Oxidation of Complexes by $(O_2CPh)_2$ and $(ER)_2$ (E = S, Se), Including Structures of $Pd(CH_2CH_2CH_2CH_2)(SePh)_2(bpy)$ (bpy = 2,2′-Bipyridine) and $MMe_2(SePh)_2(L_2)$ (M = Pd, Pt; L_2 = bpy, 1,10-Phenanthroline) and C···O and C···E Bond Formation at Palladium(IV)

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Oxidation of $PdMe_2(L_2)$ [L_2 = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen)] by diphenyl diselenide provides the first examples of stable dimethylpalladium(IV) complexes $PdMe_2(SePh)_2(L_2)$, and pallada(IV)cyclic $Pd(CH_2CH_2CH_2CH_2)(SePh)_2(bpy)$ may be similarly isolated. X-ray structural studies of the octahedral dimethylpalladium(IV) complexes and their isomorphous platinum(IV) analogues have been completed [L_2 = bpy, orthorhombic *Pnma*; L_2 = phen, triclinic $P\bar{1}$; an additional phase for $PtMe_2(SePh)_2(phen)$, tetragonal, $I4_1/a$]. The complexes $PdMe_2(SePh)_2(L_2)$ decompose at moderate temperatures in $CDCl_3$ following first-order behavior [L_2 = bpy, $E_a \sim 46$ kJ mol^{-1}, $\Delta S^{\ddagger}(20\ °C) \sim -170$ J K^{-1} mol^{-1}; L_2 = phen, $E_a \sim 36$ kJ mol^{-1}, $\Delta S^{\ddagger}(20\ °C) \sim -204$ J K^{-1} mol^{-1}] to give ethane and Se(Ph)Me, together with small quantities of $SePh_2$. Similar C···C, C···O, C···S, and C···Se bond formation processes occur on decomposition of palladium(IV) species that are too unstable to be isolated on the oxidation of $PdMe_2(bpy)$ or $Pd(CH_2CH_2CH_2CH_2)(bpy)$ by $(O_2CPh)_2$ or $(SPh)_2$.

Introduction

Since the report of $[PtIMe_3]_4$ in 1907[1] organoplatinum(IV) chemistry has become one of the most important systems for investigations of structure and reactivity at d^6 metal centers,[2,3] and the more recent development of organopalladium(IV) chemistry has provided new perspectives in d^6 chemistry.[4,5] For example, structural studies of isomorphous $[MMe_3\{(pz)_3CH\}]I$ [M = Pd, Pt; $(pz)_3CH$ = tris(pyrazol-1-yl)methane] show that Pd−N > Pt−N for nitrogen donors trans to alkyl groups,[6] and although $PtIMe_3(bpy)$ (bpy = 2,2′-bipyridine) is an exceptionally stable complex,[7] $PdIMe_3(bpy)$ undergoes facile decomposition at ambient temperature in solution allowing detailed mechanistic studies of reductive elimination at a d^6 metal center.[7,8]

It has recently been shown that platinum(IV) forms stable thiolate and selenolate complexes $PtMe_2(EPh)_2(phen)$ (E = S, Se; phen = 1,10-phenanthroline),[9] but there are no reports of thiolate or selenolate complexes in organopalladium(IV) chemistry. We have explored the formation of such complexes via oxidation of palladium(II) reagents by $(ER)_2$ in the expectation that less stable palladium(IV) complexes may be accessible and allow the study of decomposition processes at palladium(IV) in the presence of group 16 donor atoms. In addition to $(EPh)_2$ (E = S, Se) we have included $(O_2CPh)_2$ as a related group 16 oxidant.

We report here the synthesis and structural chemistry of isomorphous metal(IV) complexes $MMe_2(SePh)_2(L_2)$ (M = Pd, Pt; L_2 = bpy, phen), the structure of $Pd(CH_2CH_2CH_2CH_2)(SePh)_2(bpy)$, and studies of the formation and decomposition of a range of palladium(IV) complexes involving C···C, C···O, C···S, and C···Se bond formation processes.

Experimental Section

The reagents $[PtMe_2(SEt_2)]_2$,[10] $PdMe_2(tmeda)$ (tmeda = *N*,*N*,*N*′,N′-tetramethylethylenediamine),[11,12] $PdMe_2(L_2)$ (bpy,[12,13] phen[13]), $PtMe_2$-

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(L_2) (L_2 = bpy,[10] phen[14]), and $Pd(CH_2CH_2CH_2CH_2)(bpy)$[15] were prepared as described; other reagents were used as received. Solvents were dried and distilled, and all procedures were carried out under nitrogen. Microanalyses were by the Central Science Laboratory, University of Tasmania, and NMR spectra were recorded with a Bruker AM 300 spectrometer with chemical shifts given in ppm relative to $SiMe_4$.

Analysis of Decomposition Products. The decomposition products of palladium(IV) complexes in acetone-d_6 or $CDCl_3$ were detected by ^{1}H NMR spectroscopy and by sampling the gas/liquid phases using a microsyringe and a HP 5890 gas chromatograph connected to a HP 5970B mass selective detector (70 eV ET with He carrier gas). ^{1}H NMR spectra allowed determination of the yield of liquid-phase products containing a methyl group, e.g. E(Ph)Me (E = S, Se), and the presence of this product in GC-MS data allowed yield determination for other products. Ethane was detected by ^{1}H NMR and GC-MS, but its yield was not determined. Methane was not detected as a product in any decompositions.

Synthesis of Metal(IV) Complexes $MMe_2(ER)_2(L_2)$ (L_2 = bpy, phen). $PtMe_2(SePh)_2(bpy)$ (1). Diphenyl diselenide (0.081 g, 0.260 mmol) was added to a solution of $PtMe_2(bpy)$ (0.075 g, 0.260 mmol) in acetone (6 mL) and the solution stirred for 1 h to give a yellow solution. The solvent was evaporated in a vacuum and the residue washed with diethyl ether and dried in a vacuum to give a yellow solid (93%). Crystals may be obtained from dichloromethane/diethyl ether. ^{1}H NMR ($CDCl_3$): δ 8.67 (d, ^3J = 4.0 Hz, $^3J_{PtH}$ = 7.0 Hz, 2, H6), 7.72 (t, ^3J = 8.0 Hz, 2, H4 or 5), 7.48 (d, ^3J = 8.0 Hz, 2, H3), 7.38 (t, ^3J = 8.0 Hz, 2, H4 or 5), [6.78 (m) and 6.61 (d) and 6.46 (m), 10, Ph], 1.62 (s, $^2J_{PtH}$ = 70.6 Hz, $^3J_{SeH}$ = 7.2 Hz, 6, PtMe). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.0, 147.4, 137.5, 127.7, 122.8 (bpy); δ 137.9, 127.8, 126.4, 125.6 (Ph); δ −6.1 ($^1J_{PtC}$ = 590 Hz, PtMe). Anal. Calcd for $C_{24}H_{24}N_2PtSe_2$: C, 41.57; H, 3.49; N, 4.04. Found: C, 41.25; H, 3.49; N, 4.09.

$PtMe_2(SePh)_2(phen)$ (2). The complex was prepared as reported[9] and crystallized from chloroform/diethyl ether for X-ray diffraction studies.

$PdMe_2(SePh)_2(bpy)$ (3). Diphenyl diselenide (0.033 g, 0.100 mmol) in acetone (1 mL) at −70 °C was added to a solution of $PdMe_2(bpy)$ (0.030 g, 0.100 mmol) in acetone (1.5 mL) at −70 °C. The solution was allowed to slowly warm to −30 °C with stirring (93%). The pale yellow solution became red-orange as a dark red solid precipitated. The solid was isolated below −25 °C and dried in a vacuum at −20 °C to give a dark red crystalline solid (0.044 g, 73%). Solutions of the complex decompose quickly above −10 °C, but the solid sample can be kept for at least 1 week at −20 °C without detectable decomposition. Crystals may be obtained from chloroform/diethyl ether. ^{1}H NMR ($CDCl_3$ at −20 °C): δ 8.60 (d, ^3J = 4.0 Hz, 2, H6), 7.71 (t, ^3J = 8.0 Hz, 2, H4), 7.50 (d, ^3J = 8.0 Hz, 2, H3), 7.35 (t, ^3J = 5.3 Hz, 2, H5), [6.82 (m) and 6.701 (d) and 6.51 (m), 10, Ph], 2.07 (s, $^3J_{SeH}$ = 7.1 Hz, 6, PdMe). ^{13}C{^{1}H} NMR ($CDCl_3$, −20 °C): δ 152.5, 147.8, 137.4, 127.9, 122.3 (bpy); δ 138.0, 123.2, 126.0, 125.7 (Ph); δ 15.7 (PdMe). Anal. Calcd for $C_{24}H_{24}N_2PdSe_2$: C, 47.66; H, 4.00; N, 4.63. Found: C, 47.50; H, 3.95; N, 4.65.

$PdMe_2(SePh)_2(phen)$ (4). This complex was isolated as a dark red solid by a similar procedure to that for the bpy analogue (85%), and crystals were similarly obtained. ^{1}H NMR ($CDCl_3$ at −20 °C): δ [8.91 (d, ^3J = 5.0 Hz, 2), 8.16 (d, ^3J = 8.0 Hz, 2), 7.67 (m, 2), 7.63 (s, 2) (phen)], [6.51 (t), 6.38 (d), 6.151 (t), 10, Ph], 2.20 (s, $^3J_{SeH}$ = 11.0 Hz, 6, PdMe). ^{13}C{^{1}H} NMR ($CDCl_3$ at −20 °C): δ 147.7, 136.7, 126.9, 124.7 (bpy); δ 136.8, 127.3, 125.4 (Ph); δ 15.1 (PdMe). Anal. Calcd for $C_{26}H_{24}N_2PdSe_2$: C, 49.66; H, 3.85; N, 4.45. Found: C, 49.65; H, 3.82; N, 4.54.

$Pd(CH_2CH_2CH_2CH_2)(SePh)_2(bpy)$ (5). This complex was isolated by a similar procedure to that for the dimethylpalladium(IV) analogue (**8**) (69%), and crystals were similarly obtained. The isolated complex decomposes in solution above −20 °C to give butenes, cyclobutane, $Se(Ph)C_4H_9$ and $Se(Ph)C_4H_7$ (NMR, GC-MS identification), and a red-brown solid. ^{1}H NMR ($CDCl_3$ at −20 °C): δ 8.50 (d, ^3J = 5.2 Hz, 2, H6), 7.63 (t, ^3J = 6.3 Hz, 2, H4 or 5), 7.29 (m, 4, H3 and 4 or 5), 6.77 (t) and 6.61 (d) and 6.42 (t) (10, Ph), 4.07 (b, 2, $PdCH_2$), 1.87 (b, 2, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$ at −20 °C): δ 149.5 (bpy), 137.5, 137.4, 127.6, 125.7, 125.2, 122.0, 111.4 (Ph), 48.2 ($PdCH_2$), 35.5 (CH_2). Anal. Calcd for $C_{26}H_{26}N_2PdSe_2$: C, 49.50; H, 4.15; N, 4.44. Found: C, 49.30; H, 4.30; N, 4.95.

^{1}H NMR Studies of the Reactions of Palladium(II) Complexes with Oxidizing Agents. $PdMe_2(bpy)/(O_2CPh)_2$. Dibenzoyl peroxide (0.0074 g, 0.031 mmol) in acetone-d_6 (0.3 mL) was cooled to −70 °C and added to a precooled solution of $PdMe_2(bpy)$ (0.009 g, 0.031 mmol) in acetone-d_6 (0.3 mL) in an NMR tube. The complex $PdMe_2\{OC(O)Ph\}_2(bpy)$ was detected at −50 °C [δ 9.02 (d, 2, H6), 8.57 (d, 2 H3), 8.19 (t, 2, H4), 8.10 (d) and 7.78 (t) and 7.68 (t) (Ph), 7.16 (t, 2, H5), 1.72 (s, 6, PdMe)] but at higher temperatures decomposed to give ethane, $PhCO_2Me$ (∼35%), $PhCO_2H$ (∼15%), and a yellow solid [∼61% assuming $Pd(O_2CPh)_2(bpy)$]. The yellow solid has properties expected for $Pd(O_2CPh)_2(bpy)$: ^{1}H NMR (acetic acid-d_4): δ 8.45 (d, ^3J = 8.0 Hz, 2, H6), 8.29 (t, ^3J = 8.0 Hz, 2, H4 or 5), 7.63 (m, 2, H3), 7.50 (m, 2, H4 or 5). ^{13}C{^{1}H} NMR (acetic acid-d_4): δ 192.0 (O_2C), 157.8, 152.1, 135.8, 129.3, 125.7, 143.6, 132.1, 131.5, 130.6. IR (KBr disk): 1640 vs, 1600 vs, 1560 s, 1340 vs cm^{-1}. Anal. Calcd for $C_{24}H_{18}N_2O_4Pd$: C, 57.10; H, 3.59; N, 5.55. Found: C, 56.91; H, 3.68; N, 5.59.

$PdMe_2(bpy)/(SPh)_2$. Following a similar procedure, reaction commenced on warming to 20 °C with decomposition of an intermediate [resonance at 1.98 ppm assigned to the $Pd^{IV}Me$ group of unstable $PdMe_2(SPh)_2(bpy)$] occurring at the same temperature to form ethane, S(Ph)Me (∼17%), SPh_2 (∼49%), and an orange solid. The orange solid was very insoluble and difficult to characterize.

$Pd(CH_2CH_2CH_2CH_2)(bpy)/(O_2CPh)_2$. Following a similar procedure, reaction commenced on warming to 20 °C to form cyclobutane, butenes, $C_4H_7O_2CPh$, $C_4H_9O_2CPh$, $PhCO_2H$ and an orange solid.

$Pd(CH_2CH_2CH_2CH_2)(bpy)/(SPh)_2$. Following a similar procedure, reaction commenced on warming to 20 °C to form cyclobutane, butenes, $S(Ph)C_4H_7$, $S(Ph)C_4H_9$, SPh_2, and a red solid.

X-ray Structure Determinations. Room-temperature four-circle diffractometer data sets were as specified in Table 1 ($2\theta/\theta$ scan mode; monochromatic Mo Kα radiation), yielding N independent reflections, N_o of which, with $I > 3\sigma(I)$, were considered "observed" and used in the full matrix least-squares refinements after analytical absorption correction. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, (x, y, z, U_{iso})$_H$ being constrained at estimated values, those for the methyl groups being inferred from difference map residues as these permitted. Conventional residuals R and R_w on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being employed. Neutral atom complex scattering factors were employed,[16] computation using the XTAL 3.4 program system.[17]

Specific difficulties encountered in individual structure determinations are documented in the footnotes to Table 1. The principal difficulties encountered more generally were high absorption (analytical corrections were applied as the crystals were well formed and fiber-mounted), dominant heavy atoms located in some cases on or near crystallographic symmetry elements (where possible data were measured extensively and redundantly to assist in considerations of assignment of crystal symmetry/space group and in enhancement of precision of the determination after merging where it was considered valid to do so), and extensive decomposition of the palladium complexes on the time scale of the order of 1 day (compensated for by appropriate scaling).

Crystal data and selected geometries of the complexes are given in Tables 1 and 2, and views of the complexes are shown in Figures 1−5.

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Table 1. Specific Crystallographic Details for $MMe_2(SePh)_2(L_2)$ (L_2 = bpy, phen) and $Pd(CH_2CH_2CH_2CH_2)(SePh)_2(bpy)$[a]

	complex					
	$PdMe_2(SePh)_2$-(bpy) (**3**)[b]	$PtMe_2(SePh)_2$-(bpy) (**1**)[c]	$PdMe_2(SePh)_2$-(phen) (**4**)[d]	$PtMe_2(SePh)_2$-(phen) (**2a**)	$PtMe_2(SePh)_2$-(phen) (**2b**)[e]	$Pd(CH_2CH_2CH_2CH_2)$-$(SePh)_2$(bpy) (**5**)[f]
formula	$C_{24}H_{24}N_2PdSe_2$	$C_{24}H_{24}N_2PtSe_2$	$C_{26}H_{24}N_2PdSe_2$	$C_{26}H_{24}N_2PtSe_2$	$C_{26}H_{24}N_2PtSe_2$	$C_{26}H_{26}N_2PdSe_2$
cryst system	orthorhombic	orthorhombic	triclinic	triclinic	tetragonal	orthorhombic
space group	*Pnma* (No. 62)	*Pnma* (No. 62)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$I4_1/a$ (No. 88)	$Pna2_1$ (No. 33)
a/Å	13.906(5)	13.920(5)	11.689(8)	11.759(6)	13.874(3)	14.271(6)
b/Å	12.578(4)	12.575(4)	11.108(5)	11.094(6)		13.832(8)
c/Å	13.072(3)	13.038(6)	10.009(6)	9.976(6)	25.14(3)	12.065(9)
α/deg			66.48(4)	66.13(4)		
β/deg			85.99(4)	86.01(4)		
γ/deg			81.64(4)	81.46(4)		
V, Å^3	2286	2282	1179	1177	4839	2381
Z	4	4	2	2	8	4
M_r	604.8	693.5	628.8	717.5	717.5	630.9
D_c/g cm^{-3}	1.75_7	2.01_8	1.77_1	2.02_4	1.97_0	1.75_9
μ_{Mo}/cm^{-1}	40	94	39	91	88	39
$2\theta_{max}$/deg	50	65	46	60	60	50
N	2109	4282	3274	6833	3531	2202
N_o	1320	2361	2085	5291	2098	1867
R	0.045	0.042	0.059	0.039	0.036	0.034
R_w	0.055	0.052	0.070	0.049	0.043	0.040

[a] $R = \sum\Delta/\sum|F_o|$; $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$; $w = 1/\sigma^2(F_o)$; $T \sim 295$ K; $\lambda = 0.7107_3$ Å. [b] The molecule lies astride a crystallographic mirror plane, one of the phenyl rings being modeled as "disordered" and the other exhibiting high "thermal" motion, no disorder being resolvable. Of a number of rapidly measured data sets, that cited was the most satisfactory, R_{int} 0.07 for a hemisphere of data, scaled after 58% decomposition. [c] Isomorphous with **3**, R_{int} (orthorhombic) = 0.065 for a hemisphere of data; cf. 0.058−0.061 for the various monoclinic possibilities. [d] R_{int} = 0.077 for a full sphere of data (75% decomposition); no disorder in triclinic or tetragonal forms. [e] The subject of a previous less precise study,[9] at unspecified temperature, with a different cell volume. [f] A hemisphere of data was measured, spanning 53% decomposition. In the final model adopted, in the noncentrosymmetric $Pna2_1$ array, derivative of the centrosymmetric *Pnma* form of the dimethylmetal(IV) complexes, disorder was found in the tetramethylene array but not in the phenyl groups. Merging of data related by the *2*-axis gave R_{int} 0.048, absolute structure being indeterminate; the structure was then refined on a fully merged hemisphere (R_{int} = 0.067).

^{1}H NMR Study of the Decomposition of Palladium(IV) Complexes $PdMe_2(SePh)_2(L_2)$ (L_2 = bpy, phen). $PdMe_2(SePh)_2$(bpy) (3). A solution of $PdMe_2(SePh)_2$(bpy) (0.007 g, 0.012 mmol) in $CDCl_3$ (0.6 mL) was prepared at −70 °C in a 5 mm NMR tube, and a trace of 1,4-dioxane was added as an internal integration standard. The tube was immediately inserted into an NMR probe precooled to the temperature required for kinetic studies. Kinetic data were obtained from the $Pd^{IV}Me$ resonance with time intervals of 4−10 min depending on the temperature. First-order rate constants of 3.3×10^{-5} (−4 °C), 5.0×10^{-5} (4 °C), 1.17×10^{-4} (11 °C), 1.3×10^{-4} (19 °C), and 2.5×10^{-4} s^{-1} (25 °C) were obtained. A plot of ln *k* against 1/*T* results in estimates of $E_a \sim 46$ kJ mol^{-1} and $\Delta S^{\ddagger}$ (20 °C) ∼ −170 J K^{-1} mol^{-1}. NMR spectra show the formation of ethane and Se(Ph)Me (∼50%) during the reaction, and these products together with $SePh_2$ (∼1%) were also characterized by GC-MS. A red solid of very low solubility was obtained.

$PdMe_2(SePh)_2$(phen) (4). A study similar to that above gave first-order rate constants of 3.33×10^{-5} (0 °C), 6.67×10^{-5} (14 °C), 1.17×10^{-4} (25 °C), and 1.83×10^{-4} s^{-1} (31 °C), leading to estimates of $E_a \sim 36$ kJ mol^{-1} and $\Delta S^{\ddagger}$ (20 °C) ∼ −204 J K^{-1} mol^{-1}. NMR and GC-MS studies indicate that ethane, Se(Ph)Me (∼27%), and $SePh_2$ (8%) are formed. A red solid of very low solubility was obtained.

Results and Discussion

Studies were initially confined to MMe_2(bpy) (M = Pd, Pt), leading to the isolation of the selenolate complexes $MMe_2(SePh)_2$(bpy), and were expanded to include MMe_2(phen) and $\overline{Pd(CH_2CH_2CH_2CH_2)}$(bpy) as reagents primarily for crystallographic studies (Scheme 1). The dimethylmetal(IV) complexes exhibit simple ^{1}H NMR spectra, in particular showing one methyl environment for **1**−**4**, consistent with the configurations established for these complexes by X-ray crystallography (see below).

Dibenzoyl peroxide and $(SPh)_2$ were not explored as oxidants for $PtMe_2$(bpy) in view of the earlier report of $PtMe_2(ER)_2$(phen) (ER = O_2CPh, SPh),[9] but their reactions with palladium(II) complexes were characterized by ^{1}H NMR spectroscopy in acetone-d_6 as shown in eqs 1−4.

$$PdMe_2(bpy) + (O_2CPh)_2 \xrightarrow{-50\ ^\circ C} PdMe_2(O_2CPh)_2(bpy) \xrightarrow{-50\ ^\circ C} \underset{\sim 35\%}{MeMe} + \underset{\sim 15\%}{MeO_2CPh} + \underset{\sim 61\%}{PhCO_2H} + Pd(O_2CPh)_2(bpy) \quad (1)$$

$$PdMe_2(bpy) + (SPh)_2 \xrightarrow{20\ ^\circ C} PdMe_2(SPh)_2(bpy) \xrightarrow{20\ ^\circ C} MeMe + \underset{\sim 17\%}{MeSPh} + \underset{\sim 49\%}{SPh_2} \quad (2)$$

$$\overline{Pd(CH_2CH_2CH_2CH_2)}(bpy) + (SPh)_2 \xrightarrow{20\ ^\circ C} \overline{Pd(CH_2CH_2CH_2CH_2)}(SPh)_2(bpy) \rightarrow \underset{\text{undetected}}{} (CH_2)_4 + \text{butenes} + C_4H_7SPh + C_4H_9SPh + SPh_2 \quad (3)$$

$$\overline{Pd(CH_2CH_2CH_2CH_2)}(bpy) + (O_2CPh)_2 \xrightarrow{20\ ^\circ C} \overline{Pd(CH_2CH_2CH_2CH_2)}(O_2CPh)_2(bpy) \xrightarrow{20\ ^\circ C} \underset{\text{undetected}}{} (CH_2)_4 + \text{butenes} + C_4H_7O_2CPh + C_4H_9O_2CPh + PhCO_2H \quad (4)$$

Thus, the complexes $PdMe_2(O_2CPh)_2$(bpy) (eq 1) and $PdMe_2(SPh)_2$(bpy) (eq 2) decompose soon after they are formed and exhibit ^{1}H NMR resonances similar to those of the platinum(IV) analogues and $PdMe_2(SePh)_2$(bpy), in particular showing

Table 2. Selected Bond Distances (Å), Angles (deg), and Other Structural Data for $MMe_2(SePh)_2(bpy)$, $MMe_2(SePh)_2(phen)$, and $Pd(CH_2CH_2CH_2CH_2)(SePh)_2(bpy)$[a]

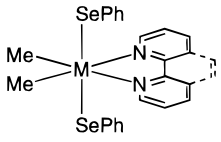
	bpy (orthorhombic)		phen (triclinic)		phen (tetragonal)	
	M = Pd (**3**)	M = Pt (**1**)	M = Pd (**4**)	M = Pt (**2a**)	M = Pt (**2b**)	$Pd(CH_2CH_2CH_2CH_2)(SePh)_2(bpy)$ (**5**)
			Bond Distances			
M−C(1)	2.036(8)	2.055(8)	2.02(1)	2.058(9)	2.056(8)	*2.08(1)*
M−C(1′)			2.03(1)	2.049(8)		*2.05(1)*
M−N(1)	2.179(5)	2.162(5)	2.160(9)	2.150(5)	2.143(6)	2.185(8)
M−N(1′)			2.20(1)	2.168(6)		2.181(8)
M-Se(1)	*2.479(1)*	*2.478(1)*	2.494(1)	2.491(1)	2.4896(9)	2.503(1)
M-Se(1′)	2.501(2)	2.498(1)	2.487(1)	2.486(1)		2.506(1)
Se(1)−C(11)	*1.90(2)*	*1.92(2)*	1.92(1)	1.911(6)	1.917(8)	1.923(8)
Se(1′)-C(11′)	1.87(1)	1.93(1)	1.91(1)	1.912(7)		1.935(9)
			Bond Angles			
C(1)-M−C(1′)	83.9(3)	86.6(3)	83.8(5)	85.7(3)	85.6(3)	*83.0(5)*
C(1)-M−N(1)	100.2(3)	98.5(3)	98.2(4)	98.0(3)	98.6(3)	*99.6(4)*
C(1)-M−N(1′)	175.8(3)	174.9(3)	174.9(4)	175.2(3)	175.8(3)	*175.3(4)*
C(1′)-M−N(1)			177.6(4)	176.2(3)		*177.4(4)*
C(1′)-M−N(1′)			101.1(5)	99.0(3)		*101.6(4)*
C(1)-M-Se(1)	*87.2(2)*	*87.6(2)*	88.7(3)	89.1(2)	87.2(2)	*90.6(3)*
C(1)-M-Se(1′)	87.4(2)	87.5(2)	88.7(3)	88.7(2)	88.9(2)	*87.7(3)*
C(1′)-M-Se(1)			85.2(3)	85.8(2)		*84.9(4)*
C(1′)-M-Se(1′)			88.4(3)	88.3(2)		*88.2(4)*
N(1)-M−N(1′)	75.6(2)	76.4(2)	76.8(3)	77.2(2)	77.2(2)	75.8(3)
N(1)-M-Se(1)	*92.8(1)*	*92.8(1)*	93.6(2)	93.6(1)	90.9(1)	94.7(2)
N(1)-M-Se(1′)	93.0(1)	92.5(1)	92.9(2)	92.4(1)	93.2(1)	92.2(2)
N(1′)-M-Se(1)			90.2(2)	90.1(1)		90.7(2)
N(1′)-M-Se(1′)			92.8(2)	92.6(1)		91.6(2)
Se(1)-M-Se(1′)	*172.69(5)*	*173.24(4)*	173.27(6)	173.82(3)	174.70(3)	173.07(5)
M−N(1)−C(2)	126.0(4)	125.3(4)	129.3(9)	128.1(5)	128.6(5)	125.7(7)
M−N(1′)-C(2′)			128.3(8)	128.0(5)		125.1(8)
M−N(1)−C(6)	115.5(4)	114.6(4)	114.5(6)	114.0(4)	114.3(4)	113.9(6)
M−N(1′)-C(6′)			112.8(7)	112.8(4)		115.8(7)
M-Se(1)−C(11)	*103.2(5)*	*103.4(4)*	105.2(3)	105.1(1)	103.7(2)	102.4(2)
M-Se(1′)-C(11′)	102.9(3)	103.1(3)	104.0(3)	104.2(2)		102.7(3)

[a] Italicized entries involve atoms adjoining regions of the structure modeled as disordered and as such inherently involving values of rather less reliability than the bulk of the structure.

Scheme 1. Synthesis of Diorganometal(IV) Complexes

$$MMe_2(L_2) + (SePh)_2 \rightarrow MMe_2(SePh)_2(L_2)$$

1: M = Pt, L_2 = bpy
2: M = Pt, L_2 = phen
3: M = Pd, L_2 = bpy
4: M = Pd, L_2 = phen



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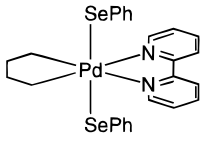
$$Pd(CH_2CH_2CH_2CH_2)(bpy) + (SePh)_2 \rightarrow$$



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PdMe resonances downfield from that of the $PdMe_2(bpy)$ reagent. The relative quantities of gas phase (ethane) and liquid-phase organic products have not been determined, but the yields of liquid-phase products were determined by a combination of NMR and GC-MS methods for the reactions of eqs 1 and 2. Benzoic acid (eq 1) is assumed to be formed by decomposition/hydrolysis of (benzoato)palladium(II) product(s) during workup. The inorganic product $Pd(O_2CPh)_2(bpy)$ (eq 1) was identified, but the very insoluble orange solids from the reactions of eqs 2−4 were not characterized. Detailed mass balances were not attempted for the reactions of eqs 1−4 since finely divided palladium metal as a product cannot be discounted, and some inorganic products may remain undetected in solution.

Despite the difficulties encountered in characterization of inorganic products, the results obtained for the reaction of eq 1 are consistent with decomposition according to eq 5, involving

$$PdMe_2(O_2CPh)_2(bpy) \rightarrow \sim 0.6[MeMe + Pd(O_2CPh)_2(bpy)] + \sim 0.4[MeO_2CPh + \text{“}PdMe(O_2CPh)(bpy)\text{”}] \quad (5)$$

C···C and C···O bond formation pathways and the presence of moisture during workup giving benzoic acid from partial decomposition of (presumably) “$PdMe(O_2CPh)(bpy)$”. For the reaction of eq 2, similar processes of C···C and C···S coupling occur; the formation of diphenyl disulfide is discussed below.

For the palladacyclopentane complexes (eqs 3 and 4) yields of products were not determined from NMR spectra because of the low solubility of the reagent and the absence of well-separated resonances for products. The intermediate palladium(IV) species could not be detected, apparently also owing to the low solubility of the $Pd(CH_2CH_2CH_2CH_2)(bpy)$ reagent resulting in the presence of a low concentration of the unstable palladium(IV) intermediate. The decomposition products are consistent with occurrence of several independent processes: fragmentation of the pallada(IV)cyclopentane ring via both C···C coupling and elimination of butenes and C···E coupling between the thiolate or carboxylate ligands and the pallada(IV)cyclopentane ring to form palladium(II) species $Pd^{II}CH_2CH_2CH_2CH_2EPh$ which decompose to form alkene (C_4H_7EPh) and alkane (C_4H_9EPh) products (E = O_2C, S).

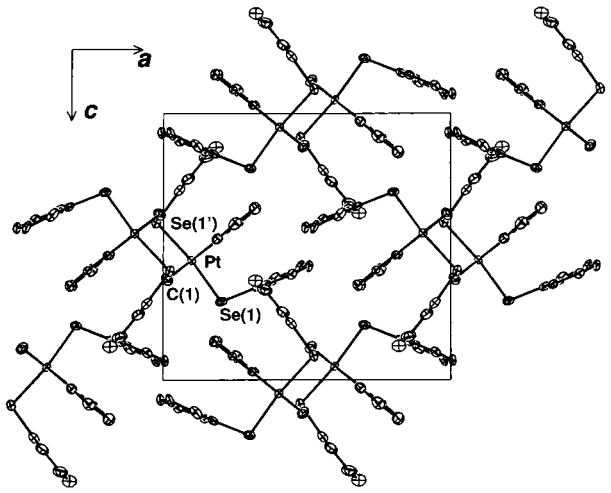

Figure 1. Unit cell contents of $PtMe_2(SePh)_2(bpy)$ (**1**) projected down *b*. The crystallographic mirror plane of space group *Pnma* lies normal to that axis.

X-ray Structural Studies of Selenophenolate Complexes $MMe_2(SePh)_2(L_2)$ (M = Pd, Pt; L_2 = bpy, phen). The 2,2′-bipyridine complexes formed isomorphous crystals in space group *Pnma*, while $PdMe_2(SePh)_2(phen)$ crystallized from chloroform/diethyl ether in the triclinic space group $P\bar{1}$. In view of an earlier structural analysis of $PtMe_2(SePh)_2(phen)$, which crystallized from acetone in the tetragonal space group $I4_1/a$,[9] this complex was also crystallized from chloroform/diethyl ether and found to form two phases, one of which is isomorphous with triclinic $PdMe_2(SePh)_2(phen)$ and the other tetragonal but with cell dimensions rather different from those reported earlier. Thus, the structural studies for isomorphous pairs of complexes $MMe_2(SePh)_2(bpy)$ (orthorhombic), $MMe_2(SePh)_2(phen)$ (triclinic), and a tetragonal phase of $PtMe_2(SePh)_2(phen)$ provide some opportunity for comparisons of coordination geometry in organopalladium(IV) and platinum(IV) chemistry where crystal packing effects, even if significant as the cell projections suggest, are constant within isomorphous pairs.

The complexes have distorted octahedral geometry containing a square-planar "$MMe_2(L_2)$" moiety and *trans*-selenophenolate groups (Figures 1−5 and Table 2). One of the selenophenolate groups in $MMe_2(SePh)_2(bpy)$ is disordered about the crystallographic mirror plane (Figure 1), and the molecules in the various structures exhibit different levels of crystallographic symmetry: $MMe_2(SePh)_2(bpy)$ (mirror plane through "MSe_2"), triclinic $MMe_2(SePh)_2(phen)$ (no crystallographic symmetry), and tetragonal $PtMe_2(SePh)_2(phen)$ (2-fold axis). In all of the complexes the phenyl groups lie above and below the bpy or phen groups.

Detailed comparisons of bond lengths for palladium and platinum complexes are rendered difficult by the disorder and other factors encountered during structure determinations (Table 1), although for the isomorphous pairs of complexes (**1** and **3**, **2a** and **4**) Pd−C < Pt−C and Pd−N > Pt−N. Similar trends, Pd−C < Pt−C and Pd-L > Pt-L, have been noted for isomorphous complexes [*fac*-$MMe_3\{(pz)_3CH$-*N*,*N*′,*N*″}]I (M = Pd, Pt)[6] and *fac*-[$MMe_3\{Co(Cp)(PR_2O)_3$-*O*,*O*′,*O*″}] (M = Pd, R = Me;[5c] M = Pt, R = Et[18]), and also for the nonisomorphous pair *fac*-[$MMe_3\{(ind)_3BH\}$] (M = Pd, Pt; $[(ind)_3BH]^-$ = tris-(indazol-1-yl)borate).[19]

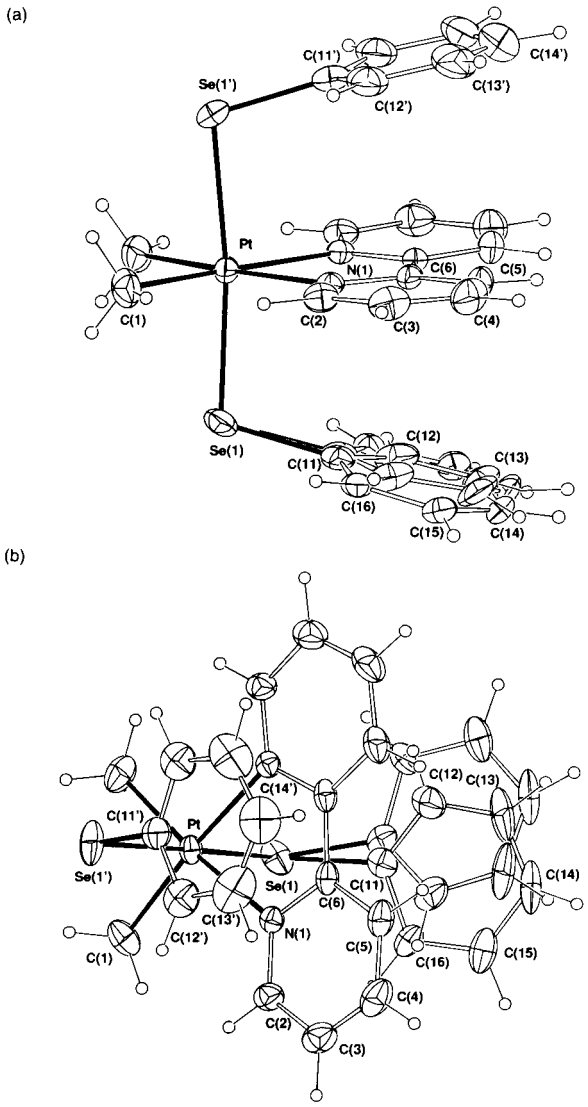

Figure 2. A single molecule of $PtMe_2(SePh)_2(bpy)$ (**1**) projected (a) approximately through the plane and (b) approximately down the Se−Pt−Se "axis", showing the disorder of the phenyl group of one of the ligands about the mirror plane in that model. Thermal ellipsoids (20%) are shown for the non-hydrogen atoms, and hydrogen atoms have been given an arbitrary radius of 0.1 Å in this and other figures.

Decomposition Reactions of Palladium(IV) Complexes. There are several reports of the decomposition of isolated triorganopalladium(IV) complexes,[4,5a,b,d,6−8] but studies of diorganopalladium(IV) complexes are restricted to unstable $PdI_2Me_2(N_2)$ [N_2 = bis(*p*-tolylimino)acenaphthene, bis(phenylimino)-camphane] which give a mixture of ethane and iodomethane.[5d] Complexes **3** and **4** represent the first isolable "simple" dialkylpalladium(IV) complexes, and thus they provide the first opportunity to compare decomposition of trialkyl- and dialkylpalladium(IV) complexes.

Trialkylpalladium(IV) complexes decompose almost exclusively by C···C bond formation, with C···X (X = halide) detected in mixtures of products of decomposition of a few complexes[5d,20] and as the major product on decomposition of an unstable dibromopallada(IV)cyclopentadiene complex.[5e] In contrast, $PdMe_2(SePh)_2(L_2)$ (**3**, **4**) decompose via both C···C and C···Se bond formation to give ethane and Se(Ph)Me, respectively, together with a small quantity of $SePh_2$ for L_2 =

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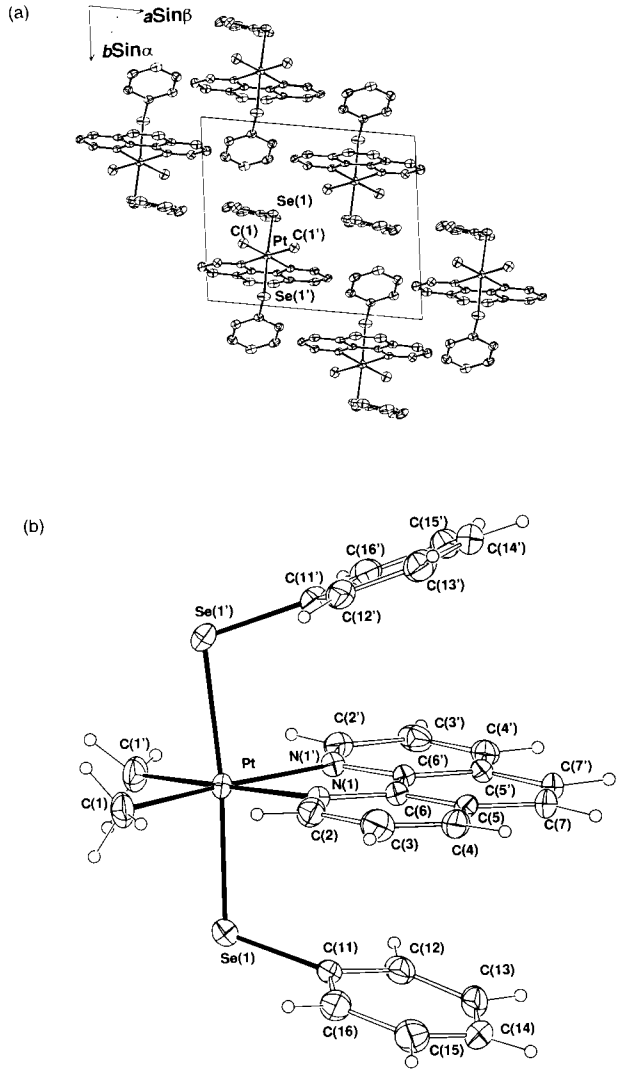

Figure 3. (a) Unit cell contents of $PtMe_2(SePh)_2(phen)$ (triclinic form) (**2a**) projected down *c*. (b) A single molecule of $PtMe_2(SePh)_2(phen)$ (**2a**).

phen (eq 6). Yields of Se(Ph)Me and $SePh_2$ were determined

$$PdMe_2(SePh)_2(L_2) \rightarrow MeMe + a\ MeSePh + b\ SePh_2 \quad (6)$$

$$L_2 = \text{bpy (\textbf{3}), } a \sim 50\%, b \sim 1\%$$
$$L_2 = \text{phen (\textbf{4}), } a \sim 27\%, b \sim 8\%$$

by a combination of NMR and GC-MS methods. Thus, the decomposition processes for **3** and **4** appear to be closely related to those for the unstable complexes $PdMe_2(O_2CPh)_2(bpy)$ and $PdMe_2(SPh)_2(bpy)$ which also exhibit carbon···carbon and carbon···chalcogen coupling (eqs 1 and 2).

The formation of SPh_2 in the reaction of $PdMe_2(bpy)$ with $(SPh)_2$, via unstable $PdMe_2(SPh)_2(bpy)$ (eq 2), and the formation of minor quantities of $SePh_2$ on the decomposition of $PdMe_2(SePh)_2(L_2)$ (L_2 = bpy, phen) are assumed to result from a similar process. It appears unlikely that EPh_2 could form directly from $PdMe_2(EPh)_2(L_2)$, and a more likely route may involve reaction of the E(Ph)Me product with a palladium(II) decomposition product, "Pd^{II}(EPh)", to give "Pd^{IV}(Ph)(EMe)(EPh)" followed by reductive elimination of EPh_2.

^{1}H NMR studies of the decompositions of **3** and **4** in $CDCl_3$ indicate first-order behavior where the bpy complex decomposes faster than the phen complex, e.g. $k \sim 1.69 \times 10^{-4}$ s^{-1} (L_2 = bpy) and $\sim 9.71 \times 10^{-5}$ s^{-1} (L_2 = phen) at 20 °C, and yield activation parameters E_a ~46 kJ mol^{-1}, $\Delta S^{\ddagger}$ (20 °C) ~ −170 J K^{-1} mol^{-1} (L_2 = bpy) and E_a ~36 kJ mol^{-1}, $\Delta S^{\ddagger}$ (20 °C) ~ −204 J K^{-1} mol^{-1} (L_2 = phen). Other solvents were found to be unsuitable for NMR studies; e.g. the complexes are insoluble in acetone, acetonitrile, and toluene.

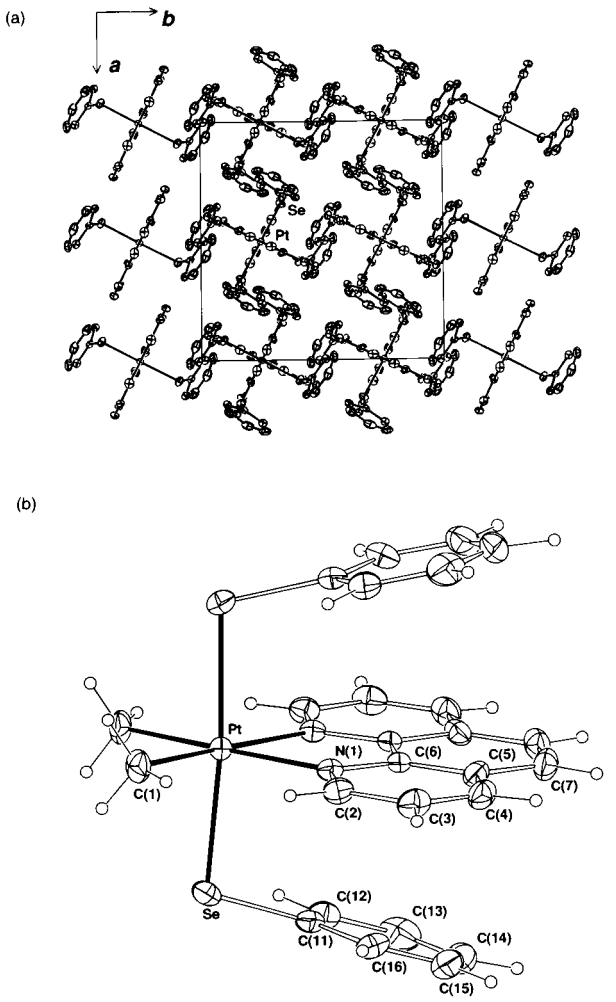

Figure 4. (a) Unit cell contents of $PtMe_2(SePh)_2(phen)$ (tetragonal form) (**2b**) projected down *c*. (b) A single molecule of $PtMe_2(SePh)_2$-(phen) (**2b**).

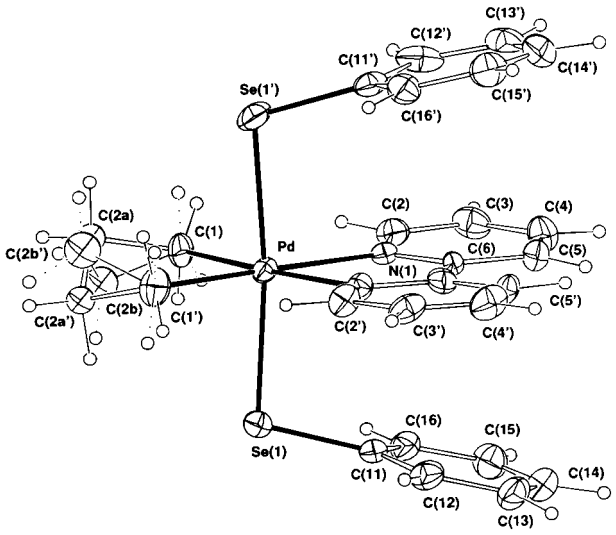

Figure 5. A single molecule of $Pd(CH_2CH_2CH_2CH_2)(SePh)_2(bpy)$ (**5**).

The complex $PdIMe_3(bpy)$ decomposes by first-order kinetics to give ethane and PdIMe(bpy),[7,8] and the negative $\Delta S^{\ddagger}$ for this reaction in acetone at 20 °C (-66 ± 34 kJ mol^{-1}), together with retardation by added iodide, was taken to indicate dissociation of I^- for the dominant pathway and formation of a (presumably) solvated intermediate $[PdMe_3(bpy)(acetone)]^+$ followed by reductive elimination. For $PdMe_2(SePh)_2(L_2)$, the highly negative values found for $\Delta S^{\ddagger}$, together with E_a values considerably lower than estimates of the Pd−Me bond energy ($\sim$130 kJ mol^{-1}),[7] are consistent with a process similar to that for $PdIMe_3(bpy)$. Thus, a polar transition state is implicated with either partial or complete ionization to form $[PdMe_2(SePh)(bpy)]^+[SePh]^-$, where the palladium center may well be solvated, followed by C···C or C···Se bond formation.

Concluding Remarks

The results reported here illustrate several new phenomena in organopalladium(IV) chemistry: isolation of stable dimethylpalladium(IV) complexes and selenolate complexes and detection of unstable thiolate complexes; formation of C···O, C···S, and C···Se bonds on decomposition; structural studies allowing detailed comparisons between palladium(IV) and platinum(IV) showing that Pd−Se = Pt−Se for the "*trans*-$M(SePh)_2$" moiety in $MMe_2(SePh)_2(L_2)$ (L_2 = bpy, phen) but Pd−C < Pt−C and Pd−N > Pt−N. The low stability of organopalladium(IV) complexes renders them ideal candidates for studies of decomposition at d^6 metal centers, and the dominance of C···C bond formation from triorganopalladium(IV) complexes is not reflected in diorganopalladium(IV) complexes in the presence of group 16 donor atoms (E) where C···E coupling becomes an important feature. The observation of C···O coupling at palladium(IV) is relevant to the proposed catalytic role of palladium(IV) in the acetoxylation of arenes.[21]

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of complexes $MMe_2(SePh)_2(bpy)$ [M = Pt (**1**), Pd (**3**)], $MMe_2(SePh)_2(phen)$ [M = Pt (**2a**,**b**), Pd (**4**)], and $Pd(CH_2CH_2CH_2CH_2)(SePh)_2(bpy)$ (**5**) are available on the Internet only. Access information is given on any current masthead page.

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