim)) and 6.81 (d, J_{45} = 1.2 Hz, 1, H5 or H4 (mim)), 4.22 (s, 2, CH_2), 3.64 (s, 3, 1-Me). IR: ν_{max} 1592, 1572, 1520, 1498, 1476, 1436, 1412, 1282, 1122, 1084, 996, 908, 752 cm^{-1}. MS: m/e 173 (M, 100%), 172 (45%), 158 (20%), 131 (15%), 93 (55%), 81 (25%), 78 (15%).

1,1-Bis(1-methylimidazol-2-yl)ethan-1-ol, $(mim)_2C(OH)Me$, 1,1-Bis(1-methylimidazol-2-yl)ethene, $(mim)_2C{=}CH_2$, and 1,1-Bis(1-methylimidazol-2-yl)ethane, $(mim)_2CHMe$. *n*-Butyllithium (95 mL, 95 mmol) was added to a suspension of 1-methylimidazole (5.5 mL, 95 mmol) in diethyl ether at −60 °C under nitrogen and the suspension allowed to warm slowly to ca. −10 °C before recooling to −60 °C to give a solution virtually free of solids. Ethyl acetate (4.6 mL, 47 mmol) was added in one portion to produce a thick suspension, which was allowed to warm slowly to ambient temperature, followed by further stirring for 2 h. The suspension was carefully hydrolyzed with 4 M HCl until the aqueous phase was acidic, the organic and aqueous phases were separated, and the organic phase was extracted with 4 M HCl (4 × 10 mL). The combined aqueous phases were basified with Na_2CO_3 and continuously extracted for 16 h with chloroform; the chloroform extract was dried over $MgSO_4$, filtered, and evaporated, and the residue was dissolved in dichloromethane. Addition of hexane and slow removal of dichloromethane under a vacuum at ambient temperature gave $(mim)_2C(OH)Me$ as a white crystalline solid, which was collected, washed with diethyl ether, and dried under high vacuum (4.7 g, 48%); mp 172–173 °C. ^1H NMR ($CDCl_3$): δ 6.96 (d, 2, H4 or H5) and 6.81 (d, J_{45} = 1.1 Hz, 2, H5 or H4), 5.51 (s (br), 1, COH), 3.28 (s, 6, 1-Me), 2.05 (s, 3, CMe). IR: ν_{max} ca. 3110, 1288, 1206, 1120, 934, 772, 730 cm^{-1}. MS: m/e 206 (M, 20%), 191 (90%), 163 (30%), 125 (35%), 109 (100%), 107 (35%), 96 (30%), 83 (60%).

A solution of $(mim)_2C(OH)Me$ (3.5 g) in concentrated H_2SO_4 (ca. 50 mL) was heated to 170 °C for 48 h. The brown solution was cooled in ice and neutralized *carefully* with saturated NaOH to give precipitated Na_2SO_4, an aqueous phase, and the crude product as an insoluble oil. The mixture was filtered, the residue

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was washed with several portions of chloroform, the phases were separated, and the aqueous phase was extracted with chloroform (4 × 10 mL). The combined organic extracts were passed through a short silica column (vacuum) and evaporated to give **$(mim)_2C{=}CH_2$** as a tan-colored oil, which crystallized on standing (63%); mp 65–70 °C. ^1H NMR ($(CD_3)_2CO$): δ 7.09 (d, 2, H4 or H5) and 6.94 (d, J_{45} = 1.0 Hz, 2, H5 or H4), 5.87 (s, 2, CH_2), 3.35 (s, 6, 1-Me). IR: ν_{max} 1708, 1620, 1524, 1472, 1410, 1284, 1146, 1078, 1042, 938, 924, 858, 760, 734 cm^{-1}. MS: *m/e* 188 (M, 100%), 187 (75%), 173 (40%), 172 (20%), 107 (30%).

The alkene $(mim)_2C{=}CH_2$ was dissolved in ethanol and quantitatively hydrogenated (^1H NMR verification) over 3 h with hydrogen (60 psi) with use of 5% Pd on charcoal as a catalyst. On completion the mixture was filtered and evaporated and the crude product recrystallized from dichloromethane/hexane to give **$(mim)_2CHMe$** as white needles (85%), mp 82–83 °C. ^1H NMR ($(CD_3)_2CO$): δ 6.94 (d, 2, H4 or H5) and 6.80 (d, J_{45} = 1.1 Hz, 2, H5 or H4), 4.56 (q, 1, CH) and 1.70 (d, J_{HMe} = 7.3 Hz, 3, CMe), 3.45 (s, 6, 1-Me). IR: ν_{max} 1500, 1408, 1280, 1142, 1132, 1088, 1042, 772, 744, 700 cm^{-1}. MS: *m/e* 190 (M, 60%), 189 (30%), 175 (45%), 109 (40%), 107 (35%), 96 (100%), 95 (50%). Anal. Calcd for $C_{10}H_{14}N_4$: C, 63.1; H, 7.4; N, 29.4. Found: C, 62.9; H, 7.4; N, 28.9.

2-(Pyridin-2-yl)-2-(1-methylimidazol-2-yl)ethan-1-ol, (py)(mim)C(OH)Me, 1-(Pyridin-2-yl)-1-(1-methylimidazol-2-yl)ethene, (py)(mim)C=CH_2, and 1-(Pyridin-2-yl)-1-(1-methylimidazol-2-yl)ethane, (py)(mim)CHMe. Phenyllithium (from 1.32 g of lithium and 9.9 mL of bromobenzene) was added to a solution of 1-methylimidazole (7.5 mL, 95 mmol) in diethyl ether (10 mL) under nitrogen at −50 °C. The resulting suspension was allowed to warm slowly to −10 °C over ca. 1 h, producing a solution virtually free of solids, and to the recooled solution (−60 °C) was added 2-acetylpyridine (10 mL, 90 mmol) in diethyl ether (10 mL) dropwise. A thick white suspension that formed slowly was warmed gradually to ambient temperature, followed by further reaction for 2 h. The suspension was hydrolyzed with 5 M HCl (30 mL), and the organic and aqueous layers were separated, followed by extraction of the organic phase with 5 M HCl (2 × 5 mL). The combined aqueous phases were basified (Na_2CO_3) and continuously extracted with chloroform for 12 h and the chloroform extract was dried ($MgSO_4$), filtered, and evaporated to give a brown oil. Distillation of the oil under high vacuum removed 1-methylimidazole and 2-acetylpyridine (NMR identification). The residue was dissolved in chloroform and passed through a short silica column (vacuum), and after evaporation a yellow oil was obtained, which crystallized on standing. Recrystallization from dichloromethane/hexane gave **(py)(mim)C(OH)Me** as white plates (64%), mp 46–49 °C. ^1H NMR ($CDCl_3$): δ 8.56 (ddd, J_{56} = 4.2 Hz, J_{46} = 1.6 Hz, J_{36} = 1.0 Hz, 1, H6), 7.67 (ddd, $J_{45} \approx J_{34} \approx$ 7.8 Hz, J_{46} = 1.7 Hz, 1, H4), 7.25 (m, 1, H5), 7.13 (m, J_{34} = 8.0 Hz, 1, H3), 6.96 (d, 1 H4 or H5 (mim)) and 6.77 (d, J_{45} = 1.2 Hz, 1, H5 or H4 (mim)), 3.35 (s, 3, 1-Me), 1.99 (s, 3, Me). IR: ν_{max} 1648, 1284, 1220, 1156, 1130, 1090, 1072, 934, 792, 764, 754, 730, 672 cm^{-1}. MS: *m/e* 203 (M, 30%), 188 (95%), 184 (20%), 160 (20%), 125 (95%), 122 (30%), 106 (50%), 93 (20%), 78 (100%).

Dehydration of (py)(mim)C(OH)Me to **(py)(mim)C=CH_2** was achieved by a method analogous to that described for $(mim)_2C{=}CH_2$. Passage through a silica column, followed by evaporation of chloroform, gave a yellow oil (76%). ^1H NMR ($(CD_3)_2CO$): δ 8.58 (ddd, J_{56} = 4.6 Hz, J_{46} = 1.6 Hz, J_{36} = 0.9 Hz, 1, H6), 7.76 (ddd, $J_{45} \approx J_{34} \approx$ 7.9 Hz, J_{46} = 1.9 Hz, 1, H4), 7.31 (m, 2, H3,5), 7.13 (d, 1, H4 or H5 (mim)) and 6.98 (d, J_{45} = 0.9 Hz, 1, H5 or H4 (mim)), 6.52 (d, 1, CH_2) and 5.70 (d, J_{HH} = 1.8 Hz, 1, CH_2), 3.50 (s, 3, 1-Me). IR: ν_{max} 2948, 1586, 1566, 1470, 1432, 1408, 1282, 1150, 924, 804, 760, 664 cm^{-1}. MS: *m/e* 185 (M, 50%), 184 (100%), 107 (10%), 78 (15%).

Hydrogenation of (py)(mim)C=CH_2 to give **(py)(mim)CHMe** was achieved by an method identical with that for $(mim)_2CHMe$. After filtration and evaporation of ethanol, the crude product was distilled at 132–144 °C and 0.15 mmHg to give a clear, slightly yellow oil (79%). ^1H NMR ($(CD_3)_2CO$): δ 8.49 (d, J_{56} = 4.4 Hz, 1, H6), 7.68 (ddd, $J_{45} \approx J_{34} \approx$ 7.6 Hz, J_{46} = 1.8 Hz, 1, H4), 7.20 (ddd, $J_{45} \approx$ 7.4 Hz, J_{56} = 4.9 Hz, J_{35} = 1.1 Hz, 1, H5), 7.11 (m, J_{34} = 7.9 Hz, 1, H3), 6.95 (d, 1, H4 or H5 (mim)) and 6.86 (d, J_{45} = 1.1 Hz, 1, H5 or H4 (mim)), 4.48 (q, 1, CH) and 1.69 (d, J_{HMe} = 7.2 Hz, 3, CMe), 3.48 (s, 3, 1-Me). IR: ν_{max} 2976, 1592, 1494, 1472, 1434, 1280, 1140, 1062, 994, 752 cm^{-1}. MS: *m/e* 187 (M, 75%), 186 (40%), 172 (25%, 109 (100%), 106 (20%), 93 (25%), 78 (20%).

Synthesis of Dimethylpalladium(II) Complexes. Method A. Halide-free LiMe (16 mL, 11.0 mmol) was added to a suspension of *trans*-$PdCl_2(SMe_2)_2$ (1.5 g, 5.0 mmol) in diethyl ether (280 mL) at −60 °C under a nitrogen atmosphere. The suspension was stirred with slow warming until a clear, colorless solution had formed (ca. −40 °C), followed by addition of $(pz)_2CMe_2$ (0.87 g, 5.0 mmol) at −60 °C and gradual warming to −15 °C. Hydrolysis (2 mL), filtration, separation and drying of the organic phase ($MgSO_4$), and slow removal of diethyl ether at 0 °C under a vacuum to half the original volume, followed by addition of hexane (30 mL) and further removal of diethyl ether at 0 °C, gave a white crystalline solid. The solid was collected, washed with cold (0 °C) diethyl ether and hexane (10 mL), and dried under high vacuum. The filtrate plus washings were evaporated further to give another crop, which was treated as above. The product formed, **$PdMe_2\{(pz)_2CMe_2\}$** (white, 1.17 g, 75%), did not require recrystallization but may be recrystallized with difficulty from acetone/hexane at −70 °C. ^1H NMR ($(CD_3)_2CO$): ambient temperature, δ 8.16 (dd, J_{45} = 2.7 Hz, J_{35} = 0.8 Hz, 2, H5), 7.67 (dd, J_{34} = 1.9 Hz, J_{35} = 0.7 Hz, 2, H3), 6.40 (dd, J_{34} = 2.1 Hz, J_{45} = 2.7 Hz, 2, H4), 2.75 (s, 6, CMe), 0.09 (s, 6, PdMe); −60 °C, δ 2.86 (s, 3, CMe) and 2.62 (s, 3, CMe), other resonances as above, T_c ca. −20 °C. A procedure identical with that above was used for the following complexes; ^1H NMR spectra are for solutions in $(CD_3)_2CO$ unless indicated otherwise.

$PdMe_2$(bpy) (yellow-orange) is insoluble in diethyl ether and was collected by filtration after hydrolysis. ^1H NMR: δ 8.78 (ddd, J_{56} = 5.3 Hz, J_{46} = 1.6 Hz, J_{36} = 0.8 Hz, 2 H6), 8.46 (m, J_{34} = 8.1 Hz, $J_{35} \approx$ 1 Hz, 2, H3), 8.17 (ddd, J_{34} = 8.1 Hz, J_{45} = 7.6 Hz, J_{46} = 1.7 Hz, 2, H4), 7.69 (ddd, J_{45} = 7.6 Hz, J_{56} = 5.2 Hz, J_{35} = 1.2 Hz, 2, H5), 0.24 (s, 6, PdMe).

$PdMe_2\{(pz)_2CH_2\}$ is white, unstable, and not amenable to recrystallization, and thus a correct microanalysis could not be obtained. ^1H NMR: ambient temperature, δ 8.02 (d, J_{45} = 2.4 Hz, 2, H5), 7.65 (d, J_{34} = 1.7 Hz, 2, H3), 6.71 (s, 2, CH), 6.40 ("t", $J_{34} \approx J_{45} \approx$ 2.1 Hz, 2, H4), 0.11 (s, 6, PdMe); −30 °C, δ 6.89 (d, 1, CH) and 6.58 (d, J_{HH} = 14.1 Hz, 1, CH), other resonances as above, T_c ca. −10 °C.

$PdMe_2\{(pz)_2CHMe\}$ (white). ^1H NMR: ambient temperature, δ 8.09 (d, 2, H5), 7.66 (d, 2, H3), 7.16 (q, 1, CH), 6.40 ("t", 2, H4), 2.53 (d, 3, CMe), 0.11 (s, 6, PdMe); −30 °C, conformer I, δ 8.06 (d, J_{45} = 2.4 Hz, 2, H5), 7.69 (d, J_{34} = 1.9 Hz, 2, H3), 7.25 (q, 1, CH) and 2.54 (d, J_{HMe} = 6.7 Hz, 3, CMe), 6.41 ("t", $J_{34} \approx J_{45}$ = 2.4 Hz, 2, H4), 0.08 (s, 6, PdMe); conformer II, δ 8.20 (d, J_{45} = 2.7 Hz, 2, H5), 7.62 (d, J_{34} = 1.8 Hz, 2, H3), 7.03 (q, 1, CH) and 2.46 (d, J_{HMe} = 7.0 Hz, 3, CMe), 6.44 ("t", $J_{34} \approx J_{45}$ = 2.3 Hz, 2, H4), 0.06 (s, 6, PdMe); conformers I and II in ca. 2:1 ratio, T_c ca. −8 °C.

$PdMe_2\{(CH_2SMe)_2\}$ (buff). ^1H NMR: δ 2.96 (s, 4, CH_2), 2.27 (s, 6, SMe), 0.12 (s, 6, PdMe).

Method B. A solution of $(py)_2CH_2$ (0.32 g, 1.90 mmol) in benzene (20 mL) was added with stirring to solid $[PdMe_2(pyd)]_n$ (0.40 g, 1.85 mmol) to give a clear, slightly yellow solution. Filtration followed by evaporation of benzene at ambient temperature under a vacuum to ca. 20 mL and addition of hexane (10–20 mL) gave a white crystalline solid. The product, **$PdMe_2\{(py)_2CH_2\}$** (cream) was collected, washed with cold (0 °C) diethyl ether (10 mL) followed by hexane (10 mL), and dried under high vacuum (0.40 g, 71%). The complex did not require recrystallization. ^1H NMR ($(CD_3)_2CO$): ambient temperature, δ 8.61 (ddd, J_{56} = 5.3 Hz, J_{46} = 1.6, J_{36} = 0.8 Hz, 2, H6), 7.88 (ddd, $J_{45} \approx J_{34} \approx$ 7.7 Hz, J_{46} = 1.7 Hz, 2, H4), 7.64 (m, $J_{34} \approx$ 8, $J_{35} \approx$ 1 Hz, 2, H3), 7.38 (ddd, J_{45} = 7.6 Hz, J_{56} = 5.4 Hz, J_{35} = 1.3 Hz, 2, H5), 4.61 (s (br), 2, CH_2), 0.12 (s, 6, PdMe); −40 °C, δ 4.68 (d, 1, CH) and 4.52 (d, J_{HH} = 13.1 Hz, 1, CH), with T_c ca. 0 °C.

A procedure similar to that described, with acetone or benzene as solvent (Table I), gave the following $Pd^{II}Me_2$ complexes.

$PdMe_2$(phen) (orange). ^1H NMR: δ 9.12 (dd, J_{23} = 4.9 Hz, J_{24} = 1.5 Hz, 2, H2,9), 8.76 (dd, J_{34} = 8.2 Hz, J_{24} = 1.5 Hz, 2, H4,7), 8.17 (s, 2, H5,6), 8.04 (dd, J_{23} = 4.9 Hz, J_{34} = 8.2 Hz, 2, H3,8), 0.38 (s, 6, PdMe).

$PdMe_2${py(mim)} (yellow). ^1H NMR: δ 9.31 (d, J_{56} = 5.0 Hz, 1, H6), ca. 8.15 (m, 2, H3,4), 7.56 (ddd, J_{56} = 5.2 Hz, J_{45} = 7.1 Hz, J_{35} = 1.8 Hz, 1, H5), 7.42 (s, 1, H4 or H5 (mim)) and 7.12 (s, 1, H5 or H4 (mim)), 4.22 (s, 3, 1-Me), 0.24 (s, 3, PdMe trans to py), 0.05 (s, 3, PdMe trans to mim).

$PdMe_2${(py)(mim)C=O} (red). ^1H NMR: δ 8.89 (dd, J_{56} = 5.4 Hz, J_{46} = 1 Hz, 1, H6), 8.22 (m, 2, H3,4), 7.76 (ddd, J_{56} = 5.3 Hz, J_{45} = 7.8 Hz, J_{35} = 1.9 Hz, 1, H5), 7.63 (d, 1, H4 or H5 (mim)) and 7.32 (d, J_{45} = 1.1 Hz, 1, H5 or H4 (mim)), 4.10 (s, 3, 1-Me), 0.08 (s, 3, PdMe trans to py), −0.06 (s, 3, PdMe trans to mim).

$PdMe_2${$(mim)_2C$=O} (orange). ^1H NMR: δ 7.59 (d, 2, H4 or H5) and 7.39 (d, J_{45} = 1.2 Hz, 2, H5 or H4), 4.17 (s, 6 1-Me), 0.10 (s, 6, PdMe).

$PdMe_2${(py)(mim)C=CH_2} (pale orange). ^1H NMR: δ 8.72 (d, J_{56} = 5.3 Hz, 1, H6), 7.98 (ddd, $J_{45} \approx J_{34}$ = 7.7 Hz, J_{46} = 1.6 Hz, 1, H4), 7.78 (d, J_{34} = 7.8 Hz, 1, H3), 7.45 (ddd, J_{56} = 5.4 Hz, J_{45} = 7.7 Hz, J_{35} = 1.3 Hz, 1, H5), 7.25 (d, 1, H4 or H5 (mim)) and 7.03 (d, J_{45} = 1.3 Hz, 1, H5 or H4 (mim)), 6.25 (s, 1, CH trans to py), 6.01 (s, 1, CH trans to mim), 3.88 (s, 3, 1-Me), 0.08 (s, 3, PdMe trans to py), −0.10 (s, 3, PdMe trans to mim).

$PdMe_2${$(mim)_2C$=CH_2} (white). ^1H NMR: δ 7.20 (d, 2, H4 or H5) and 7.05 (d, J_{45} = 1.4 Hz, 2, H5 or H4), 6.16 (s, 2, CH_2), 3.92 (s, 6, 1-Me), −0.03 (s, 6, PdMe).

$PdMe_2${$(py)_2$CHMe} (white, Figure 3). ^1H NMR: 50 °C, δ 8.68 (d, 2, H6), 7.87 (ddd, 2, H4), 7.58 (m, 2, H3), 7.34 (ddd, 2, H5), ca. 5.2 (s, 1, CH), ca. 2.4 (s, 3, CMe), 0.14 (s, 6, PdMe); −10 °C conformer A, δ 5.26 (q, 1, CH(ax)) and 1.95 (d, J_{HMe} = 7.5 Hz, 3, CMe(eq)); conformer B, δ 4.70 (q, 1, CH(eq)) and 2.45 (d, J_{HMe} = 7.2 Hz, 3, CMe(ax)); conformers A and B, δ 8.69 (d, J_{56} = 5.4 Hz, 1, H6), 8.59 (d, J_{56} = 5.2 Hz, 1, H6), 7.92 (m, 2, H4), 7.63 (m, 2, H3), 7.40 (m, 2, H5), 0.11 (s, 3, PdMe), 0.09 (s, 3, PdMe).

$PdMe_2${$(py)_2CMe_2$} (white). ^1H NMR: ambient temperature, δ 8.78 (dd, J_{56} = 5.2 Hz, J_{46} = 1.9 Hz, 2, H6), 7.89 (ddd, $J_{45} \approx J_{34} \approx$ 7.8 Hz, J_{46} = 1.9 Hz, 2, H4), 7.73 (d, J_{34} = 7.8 Hz, 2, H3), 7.34 (m, 2, H5), ~3.0 (CMe(ax), obscured by weater), ~2.2 (CMe(eq), obscured by acetone), 0.14 (s, 6, PdMe); −10 °C, δ 2.84 (s, 3, CMe(ax)), 2.22 (s, 3, CMe(eq)), other resonances as at ambient temperature, T_c ca. 35 °C.

$PdMe_2${$(mim)_2CH_2$} (white). ^1H NMR ($(CD_3)_2SO$): δ 7.26 (d, 2, H4 or H5) and 6.96 (d, J_{45} = 1.4 Hz, 2, H5 or H4), 4.26 (s, 2, CH_2), 3.80 (s, 6, 1-Me), −0.09 (s, 6, PdMe).

$PdMe_2${$(mim)_2$CHMe} (white). ^1H NMR: δ 7.03 (d, 2, H4 or H5) and 6.96 (d, J_{45} = 1.4 Hz, 2, H5 or H4), 4.68 (q, 1, CH(eq)) and 1.70 (d, J_{HMe} = 7.0 Hz, 3, CMe(ax)), 3.86 (s, 6, 1-Me), −0.02 (s, 6, PdMe).

$PdMe_2${(py)(pz)CH_2} (pale yellow). ^1H NMR: ambient temperature, δ 8.69 (dd, J_{56} = 5.2 Hz, J_{46} = 1.4 Hz, 1, H6), 7.97 (m, 2, H4 (py) and H5 (pz)), 7.70 (d, J_{34} = 7.6 Hz, 1, H3), 7.57 (d, J_{34} = 1.6 Hz, 1, H3 (pz)), 7.51 (ddd, J_{45} = 7.8 Hz, J_{56} = 5.4 Hz, J_{35} = 1.2 Hz, 1, H5), 6.34 ("t", $J_{34} \approx J_{45}$ = 2.2 Hz, 1, H4 (pz)), 5.71 (s, 2, CH_2), 0.14 (s, 3, PdMe), 0.08 (s, 3, PdMe); −50 °C, δ 5.71 (d, 1, CH) and 5.64 (d, J_{HH} = 14.4 Hz, 1, CH).

$PdMe_2${(pz)(mim)CH_2} (white). ^1H NMR: δ 7.95 (dd, J_{45} = 2.5 Hz, J_{35} = 0.7 Hz, 1, H5), 7.60 (dd, J_{34} = 2.1 Hz, J_{35} = 0.8 Hz, 1, H3), 7.11 (d, 1, H4 or H5 (mim)) and 6.96 (d, J_{45} = 1.3 Hz, 1, H5 or H4 (mim)), 6.32 (dd, J_{45} = 2.5 Hz, J_{34} = 2.1 Hz, 1, H4), 3.9 (s, 3, 1-Me), 5.57 (s, 2, CH_2), 0.09 (s, 3, PdMe trans to pz), −0.01 (s, 3, PdMe trans to mim).

$PdMe_2${(py)(mim)CH_2} (yellow). ^1H NMR: δ 8.65 (dd, J_{56} = 5.4 Hz, $J_{46} \approx$ 1.3 Hz, 1, H6), 7.90 (ddd, $J_{45} \approx J_{34} \approx$ 7.6 Hz, J_{46} = 1.7 Hz, 1, H4), 7.68 (d, J_{34} = 7.6 Hz, 1, H3), 7.42 (ddd, J_{56} = 5.4 Hz, J_{45} = 7.6 Hz, J_{35} = 1.3 Hz, 1, H5), 7.11 (d, 1, H4 or H5 (mim)) and 6.88 (d, J_{45} = 1.4 Hz, 1, H5 or H4 (mim)), 4.34 (s, 2, CH_2), 3.86 (s, 3, 1-Me), 0.07 (s, 3, PdMe trans to py), −0.07 (s, 3, PdMe trans to mim).

$PdMe_2${(py)(mim)CHMe} (white). ^1H NMR: δ 8.76 (dd, J_{56} = 5.1 Hz, J_{46} = 1.4 Hz, 1, H6), 7.87 (ddd, $J_{45} \approx J_{34} \approx$ 7.6 Hz, J_{46} = 1.8 Hz, 1, H4), 7.60 (m, J_{34} = 7.8 Hz, 1, H3), 7.36 (m, 1, H5), 7.04 (d, 1, H4 or H5 (mim)) and 6.92 (d, J_{45} = 1.4 Hz, 1, H5 or H4 (mim)), 4.71 (q, 1, CH(eq)) and 2.14 (d, J_{HMe} = 7.1 Hz, 3, CMe(ax)), 3.86 (s, 3, 1-Me), 0.11 (s, 3, PdMe trans to py), −0.03 (s, 3, PdMe trans to mim).

Synthesis of Methylpalladium(II) Complexes. Method C. Iodomethane (0.5 mL, 8.03 mmol) and 2,2′-bipyridyl (0.09 g, 0.61 mmol) were added to a suspension of $Pd_2(dba)_3(CHCl_3)$ (0.275 g, 0.27 mmol) in benzene (30 mL) at 0 °C with stirring under nitrogen. The mixture was slowly warmed to ca. 50 °C to give a yellow solution containing an orange-tan solid. Evaporation to dryness, followed by extraction of the solid with diethyl ether (4 × 10 mL) to remove dba, gave crude PdMeI(bpy). Recrystallization from hot acetone or dichloromethane/hexane gave pure yellow **PdIMe(bpy)** (0.17 g, 79%, NMR identification).

A similar procedure, with recrystallization from acetone/hexane, gave PdIMe{$(pz)_2CH_2$} and PdIMe{$(py)_2CH_2$} in 11% and 39% yields, respectively.

Method D. An acetone solution (10 mL) of 2,2′-bipyridyl (0.15 g, 0.96 mmol) was added to a stirred suspension of $[PdIMe(SMe_2)]_2$ (0.30 g, 0.48 mmol) in acetone (20 mL). The suspension quickly cleared to give a yellow solution; filtration followed by addition of hexane (20 mL) and slow removal of acetone under a vacuum at ambient temperature gave **PdIMe(bpy)** as a yellow powder (79%). ^1H NMR ($(CD_3)_2CO$, incorrectly reported in preliminary communication):[29] py trans to PdMe, δ 9.53 (ddd, J_{56} = 5.3 Hz, J_{46} = 1.7 Hz, J_{36} = 0.8 Hz, 1, H6), 8.51 (m, J_{34} = 8.1 Hz, $J_{35} \approx$ 1 Hz, 1, H3), 8.20 (ddd, J_{34} = 8.1 Hz, J_{45} = 7.6, J_{46} = 1.7 Hz, 1, H4), 7.70 (ddd, J_{45} = 7.6 Hz, J_{56} = 5.3 Hz, J_{35} = 1.2 Hz, 1, H5); py trans to PdI, δ 8.70 (m, J_{56} = 5.6 Hz, 1, H6), 8.58 (m, J_{34} = 8.1 Hz, J_{35} = 1.4 Hz J_{36} = 0.8 Hz, 1, H3), 8.34 (ddd, J_{34} = 8.1 Hz, J_{45} = 7.6 Hz, J_{46} = 1.6 Hz, 1, H4), 7.85 (ddd, J_{45} = 7.6 Hz, J_{56} = 5.6 Hz, J_{35} = 1.4 Hz, 1, H5); δ 0.83 (s, 3, PdMe).

A procedure similar to that described, with acetone or benzene as a solvent (Table I), gave the following $Pd^{II}Me$ complexes.

PdIMe(phen) (yellow). ^1H NMR: ring trans to PdMe (H2,3,4), δ 9.77 (dd, J_{23} = 4.9 Hz, J_{24} = 1.7 Hz, 1, H2), 8.81 (dd, J_{34} = 8.2 Hz, J_{24} = 1.8 Hz, 1, H4), 8.06 (dd, J_{34} = 8.2 Hz, J_{23} = 4.9 Hz, 1, H3); ring trans to PdI (H7,8,9), δ 9.08 (dd, J_{89} = 5.1 Hz, $J_{79} \approx$ 1.2 Hz, 1, H9), 8.94 (dd, J_{78} = 8.1 Hz, J_{79} = 1.4 Hz, 1, H7), 8.19 (dd, J_{78} = 8.2 Hz, J_{89} = 5.2 Hz, 1, H8); other protons, δ 8.25 (s, 2, H5,6), 1.00 (s, 3, PdMe).

PdIMe{py(mim)} (cream). ^1H NMR: δ 9.31 (ddd, J_{56} = 5.2 Hz, J_{46} = 1.7 Hz, J_{36} = 0.9 Hz, 1, H6), 8.21 (d, J_{34} = 8.1 Hz, 1, H3), 8.14 (ddd, $J_{45} \approx J_{34} \approx$ 8.1 Hz, J_{46} = 1.7 Hz, 1, H4), ca. 7.58 (m, H5, obscured), 7.56 (d, 1, H4 or H5 (mim)) and 7.21 (d, J_{45} = 1.4 Hz, 1, H5 or H4 (mim)), 4.31 (s, 3, 1-Me), 0.91 (s, 3, PdMe).

PdIMe{(py)(mim)C=O} (orange). ^1H NMR: isomer A (py trans to PdMe), δ 9.69 (ddd, J_{56} = 5.3 Hz, J_{46} = 1.5 Hz, J_{36} = 0.8 Hz, 1, H6), ca. 8.25 (m, H3,4, obscured), 7.73 (ddd, J_{45} = 7.8 Hz, J_{56} = 5.4 Hz, J_{35} = 2.4 Hz, 1, H5), 7.78 (d, 1, H4 or H5 (mim)) and 7.38 (d, J_{45} = 1.3 Hz, 1, H5 or H4 (mim)), 4.12 (s, 3, 1-Me), 0.82 (s, 3, PdMe); isomer B resonances are of low intensity (isomer ratio ca. 10:1), with py resonances at ca. 8.8, 8.4, 7.91 ppm and mim resonances at ca. 7.8 and 7.6 ppm, with 0.63 ppm (s, PdMe).

PdIMe{(py)(mim)C=CH_2} (pale yellow). ^1H NMR: isomer A (py trans to PdMe), δ 9.45 (ddd, J_{56} = 5.4 Hz, J_{46} = 1.7 Hz, J_{36} = 0.7 Hz, 1, H6), 8.01 (ddd, $J_{45} \approx J_{34} \approx$ 7.7 Hz, J_{46} = 1.8 Hz, 1, H4), 7.82 (m, 1, H3), ~7.40 (m, H5 (py) and H4 or H5 (mim)), 7.10 (d, J_{45} = 1.6 Hz, 1, H5 or H4 (mim)), 6.42 (s, 1, CH_2) and 6.20 (s, 1, CH_2), 3.95 (s, 3, 1-Me), 0.77 (s, 3, PdMe); isomer B resonances are of low intensity (isomer ratio ca. 10:1) with mim resonances at 7.34, 7.06 (H4 and H5), 3.89 (1-Me), and 0.52 ppm (PdMe).

PdIMe{$(mim)_2C$=CH_2} (cream). ^1H NMR: mim trans to PdMe, δ 7.56 (d, 1, H4 or H5) and 7.15 (d, J_{45} = 1.4 Hz, 1, H5 or H4), 3.93 (s, 3, 1-Me); mim trans to PdI, δ 7.37 (d, 1, H4 or H5) and 7.08 (d, J_{45} = 1.6 Hz, 1, H5 or H4), 4.00 (s, 3, 1-Me); 6.33 (m, 2, CH_2), 0.60 (s, 3, PdMe).

PdIMe{$(py)_2CH_2$} (orange). Ambient temperature, py trans to PdMe, δ 9.12 (ddd, J_{56} = 5.4 Hz, J_{46} = 1.7 Hz, J_{36} = 0.8 Hz, 1, H6), 7.90 (ddd, $J_{45} \approx J_{34} \approx$ 7.7 Hz, J_{46} = 1.7 Hz, 1, H4), 7.66 (d, J_{34} = 7.7 Hz, 1, H3), 7.35 (m, 1, H5); py trans to PdI, δ 8.61 (m, 1, H6), 8.05 (ddd, $J_{45} \approx J_{34} \approx$ 7.7 Hz, J_{46} = 1.6 Hz, 1, H4), 7.81 (d, J_{34} = 7.6 Hz, 1, H3), 7.54 (m, 1, H5), 4.91 (s, 1, CH) and 4.61 (s, 1, CH), 0.77 (s, 3, PdMe); 0 °C, 4.92 (d, 1, CH) and 4.61 (d, J_{HH} = 13.6 Hz, 1, CH), other resonances similar to above, T_c ca. 34 °C.

PdIMe{$(py)_2$CHMe} (pale orange). ^1H NMR: conformer A, δ 9.08 (d, $J_{56} \approx$ 5.9 Hz, H6 trans to PdMe), 8.60 (d, $J_{56} \approx$ 4.5 Hz, 1, H6 trans to PdI), 5.42 (q, J_{HMe} = 7.1 Hz, 1, CH(ax)), ~2.04 (CMe(eq), obscured by acetone), 0.78 (s, 3, PdMe); conformer B, δ 9.31 (d, J_{56} = 5.6 Hz, 1, H6 trans to PdMe), 8.67 (d, $J_{56} \approx$ 4.5 Hz, 1, H6 trans to PdI), 4.86 (q, 1, CH(eq)) and 2.59 (d, J_{HMe} = 7.2 Hz, 3, CMe(ax)), 0.77 (s, 3, PdMe); conformers A and B, δ 8.06

and 7.88 (2, H4), 7.75 and 7.65 (2, H3), 7.54 and 7.35 (2, H5); conformers A and B in 4:5 ratio.

PdIMe{(py)$_2$CMe$_2$} (buff). ^{1}H NMR: py trans to PdMe, δ 9.44 (m, 1, H6), 7.92 (m, H4, obscured), 7.66 (d, J_{34} = 8.3 Hz, 1, H3), 7.32 (m, 1, H5); py trans to PdI, δ 8.74 (dd, J_{56} = 5.7 Hz, $J_{46} \approx$ 1.6 Hz, 1, H6), 8.05 (ddd, $J_{45} \approx J_{34} \approx$ 8.2 Hz, J_{46} = 1.8 Hz, 1, H4), 7.89 (m, H3, obscured), 7.51 (m, 1, H5), 3.01 (s, 3, CMe(ax)), 2.16 (s, 3, CMe(eq)), 0.79 (s, 3, PdMe).

PdIMe{(mim)$_2$CH$_2$} (cream). ^{1}H NMR: mim trans to PdMe, δ 7.52 (d, 1, H4 or H5) and 7.00 (d, J_{45} = 1.5 Hz, 1, H5 or H4), 3.83 (s, 3, 1-Me); mim trans to PdI, δ 7.22 (1, H4 or H5) and 6.99 (d, J_{45} = 1.6 Hz, 1, H5 or H4), 3.93 (s, 3 1-Me) 4.31 (s, 2, CH_2), 0.60 (s, 3, PdMe).

PdIMe{(mim)$_2$CHMe} (yellow). ^{1}H NMR: mim trans to PdMe, δ 7.49 (d, 1, H4 or H5) and 6.97 (d, J_{45} = 1.4 Hz, 1, H5 or H4), 3.86 (s, 3, 1-Me); mim trans to PdI, δ 7.19 (d, 1, H4 or H5) and 6.99 (d, J_{45} = 1.5 Hz, 1, H5 or H4), 3.95 (s, 3, 1-Me), 4.80 (1, CH(ax)) and 1.82 (d, J_{HMe} = 7.0 Hz, 3, CMe(eq)), 0.62 (s, 3, PdMe).

PdIMe{(py)(pz)CH$_2$} (orange). ^{1}H NMR: isomer A, py trans to PdMe, δ 9.29 (ddd, J_{56} = 5.4 Hz, J_{46} = 1.7 Hz, J_{36} = 0.8 Hz, 1, H6), 8.00 (ddd, $J_{45} \approx J_{34} \approx$ 7.7 Hz, J_{46} = 1.7 Hz, 1, H4), ~7.70 (m, H3, obscured), 7.50 (ddd, J_{45} = 7.6 Hz, J_{56} = 5.4 Hz, J_{35} = 1.4 Hz, 1, H5); pz trans to PdI, δ 8.13 (dd, J_{45} = 2.6 Hz, J_{35} = 0.6 Hz, 1, H5), ~7.70 (m, H3, obscured), 6.51 ("t", $J_{34} \approx J_{45}$ = 2.4 Hz, 1, H4), 5.85 (s, 2, CH_2), 0.87 (s, 3, PdMe); isomer B, py trans to PdI δ 8.68 (d, $J_{56} \approx$ 4.5 Hz, 1, H6), 8.15 (m, H4, obscured), 7.87 (d, $J_{34} \approx$ 7.1 Hz, 1, H3), ~7.69 (m, H5, obscured); pz trans to PdMe, δ 7.95 (d, J_{45} = 2.4 Hz, 1, H5), 7.82 (d, J_{34} = 1.7 Hz, 1, H3), 6.32 ("t", $J_{34} \approx J_{45}$ = 2.3 Hz, 1, H4) 5.87 (s, 2, CH_2), 0.75 (s, 3, PdMe); isomers A and B in ca. 4:1 ratio.

PdIMe{(pz)(mim)CH$_2$} (buff). ^{1}H NMR: isomer A, pz trans to PdMe, δ 8.06 (dd, J_{34} = 2.1 Hz, J_{35} = 0.8 Hz, 1, H5), 7.95 (dd, J_{45} = 2.4 Hz, J_{35} = 0.8 Hz, 1, H3), 6.30 ("t", $J_{34} \approx J_{45}$ = 2.3 Hz, 1, H4); mim trans to PdI, δ 7.29 (d, 1, H4 or H5) and 7.05 (d, J_{45} = 1.6 Hz, 1, H5 or H4), 4.00 (s, 3, 1-Me) 5.70 (s, 2, CH_2), 0.76 (s, 3, PdMe); isomer B, pz trans to PdI, δ 8.17 (d, J_{45} = 2.3 Hz, 1, H5), 7.72 (d, J_{34} = 2.2 Hz, 1, H3), 6.48 (m, 1, H4); mim trans to PdMe, δ 7.33 (d, 1, H4 or H5) and 7.08 (d, J_{45} = 1.3 Hz, 1, H5 or H4), 3.91 (s, 3, 1-Me), 5.73 (s, 2, CH_2), 0.66 (s, 3, PdMe); isomers A and B in ca. 4:1 ratio.

PdIMe{(py)(mim)CH$_2$} (pale yellow). ^{1}H NMR: isomer A, py trans to PdMe, δ 9.35 (ddd, J_{56} = 5.4 Hz, J_{46} = 1.8 Hz, J_{36} = 0.8 Hz, 1, H6), 7.89 (ddd, $J_{45} \approx J_{34} \approx$ 7.7 Hz, J_{46} = 1.8 Hz, 1, H4), 7.66 (d, J_{34} = 7.5 Hz, 1, H3), 7.35 (m, 1, H5); mim trans to PdI, δ 7.20 (d, 1, H4 or H5) and 6.96 (d, J_{45} = 1.6 Hz, 1, H5 or H4), 3.94 (s, 3, 1-Me), 4.50 (s, 2, CH_2), 0.80 (s, 3, PdMe); isomer B, py and mim resonances are broad and of low intensity, δ 3.86 (s, 3, 1-Me), 0.59 (s, 3, PdMe), isomers A and B in ca. 19:1 ratio.

PdIMe{(py)(mim)CHMe} formed as an oil that crystallized on standing at ca. −20 °C but could not be recrystallized. ^{1}H NMR: δ 9.46 (ddd, J_{56} = 5.4 Hz, J_{46} = 1.7 Hz, J_{36} = 0.6 Hz, 1, H6), 7.89 (ddd, $J_{45} \approx J_{34} \approx$ 7.6, J_{46} = 1.7 Hz, 1, H4), 7.65 (m, 1, H3), 7.34 (ddd, J_{45} = 7.6 Hz, J_{56} = 5.4 Hz, J_{35} = 1.5 Hz, 1, H5), 7.21 (d, 1, H4 or H5) and 6.98 (d, J_{45} = 1.6 Hz, 1, H5 or H4), 4.86 (q, 1, CH(eq)) and 2.24 (d, J_{HMe} = 7.1 Hz, 3, CMe(ax)), 3.95 (s, 3, 1-Me), 0.80 (s, 3, PdMe).

Method E. A saturated solution of $AgNO_3$ (0.20 g, 1.15 mmol) in acetonitrile (3.6 mL) was added to a stirred solution of [PdIMe(SMe$_2$)]$_2$ (0.30 g, 0.48 mmol) in acetonitrile (50 mL). Filtration to remove AgI, followed by addition of an aqueous solution of KBr (0.23 g, 1.92 mmol) and filtration to remove some AgBr, gave a clear yellow solution. Gentle heating (50 °C) for ca. 15 min followed by addition of 2,2′-bipyridyl (0.15 g, 0.96 mmol) and removal of organic solvents under a vacuum at ca. 50 °C gave an orange powder, which was collected by filtration and dried under high vacuum. Recrystallization could be effected from acetone/hexane to give yellow-orange **PdBrMe(bpy)** (0.26 g, 75%). ^{1}H NMR ($CDCl_3$): δ 9.39 (ddd, J_{56} = 5.3 Hz, J_{46} = 1.7 Hz, J_{36} = 0.9 Hz, 1, H6 trans to PdMe), 8.70 (d, $J_{56} \approx$ 4.9 Hz, 1, H6 trans to PdBr), 8.14–7.95 (m, 4, H3,4), 7.61–7.51 (m, 2, H5), 1.04 (s, 3, PdMe).

PdClMe(bpy) (pale yellow). ^{1}H NMR ($CDCl_3$): δ 9.22 (m, 1, H6 trans to PdMe), 8.69 (d, J_{56} = 5.0 Hz, 1, H6 trans to PdCl), 8.14–7.96 (m, 4, H3,4), 7.55 (m, 2, H5), 1.04 (s, 3, PdMe).

PdBrMe{(pz)$_2$CMe$_2$} (pale orange). ^{1}H NMR ($(CD_3)_2CO$): ambient temperature, pz trans to PdMe, δ 8.13 (dd, J_{45} = 2.7 Hz, J_{35} = 0.8 Hz, 1, H5), 8.00 (d, J_{34} = 2.0 Hz, 1, H3), 6.39 ("t", $J_{34} \approx J_{45}$ = 2.3 Hz, 1, H4); pz trans to PdBr, δ 8.29 (dd, J_{45} = 3.0 Hz, J_{35} = 0.8 Hz, 1, H5), 7.80 (d, J_{34} = 2.2 Hz, 1, H3), 6.54 (dd, J_{45} = 3.0 Hz, J_{34} = 2.2 Hz, 1, H4), 2.72 (s, 6, CMe), 0.84 (s, 3, PdMe); −30 °C, δ 2.93 (s, 3, CMe) and 2.69 (s, 3, CMe), other resonances similar to above, T_c ca. −13 °C.

PdClMe{(pz)$_2$CMe$_2$} (yellow). ^{1}H NMR ($(CD_3)_2CO$): ambient temperature, pz trans to PdMe δ 8.15 (dd, J_{45} = 2.7 Hz, J_{35} = 0.8 Hz, 1, H5), 7.90 (m, 1, H3), 6.39 (dd, J_{45} = 2.7 Hz, J_{34} = 2.0 Hz, 1, H4); pz trans to PdCl, δ 8.29 (dd, J_{45} = 3.0 Hz, J_{35} = 0.8 Hz, 1, H5), 7.78 (m, 1, H3), 6.52 (dd, J_{45} = 2.9 Hz, J_{34} = 2.2 Hz, 1, H4), 2.79 (s, 6, CMe), 0.85 (s, 3, PdMe); −40 °C, δ 2.86 (s, 3, CMe) and 2.66 (s, 3, CMe), other resonances similar to above, T_c ca. −30 °C.

Method F. Methyllithium (from Li and MeI, standardized, 3.3 mmol) was added to a suspension of *trans*-PdCl$_2$(SMe$_2$)$_2$ (0.50 g, 1.66 mmol) in diethyl ether (70 mL) at −70 °C under a nitrogen atmosphere and the suspension stirred at −60 to −40 °C for 1 h to give a near-colorless solution with no unreacted reagent evident. Addition of (pz)$_2$CMe$_2$ (0.29 g, 1.66 mmol) with continual stirring while the solution was slowly warmed to ca. −10 °C gave a yellow solution, with little or no reduced palladium present. Hydrolysis (2 mL), followed by filtration, separation, and drying of the organic phase ($MgSO_4$) and evaporation of diethyl ether under a vacuum at ca. 5 °C, gave crude **PdIMe{(pz)$_2$CMe$_2$}**. The product was readily recrystallized from acetone/hexane to give yellow plates (0.51 g, 73%). ^{1}H NMR ($(CD_3)_2CO$): ambient temperature, pz trans to PdMe, δ 8.14 (dd, J_{45} = 2.7 Hz, J_{35} = 0.6 Hz, 1, H5), 8.11 (dd, J_{34} = 2.1 Hz, J_{35} = 0.5 Hz, 1, H3), 6.37 (dd, J_{34} = 2.1 Hz, J_{45} = 2.7 Hz, 1, H4); pz trans to PdI, δ 8.30 (dd, J_{45} = 2.8 Hz, J_{35} = 0.6 Hz, 1, H5), 7.81 (dd, J_{34} = 2.3 Hz, J_{35} = 0.7 Hz, 1, H3), 6.55 (dd, J_{34} = 2.4 Hz, J_{45} = 2.8 Hz, 1, H4) 2.83 (s, 6, CMe), 0.83 (s, 3, PdMe); −20 °C, δ 2.95 (s, 3, CMe) and 2.70 (s, 3, CMe), other resonances similar to above, T_c ca. −8 °C.

PdIMe{(pz)$_2$CH$_2$} (pale orange). ^{1}H NMR: ambient temperature, pz trans to PdMe, δ 8.03 (d, J_{45} = 2.6 Hz, 1, H5), 7.98 (d, J_{34} = 2.1 Hz, 1, H3), 6.38 ("t", $J_{34} \approx J_{45}$ = 2.2 Hz, 1, H4); pz trans to PdI, δ 8.21 (d, J_{45} = 2.7 Hz, 1, H5), 7.82 (d, J_{34} = 2.3 Hz, 1, H3), 6.57 ("t", $J_{34} \approx J_{45}$ = 2.4 Hz, 1, H4), 6.85 (s, 2, CH_2), 0.83 (s, 3, PdMe); −30 °C, δ 7.01 (d, 1, CH) and 6.73 (d, J_{HH} = 14.36 Hz, 1, CH), other resonances similar to above.

PdIMe{(pz)$_2$CHMe} (buff). ^{1}H NMR: ambient temperature, δ 8.21 (s (br), 1, H5), 8.05 (s (br), 2, H3,5), 7.81 (s (br), 1, H3), 7.28 (s, 1, CH), 6.60 ("t", 1, H4), 6.38 ("t", 1, H4), 2.59 (d, 3, CMe), 0.84 (s, 3, PdMe); −15 °C, conformer I, pz trans to PdMe, δ 8.07 (d, J_{45} = 2.5 Hz, 1, H5), 8.06 (d, J_{34} = 1.7 Hz, 1, H3), ~6.40 (m, H4, obscured); pz trans to PdI, δ 8.23 (d, J_{45} = 2.5 Hz, 1, H5), 7.88 (d, J_{34} = 1.8 Hz, 1, H3), ~6.58 (m, H4, obscured), 7.37 (q, 1, CH) and 2.62 (d, J_{HMe} = 6.7 Hz, 3, CMe), 0.82 (s, 3, PdMe); conformer II, pz trans to PdMe, δ 8.17 (d, J_{45} = 2.5 Hz, 1, H5), 7.90 (d, J_{34} = 2.2 Hz, 1, H3), ~6.41 (m, H4, obscured); pz trans to PdI, δ 8.32 (d, J_{45} = 2.7 Hz, 1, H5), 7.15 (q, 1, CH) and 2.53 (d, J_{HMe} = 6.8 Hz, 3, CMe), 0.79 (s, 3, PdMe); conformers I and II in ca. 6:4 ratio.

PdIMe{(CH$_2$SMe)$_2$}. ^{1}H NMR: δ 3.18 b (m, 2, CH_2) and 3.06 b (m, 2, CH_2), 2.53 (s, 3, SMe), 2.41 (s, 3, SMe), 0.83 (s, 3, PdMe).

The complexes PdIMe(L$_2$) (L$_2$ = bpy, (pz)$_2$CH$_2$, (pz)$_2$CHMe, (pz)$_2$CMe$_2$) were also synthesized by using MgIMe and following a procedure similar to that above, including similar solvent volumes.

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