(η^3-CPh$_3$)(acac) (M = Pd, Pt),[60] and [Pt{*t*-Bu$_2$P(CH$_2$)$_3$P-*t*-Bu$_2$}(η^3-*anti*-1-MeCHAr)]$^+$ [47] the metal undergoes a [1,5]-suprafacial shift between equivalent η^3-benzyl sites which, in the first two cases, is rapid on the ^{1}H NMR time scale, even at low temperature.

Supplementary Material Available: Summary tables of crystal data and data collection and refinement details and listings of anisotropic thermal parameters for **2** and **3** and a table of hydrogen atom coordinates for **2** (9 pages). Ordering information is given on any current masthead page.

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^{1}H NMR Detection of Cationic Organopalladium(IV) Intermediates in Oxidative-Addition Reactions and the Structure of *fac*-PdBrMe$_2$(CH$_2$COPh)(bpy)

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Phenacyl bromides react with dimethylpalladium(II) complexes PdMe$_2$(L$_2$) (L$_2$ = bpy, phen) to form the palladium(IV) complexes *fac*-PdBrMe$_2$(CH$_2$COAr)(L$_2$) (Ar = Ph, *p*-C$_6$H$_4$Br), which have both methyl groups trans to the bidentate nitrogen donor ligand. ^{1}H NMR studies of the oxidative addition of phenacyl bromides to PdMe$_2$(bpy) in (CD$_3$)$_2$CO at −5 °C indicate the formation of two similar cationic intermediates, prior to formation of the neutral product. As the cations have only one of the methyl groups trans to bpy, configurational changes at palladium occur on cation formation and on conversion of the cations to the neutral product. It is proposed that one of the cations may be stabilized via an intramolecularly coordinated phenacyl group, [PdMe$_2$(CH$_2$COAr-*C,O*)(L$_2$)]$^+$. A single cation, exhibiting NMR spectra similar to those of the cations of the bpy complexes, is detected as an intermediate in the reaction of PdMe$_2$(phen) with ArCOCH$_2$Br. A cation has also been detected for the reaction of PdMe$_2$(bpy) with CD$_3$I in (CD$_3$)$_2$CO at −50 °C, prior to formation of PdIMe$_2$(CD$_3$)(bpy). Both the cation, most likely [PdMe$_2$(CD$_3$)(bpy)((CD$_3$)$_2$CO)]$^+$, and the neutral product display scrambled Me and CD$_3$ groups, in contrast to the trans oxidative addition reported for the analogous reaction of PtMe$_2$(bpy) with CD$_3$I. Crystals of PdBrMe$_2$(CH$_2$COAr)(bpy) are orthorhombic, space group *Pbca*, with *a* = 19.554 (3) Å, *b* = 15.007 (9) Å, *c* = 13.282 (4) Å, and *Z* = 8.

Introduction

The classic S$_N$2 mechanism for oxidative addition of alkyl halides to d^8 metal centers is expected to require the formation of a cation intermediate (eq 1).[2,3] However, spectroscopic detection of intermediate cations appears to be restricted to two platinum(II,IV) systems,[4,5] presumably because reaction ii is very fast under the conditions usually required for monitoring reaction i.

$$\underset{d^8}{M} + RX \xrightarrow{(i)} \underset{d^6}{MR^+X^-} \xrightarrow{(ii)} \underset{d^6}{MXR} \qquad (1)$$

The recent emergence of an organometallic chemistry of palladium(IV),[6-9] involving the reaction of alkyl halides with palladium(II) d^8 complexes, is providing new systems for the examination of mechanisms in oxidative-addition chemistry. Kinetic studies indicate occurrence of the S$_N$2 mechanism for the reaction of PdMe$_2$(L$_2$) (L$_2$ = 2,2′-bipyridyl (bpy), 1,10-phenanthroline (phen)) with iodomethane and benzyl bromide.[10] Consistent with this mechanism, the tetramethylethylenediamine complex PdMe$_2$(tmeda) reacts with methyl triflate in CD$_3$CN to form [PdMe$_3$(tmeda)(NCCD$_3$)]$^+$SO$_3$CF$_3^-$.[8a] We report here further developments in the synthetic chemistry of palladium(IV), resulting in ^{1}H NMR detection of cation intermediates in oxidative-addition reactions. The studies reveal facile isomerization processes during oxidative addition of phenacyl bromides to PdMe$_2$(L$_2$), and a reexamination of the reaction of iodomethane with PdMe$_2$(bpy) at −50 °C has also revealed the occurrence of a cation intermediate. A preliminary report of part of this work has appeared.[11]

Results and Discussion

Synthesis and Characterization of Palladium(IV) Complexes PdBrMe$_2$(CH$_2$COAr)(L$_2$) (L$_2$ = bpy, phen; Ar = Ph, *p*-C$_6$H$_4$Br). The complexes formed on reaction of PdMe$_2$(L$_2$) with the organo bromides at 0 °C and were isolated by workup at this temperature. ^{1}H NMR spectra for CDCl$_3$ solutions are readily interpretable, with singlets for PdMe and CH$_2$ groups, and equivalence of pyridyl rings

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Table I. Positional Parameters for $PdBrMe_2(CH_2COPh)(bpy)$

atom	x	y	z
Pd	0.13375 (3)	0.19351 (3)	0.12512 (4)
Br	0.06460 (4)	0.23617 (5)	−0.03113 (6)
C(a)	0.2232 (4)	0.2347 (5)	0.0600 (6)
N(a1)	0.0408 (3)	0.1343 (4)	0.1870 (4)
C(a2)	0.0297 (3)	0.0493 (5)	0.1592 (5)
C(a3)	−0.0288 (4)	0.0052 (5)	0.1907 (6)
C(a4)	−0.0748 (4)	0.0472 (7)	0.2516 (7)
C(a5)	−0.0639 (4)	0.1324 (6)	0.2787 (6)
C(a6)	−0.0053 (4)	0.1746 (5)	0.2453 (6)
C(b)	0.1229 (4)	0.3203 (4)	0.1771 (6)
N(b1)	0.1359 (3)	0.0563 (3)	0.0710 (4)
C(b2)	0.0813 (4)	0.0064 (5)	0.0937 (5)
C(b3)	0.0759 (4)	−0.0805 (5)	0.0597 (6)
C(b4)	0.1269 (6)	−0.1166 (5)	0.0034 (6)
C(b5)	0.1825 (5)	−0.0652 (7)	−0.0192 (6)
C(b6)	0.1849 (4)	0.0203 (6)	0.0143 (6)
C(c′)	0.1890 (4)	0.1707 (5)	0.2563 (5)
C(c)	0.2142 (4)	0.0785 (6)	0.2558 (6)
O(c)	0.2675 (3)	0.0583 (5)	0.2156 (5)
C(c1)	0.1730 (4)	0.0081 (6)	0.3062 (6)
C(c2)	0.1234 (4)	0.0250 (5)	0.3772 (6)
C(c3)	0.0879 (5)	−0.0432 (7)	0.4220 (7)
C(c4)	0.1005 (6)	−0.1289 (7)	0.3967 (9)
C(c5)	0.1496 (6)	−0.1468 (7)	0.3277 (8)
C(c6)	0.1863 (5)	−0.0801 (8)	0.2839 (6)

Table II. Selected Bond Distances (Å) and Angles (deg) for $PdBrMe_2(CH_2COPh)(bpy)$[a]

	Bond Distances		
Pd–C(a)	2.047 (7)	Pd–N(a1)	2.184 (5)
Pd–C(b)	2.035 (7)	Pd–N(b1)	2.181 (5)
Pd–C(c′)	2.078 (7)	Pd–Br	2.558 (1)
	Bond Angles		
C(a)–Pd–C(b)	87.1 (3)	N(a1)–Pd–Br	88.1 (1)
C(a)–Pd–C(c′)	87.7 (3)	N(b1)–Pd–Br	88.8 (1)
C(b)–Pd–C(c′)	85.6 (3)	N(a1)–Pd–N(b1)	75.9 (2)
C(a)–Pd–N(a1)	173.3 (3)	Pd–N(a1)–C(a2)	114.6 (4)
C(a)–Pd–N(b1)	97.5 (3)	Pd–N(a1)–C(a6)	126.6 (5)
C(a)–Pd–Br	91.9 (2)	Pd–N(b1)–C(b2)	116.1 (4)
C(b)–Pd–N(a1)	99.5 (3)	Pd–N(b1)–C(b6)	125.6 (5)
C(b)–Pd–N(b1)	175.0 (3)	Pd–C(c′)–C(c)	109.0 (5)
C(b)–Pd–Br	89.2 (2)	C(c′)–C(c)–C(c1)	119.0 (7)
C(c′)–Pd–N(a1)	92.9 (2)	C(c′)–C(c)–O(c)	121.9 (8)
C(c′)–Pd–N(b1)	96.4 (3)	C(c1)–C(c)–O(c)	119.1 (8)
C(c′)–Pd–Br	174.8 (2)	N(a1)–C(a2)–C(b2)	117.7 (6)
		N(b1)–C(b2)–C(a2)	115.6 (6)

[a] The pyridyl rings are planar (rings a and b have $\chi^2 = 1.3, 2.0$) and form a dihedral angle of 2.0 (3)°, and the rings form dihedral angles of 3.4 (2) and 4.1 (2)° with the "C_2N_2" mean plane (which has $\chi^2 = 15.1$); the Pd atom is 0.06 (1) and 0.08 (1) Å from the mean planes of rings a and b, respectively. The phenyl ring is planar ($\chi^2 = 3.0$), and deviations of C(c), C(c′), and O(c) from this plane are 0.01 (2), −0.39 (2), and 0.35 (2) Å, respectively.

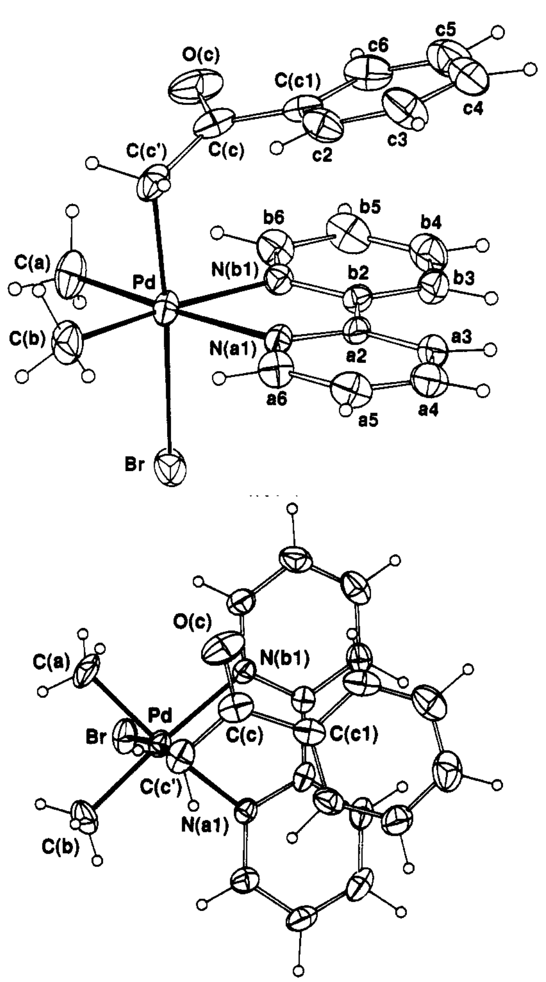

Figure 1. Two projections of $PdBrMe_2(CH_2COPh)(bpy)$. The bottom projection is a view normal to the phenyl plane; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms have been given an arbitrary radius of 0.1 Å.

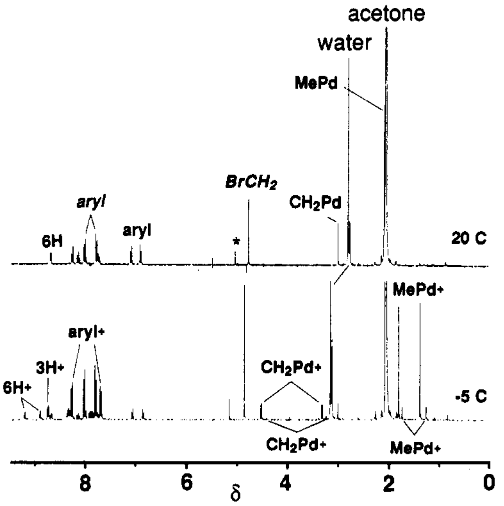

Figure 2. ^1H NMR spectra obtained on addition of an excess of p-$BrC_6H_4COCH_2Br$ to $PdMe_2(bpy)$ in $(CD_3)_2CO$ at −5 °C, followed by warming to 20 °C. Selected assignments are shown, with peaks for the unchanged reagent being in italics. The asterisk indicates an impurity.

indicating trans oxidative addition of the organo bromides to $PdMe_2(L_2)$.

Crystals of $PdBrMe_2(CH_2COPh)(bpy)$ obtained directly from the synthesis were suitable for crystallographic studies. Selected structural parameters are given in Tables I and II, and projections of the structure are shown in Figure 1. The phenacyl group is located above the 2,2′-bipyridyl ligand, as found in the related p-bromobenzyl complex $PdBrMe_2(CH_2$-p-$C_6H_4Br)(phen)$.[12] Bond lengths and angles for the coordination geometry are similar to those of $PdBrMe_2(CH_2$-p-$C_6H_4Br)(phen)$.[12]

^1H NMR Studies of Oxidative Addition of Organo Halides to $PdMe_2(L_2)$. Addition of excess $ArCOCH_2Br$ to $PdMe_2(phen)$ in $(CD_3)_2CO$ at −5 °C gave ^1H NMR spectra showing immediate reaction of $PdMe_2(phen)$, exhibiting resonances for $PdBrMe_2(CH_2COAr)(phen)$ and other resonances assigned to an intermediate. When the temperature is raised to 20 °C, resonances of the intermediate vanish to give a spectrum showing only $PdBrMe_2(CH_2COAr)(phen)$ and unreacted organo halide.

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Table III. Selected ^{1}H NMR Data (δ) for Palladium(IV) Species in $(CD_3)_2CO$, Detected during the Reaction

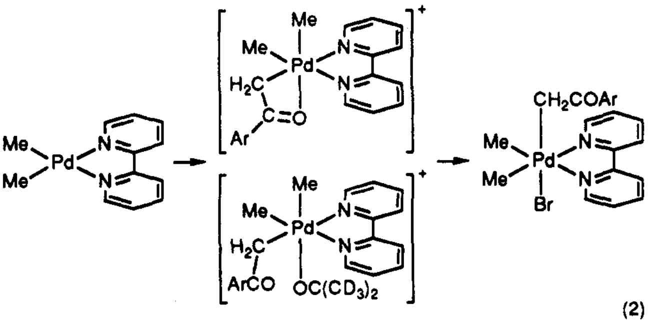
$$Pd^{II}Me_2(L_2) \xrightarrow[-5\ °C]{ArCOCH_2Br} \text{“}[Pd^{IV}Me_2(CH_2COAr)(L_2)]^{+}\text{”}^{a} \xrightarrow[20\ °C]{} Pd^{IV}BrMe_2(CH_2COAr)(L_2)$$

		“$[Pd^{IV}Me_2(CH_2COAr)(L_2)]^+$”^{a,b}		$Pd^{IV}BrMe_2(CH_2COAr)(L_2)^b$	
Ar	L_2	PdMe^c	$PdCH_2$^{d}	PdMe	$PdCH_2$
Ph	bpy	1.86, 1.36 1.78,^{e} 1.26^e	4.60 d, 3.40 d 4.50 d,^{e} 3.32 d^e	2.09	3.02
Ph	phen	2.00, 1.46	4.67 d, 3.58 d	2.24	3.12
p-C_6H_4Br	bpy	1.81, 1.39 1.54,^{e} 1.26^e	4.67 d, 3.46 d 4.41 d,^{e} 3.25 d^e	2.11	2.99
p-C_6H_4Br	phen	1.92, 1.47	4.70 d, 3.47 d	2.24	3.09

[a] Assumed octahedral with solvent coordination or intramolecular phenacyl coordination. [b] At −5 °C. [c] Me group trans to L_2 is at a higher δ value in each set. [d] ^2J(HH) = ca. 6 Hz. [e] Very low intensities.

The final spectra do not alter on recooling, indicating that resonances assigned to the intermediate do not arise from an equilibrium with the neutral product.

Spectra for the reaction of $PdMe_2$(bpy) with $ArCOCH_2Br$ indicate the presence of two intermediates, as shown in Figure 2 for the reaction of p-$BrC_6H_4COCH_2Br$. The spectra are very similar to those of the phen analogues, except that they exhibit a second set of low-intensity PdMe and $PdCH_2$ resonances (assigned below the base line in Figure 2). Detailed assignments are given in Table III. The spectrum obtained at −5 °C (Figure 2) exhibits four methylpalladium resonances, upfield from the value for the neutral product $PdBrMe_2(CH_2COC_6H_4Br)$(bpy), and the 1:1 relative intensities for the two sets of resonances are maintained during their disappearance at 20 °C. The upfield shift is consistent with assignment of the intermediates as cations, since $Pt^{IV}Me$ resonances in cations occur upfield from those of closely related neutral complexes.[5] The close relationship between the singlets for the PdMe group of each intermediate suggests that the geometry and donor atoms in each intermediate are similar. The methylene protons in $PdCH_2COC_6H_4Br$ are inequivalent in both intermediates, occurring as an AB pattern with $^2J_{HH}$ = ca. 6 Hz separated by ca. 1.2 ppm. Again, a close relationship appears to occur between the environments in each intermediate. The lack of symmetry at palladium is also indicated by the presence of an unsymmetrical 2,2′-bipyridyl group, as two H6 resonances occur for the major cation. Assuming that the expected[7] *fac*-PdC_3 geometry occurs, and that one of the donor groups is a solvent molecule in one intermediate, the other intermediate may be either a similar structure with a different orientation along the Pd–CH_2 axis or an intramolecular coordination system (eq 2).



(2)

Intramolecular coordination involving Pd–CH_2 in the axial position is very unlikely, as this would require a *mer*-PdC_3 geometry. The intramolecular system as shown in eq 2 may occur as a means of stabilization for the major cation, and this assignment is also consistent with the extreme difficulty found in detecting cations for the oxidative addition of closely related benzyl bromides to $PdMe_2(L_2)$. In some cases benzyl bromides gave very low intensity resonances assigned tentatively to cations with both methyl groups trans to L_2 in “$[PdBrMe_2(CH_2Ar)(L_2)((CD_3)_2CO)]^+$”, e.g. for Ar = p-BrC_6H_4 at −20 °C, the cation has singlets at 2.98 and 1.80 ppm, assigned as $PdCH_2$ and PdMe, respectively.

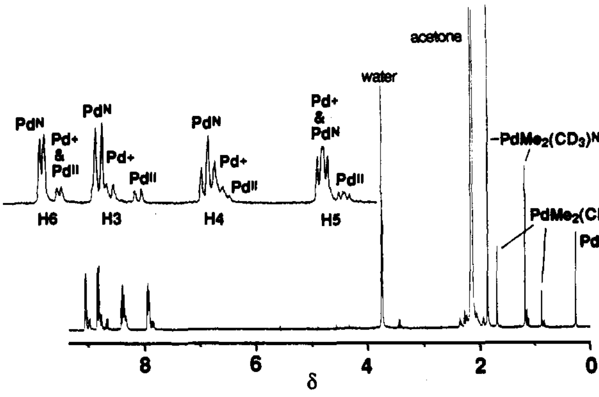


Figure 3. ^{1}H NMR spectrum obtained on addition of excess CD_3I to $PdMe_2$(bpy) at −50 °C in $(CD_3)_2CO$, showing unreacted $PdMe_2$(bpy), the cation $[PdMe_2(CD_3)(bpy)((CD_3)_2(CO)]^+$, and the neutral product $PdIMe_2(CD_3)$(bpy). PdMe resonances for both the cation $(PdMe_2(CD_3))^+$ 1.61, 0.82 ppm) and the neutral product $(PdMe_2(CD_3))^N$ 1.77, 1.11 ppm) have 2:1 intensity ratios for the methyl groups trans to bpy and $(CD_3)_2CO$ (cation) or iodide (neutral product).

The detection of cations described above prompted an examination of the reaction of $PdMe_2$(bpy) with CD_3I in $(CD_3)_2CO$ at −50 °C. At this temperature, an intermediate cation was observed, and as the temperature was raised it irreversibly converted to the neutral product $PdIMe_2(CD_3)$(bpy) (Figure 3). In contrast to the analogous platinum experiment, where the methyl groups remain trans to bpy in the cation and neutral product,[5] the methyl and CD_3 groups are scrambled between positions trans to bpy and solvent (or iodide), reflecting more facile intramolecular motion for palladium(IV). Scrambling is assumed to occur in the cation intermediate, perhaps during oxidative addition in a five-coordinate intermediate prior to solvent coordination.

Conclusions

Phenacyl bromides react with dimethylpalladium(II) complexes of 2,2′-bipyridyl and 1,10-phenanthroline in acetone at −5 °C to give cationic species that react with bromide to give the isolable complexes $PdBrMe_2(CH_2COAr)(L_2)$. Subtle configurational changes occur during the reaction: methyl groups trans to L_2 in square-planar $PdMe_2(L_2)$ occupy one position trans to L_2 and one trans to an axial site in the octahedral intermediate cations and revert to positions trans to L_2 in the octahedral neutral product. Similar flexibility occurs during oxidative addition of CD_3I to $PdMe_2$(bpy) at −50 °C, where the methyl and CD_3 groups are scrambled in the intermediate cation $[PdMe_2(CD_3)(bpy)((CD_3)_2CO)]^+$ and in the final neutral product $PdIMe_2(CD_3)$(bpy). This study provides one of very few reports of the detection of cations for oxidative addition of organo halides to d^8 centers, the first for addition to palladium(II), and also illustrates interesting differences from related platinum chemistry.

Experimental Section

The reagents $PdMe_2$(bpy) and $PdMe_2$(phen) were prepared as described,[13] and the solvents were distilled. Microanalyses were by the Canadian Microanalytical Service, Vancouver, Canada, and the ^{1}H NMR spectra were recorded with a Bruker AM 300 spectrometer, with chemical shifts given in ppm relative to Me_4Si.

Synthesis of Complexes. $PdBrMe_2(CH_2COPh)(bpy)$. $PhCOCH_2Br$ (0.072 g, 0.36 mmol) was added to a stirred, filtered solution of $PdMe_2(bpy)$ (0.102 g, 0.35 mmol) in acetone at 0 °C (ca. 15 mL, warmed to dissolve if necessary). The yellow solution became decolorized immediately, hexane (10 mL) was added, and the solution was evaporated under reduced pressure at 0 °C to give a white crystalline solid at ca. half volume (yield 47%). The complex was washed with hexane and vacuum-dried. ^{1}H NMR ($CDCl_3$): δ 8.60 (d, ^3J = 4.7 Hz, 2, H6), 7.85 (m, 4, H3 and H4), 7.49 (m, 2 H5), 7.24 (t, 1, Ph(4)), 6.94 (m, 4, Ph(2,3,5,6)), 3.02 (s, 2, $PdCH_2$), 2.20 (s, 6, PdMe). Anal. Calcd for $C_{20}H_{21}BrN_2OPd$: C, 48.9; H, 4.3; N, 5.7. Found: C, 49.2; H, 4.3; N, 5.6.

The following complexes were obtained as pale yellow solids by using a similar procedure.

$PdBrMe_2(CH_2COPh)(phen)$: yield 46%; ^{1}H NMR ($CDCl_3$) δ 8.95 (dd, ^3J = 4.9 Hz, ^4J = 1.5 Hz, H2,9), 8.33 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, H4,7), 7.82 (m, 2, H3,8), 7.75 (s, 2, H5,6), 6.87 (t(b), 1, Ph(4)), 6.65 (m, 2, Ph(3,5)), 6.54 (m, 2, Ph(2,6)), 3.12 (s, 2, $PdCH_2$), 2.35 (s, 6, PdMe). Anal. Calcd for $C_{22}H_{21}BrN_2OPd$: C, 51.2; H, 4.1; N, 5.4. Found: C, 50.6; H, 4.1; N, 5.7.

$PdBrMe_2(CH_2CO\text{-}p\text{-}C_6H_4Br)(bpy)$: yield 37%; ^{1}H NMR ($CDCl_3$) δ 8.61 (d, ^3J = 6 Hz, 2, H6), 7.92 (m, 4, H3 and H4), 7.53 (m, 2, H5), 7.05 (d, 2, Ph(3,5)) and 6.84 (d, ^3J = 8.5 Hz, 2, Ph(2,6)), 2.97 (s, 2, $PdCH_2$), 2.20 (s, 6, PdMe). Anal. Calcd for $C_{20}H_{20}Br_2N_2OPd$: C, 42.1; H, 4.2; N, 4.9. Found: C, 42.2; H, 3.6; N, 4.8.

$PdBrMe_2(CH_2CO\text{-}p\text{-}C_6H_4Br)(phen)$: yield 35%; ^{1}H NMR ($CDCl_3$) δ 8.97 (d(b), 2, H2,9), 8.38 (d(b), 2, H4,7), 7.85 (m(b), 4, H3,5,6,8), 6.58 (d, 2, Ph(3,5)) and 6.44 (d, ^3J = 8.5 Hz, 2, Ph(2,6)), 3.06 (s, 2, $PdCH_2$), 2.36 (s, 6, PdMe). Anal. Calcd for $C_{22}H_{20}Br_2N_2OPd$: C, 4.44; H, 3.4; N, 4.7. Found: C, 44.8; H, 3.5; N, 4.7.

X-ray Structure Determination. A unique data set was measured to $2\theta_{max}$ = 55° with an Enraf-Nonius CAD-4 diffractometer operating in the conventional 2θ-θ scan mode. A total of 4213 independent reflections were obtained at ca. 295 K, 2019 with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after Gaussian absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for non-hydrogen atoms; although hydrogen atoms of the methyl groups were located, all $(x, y, z, U_{iso})_H$ values were included constrained at estimated values. Residuals R and R_w on $|F|$ at convergence were 0.040 and 0.035; statistical weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ were employed. Neutral-atom complex scattering factors were used;[14] computation was with the XTAL 3.0 program system implemented by Hall.[15] Crystal data and collection parameters: $PdBrMe_2(CH_2COPh)(bpy)$, $C_{20}H_{21}BrN_2OPd$, M_r = 491.7, orthorhombic, space group *Pbca*, a = 19.554 (3) Å, b = 15.007 (9) Å, c = 13.282 (4) Å, V = 3897.6 Å^3, $D_c(Z = 8)$ = 1.68 g cm^{-3}, $F(000)$ = 1952, specimen size 0.11 × 0.25 × 0.18 mm, monochromatic Mo Kα radiation, λ = 0.71073 Å, μ = 28.9 cm^{-1}, $A^*_{min,max}$ = 1.36, 1.65.

Acknowledgment. We thank the Australian Research Council and the University of Tasmania for financial support and Johnson Matthey Ltd. for a generous loan of palladium salts.

Supplementary Material Available: Listings of thermal parameters, hydrogen atom parameters, and ligand and phenacyl geometries (3 pages). Ordering information is given on any current masthead page.

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Stable Silene Geometric Isomers

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Photolysis of the acylsilane $(Me_3Si)_2MesSiCOAd$ (**1**) at room temperature gave rise to two geometric isomers of $(Me_3Si)MesSi{=}C(OSiMe_3)Ad$ (**2a,b**) the first reported silene geometric isomers detectable and stable in solution at room temperature. Warming to 100 °C caused the slow decomposition of both isomers so that, at the end of 7 days, the minor isomer was completely decomposed while 60% of the major isomer remained. Addition of methanol to the silenes in the dark gave the pair of diastereomeric adducts **3a,b**, identical with the products of photolysis of **1** in the presence of methanol. Treatment of 1.4:1 mixtures of the silenes with phenylacetylene or (trimethylsilyl)acetylene gave rise to 1.4:1 mixtures of the anticipated silacyclobutenes **4a,b** and **5a,b**, indicating that the cycloaddition reactions were highly stereospecific. Crystal structures obtained for the major silacyclobutene derived from phenylacetylene, **4a**, and the major isomer derived from (trimethylsilyl)acetylene, **5a**, confirmed the regiochemistry and stereochemistry of their structures and indicated that the major silene isomer **2a** had *E* geometry. Silenes **2a,b** failed to react with 2,3-dimethylbutadiene or diphenylacetylene but reacted with butadiene, yielding only [2 + 2] cycloadducts **6**. Reaction of the silenes with oxygen gave the ester **8**. When the silenes **2a,b** were further photolyzed in inert solvent with ≥360 nm radiation, they were slowly converted to a complex mixture which contained the silaindanes **10a,b**. A crystal structure of the silacyclobutene adduct of the silene $(Me_3Si)_2Si{=}C(OSiMe_3)CMe_3$ with 1-phenylpropyne, **11**, indicated that the $=$CMe group of the silacyclobutene was adjacent to the ring silicon atom, consistent with the findings for **4** and **5** and contrary to a previous proposal.

The 1,3-shift of a trimethylsilyl group from silicon to oxygen during the photolysis of acylpolysilanes under mild photochemical conditions ($\lambda \geq$ 360 nm) gives rise to silenes, as is now well-established.[1-3] For acylsilanes with the