

Organopalladium Compounds with a Chiral Palladated Carbon Atom. Facile Isolation of Optically Active Cyclopalladated Complexes Containing the (*S*)- or (*R*)-[2-NMe₂C₆H₄CH(SiMe₃)] Monoanion.¹ Molecular Structure of {2-[1-(*S*)-(Dimethylamino)ethyl]phenyl}[2-(dimethylamino)- α -(trimethylsilyl)benzyl]palladium(II)

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A series of mixed metallobicyclic compounds of general formula [Pd($\widehat{N}C$)(dmat-Si)], in which dmat-Si is the monoanionic 2-NMe₂C₆H₄CH(SiMe₃) chelate and $\widehat{N}C$ is one of the monoanionic chelates 2-NMe₂CH₂C₆H₄ (dmba), 8-C₉H₆NCH₂ (8-mq), or the pure *S* enantiomer of 2-NMe₂CH(Me)C₆H₄ ((*S*)-dmba), has been synthesized via the transmetalation reaction of dmat-SiLi (1) with one of the dimers [Pd($\widehat{N}C$)(μ -Cl)]₂. The 2:1 molar reaction of 1 with [Pd(SEt₂)₂Cl₂] afforded as the main product the C-C coupled compound [dmat-Si]₂ (3) and the symmetric product [Pd(dmat-Si)]₂ (2) in only 4% yield. [Pd-((*S*)-dmba)(dmat-Si)] (6) is formed as a mixture of the two diastereomers, arising from the configuration (either *R* in 6a or *S* in 6b) of the benzylic carbon atom of the dmat-Si chelate. These diastereomers can be separated by fractional crystallization. The molecular structure of the most accessible diastereomer 6b has been determined by an X-ray diffraction study: C₂₂H₃₄N₂PdSi, monoclinic, *P*2₁, *a* = 10.027 (2) Å, *b* = 11.481 (4) Å, *c* = 10.833 (2) Å, β = 115.08 (2)°, *V* = 1129.5 Å³, *Z* = 2 for 1843 (*I* > $\sigma(I)$) reflections, μ (Mo K α) = 8.7 cm⁻¹, *R* = 0.0200, *R*_w = 0.0289. The square-planar configuration about the Pd atom contains the $\widehat{N}C$ chelates in the *cis* arrangement while the absolute configuration of the benzylic carbon atom bearing the SiMe₃ group is *S*. Reactions of [Pd($\widehat{N}C$)(dmat-Si)] with either methyl vinyl ketone or acetyl chloride did not afford functionalized dmat-Si ligands via the cross-coupling reaction. Instead reaction of [Pd-(dmba)(dmat-Si)] (4) with PhCH₂Br yielded the ammonium salt of the cross-coupled product [2-((PhCH₂)NMe₂CH₂)C₆H₄CH₂Ph]⁺Br⁻ together with [Pd(dmat-Si)(μ -Br)]₂ (7). The latter compound is a mixture of *cis* and *trans* isomers and gives the monomer [Pd(dmat-Si)PyBr] (8) on reaction with pyridine.

Introduction

The chemistry of organopalladium compounds in which the metal is part of a heterocyclic unit has received much attention.³ Particularly, the compounds derived from palladation of tertiary amines have been shown to display useful reactivity as intermediates in organic synthetic reactions.⁴ While looking for some applications of cyclopalladated derivatives in enantioselective syntheses,⁵ Sokolov et al. found that chiral ferrocenylpalladium com-

pounds are good candidates for the syntheses of precursors of natural prostaglandins.^{4,6} They also showed that these optically active starting materials were easily accessible. This contrasts with the fact that up to now only a few optically active organopalladium compounds with a chiral metalated carbon center have been reported. Moreover, it appeared to be difficult to obtain these compounds enantiomerically pure.⁷ We have now embarked on a study directed to find a reliable way to obtain such complexes.

It has been shown that lithiated tertiary amines or phosphines are easily transmetalated onto Pd(II) or Pt(II) centers affording either symmetrical or asymmetrical bicyclic organometallic products.⁸ We decided to use this

(1) Reactivity of cyclopalladated compounds. 13. Part 12: Maassarani, F.; Pfeffer, M.; Le Borgne, G.; Grandjean, D. *Organometallics* 1986, 5, 1511.

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(7) (a) The direct synthesis of an optically pure compound by the cyclopalladation of 8-ethylquinoline according to Sokolov's report^{7b} was impossible in our hands. These authors have published alternative methods based on transmetalation reactions that are however much more complicated to achieve.^{7cd} (b) Sokolov, V. I.; Sorokina, T. A.; Troitskaya, L. L.; Solovieva, L. I.; Reutov, O. A. *J. Organomet. Chem.* 1972, 36, 389. (c) Sokolov, V. I.; Bashilov, V. V.; Musaev, A. A.; Reutov, O. A. *J. Organomet. Chem.* 1982, 225, 57. (d) Bashilov, V. V.; Maskaeva, E. V.; Petrovskii, P. V.; Sokolov, V. I. *J. Organomet. Chem.* 1985, 292, 89.

strategy to synthesize organopalladium complexes with a chiral palladated carbon center rather than the route involving the direct palladation reaction of the prochiral ligand. In this paper the transmetalation reaction of lithiated 2-(dimethylamino)- α -(trimethylsilyl)toluene to chloropalladium complexes is reported. In one case this approach has led to the facile isolation of an optically active organopalladium compound, i.e., $[(S)-2-NMe_2CH(Me)C_6H_4]Pd\{[(S)-CH(SiMe_3)C_6H_4NMe_2-2]\}$ of which the structure has been determined by an X-ray diffraction study. The first results directed to the use of these novel chiral palladium compounds in organic syntheses are described.

Experimental Section

General Data. All manipulations were performed under dry oxygen-free nitrogen by using standard Schlenk techniques unless otherwise stated. The 1H and ^{13}C $\{^1H\}$ NMR spectra were recorded at 200.00 and 50.32 MHz, respectively, on a Bruker SY 200 instrument. Proton and carbon chemical shifts (δ) are positive downfield relative to external $SiMe_4$. The 2-D NMR spectrum (200 MHz 1H); ^{13}C , 1H , correlated) of **4** dissolved in CD_2Cl_2 was recorded on a Bruker AC 200 instrument. 1H and ^{13}C NMR data are given in Tables I and II, respectively. CD spectra were measured in toluene solutions in a 1-dm cell thermostated to 20 °C by use of a Perkin-Elmer Model 241 MC polarimeter. Elemental analyses were carried out by the Service Central de Microanalyses du CNRS (Strasbourg, France).

Syntheses. All solvents were dried and distilled under nitrogen prior to use. $[Pd(SEt_2)_2Cl_2]$,⁹ $\{[Pd(dmab)(\mu-Cl)]_2\}$,¹⁰ $\{[Pd(8-mq)(\mu-Cl)]_2\}$,¹¹ and $\{[Pd((S)-dmab)(\mu-Cl)]_2\}$ ¹² were prepared as previously reported. Synthesis and lithiation of 2-(dimethylamino)[(trimethylsilyl)methyl]benzene to 2-(dimethylamino)- α -lithio- $[\alpha$ -(trimethylsilyl)methyl]benzene [**1**, Li(dmat-Si)] were performed as described in the literature.¹³⁻¹⁵

$\{[2-NMe_2C_6H_4CH(SiMe_3)]Pd\{CH(SiMe_3)C_6H_4NMe_2-2\}\}$ (**2**). A solution of **1**^{15b} (1.21 g, 5.7 mmol) in Et_2O (12 mL) was added dropwise to a solution of $[Pd(SEt_2)_2Cl_2]$ (0.85 g, 2.38 mmol) in Et_2O (35 mL) at -20 °C. The mixture was allowed to warm up slowly to room temperature. The solvent was removed from the black solution in vacuo and pentane (35 mL) added to the residue. The solution was then filtered on a short column of alumina ($l = 5$ cm) and the column eluted with toluene (15 mL) which yielded a yellow solution. This solution was evaporated to dryness and the resulting yellow oil dissolved in pentane (15 mL) from which the white compound **3** crystallized at -20 °C (0.04 g, 3.4%). Anal. Calcd for $(C_{12}H_{20}NSi)_2$ (**3**): C, 69.83; H, 9.77; N, 6.79. Found: C, 69.30; H, 9.68; N, 6.74. Compound **2** could not be isolated pure in this way because of its high solubility in pentane. It was always

contaminated by **3** and protonated dmat-Si (i.e. $NMe_2C_6H_4CH_2(SiMe_3)$).

$\{[2-NMe_2CH_2C_6H_4]Pd\{CH(SiMe_3)C_6H_4NMe_2-2\}\}$ (**4**). A solution of **1**^{15b} (0.51 g, 2.39 mmol) in Et_2O (10 mL) was added dropwise to a suspension of $\{[Pd(dmab)(\mu-Cl)]_2\}$ (0.66 g, 1.19 mmol) in Et_2O (50 mL) at -50 °C. The solution was stirred for 1.5 h and then warmed to 25 °C. The solvent was removed from the black solution in vacuo, and the resulting residue was extracted with toluene (50 mL). The combined toluene extracts were filtered on an alumina column ($l = 4$ cm) in order to remove any traces of metallic palladium and the LiCl formed during the reaction. The solvent was removed, and the residue was washed with pentane (2×10 mL) which afforded **4** as a white solid (0.64 g, 60%). In one case compound **4** was crystallized at -20 °C from a toluene/pentane solution (white crystals, 0.35 g, 33%). Anal. Calcd for $C_{22.4}H_{33.6}N_2PdSi$ ($4 + 0.2C_7H_8$): C, 57.83; H, 7.23; N, 6.02. Found: C, 57.41; H, 7.69; N, 6.24. (The amount of toluene was quantitatively determined by 1H NMR spectroscopy).

$\{[2-NC_6H_4CH_2]Pd\{CH(SiMe_3)C_6H_4NMe_2-2\}\}$ (**5**). To a suspension of $\{[Pd(8-mq)(\mu-Cl)]_2\}$ (0.3 g, 0.52 mmol) cooled to -60 °C was added a solution of **1** (0.22 g, 1.05 mmol) in Et_2O (6 mL) dropwise. The solution was allowed to warm to room temperature, and the solvent was evaporated from the resulting dark colored solution. The residue was dissolved in toluene and filtered on an alumina column ($l = 4$ cm) to give, after removal of the toluene, a yellow liquid which crystallized at -20 °C from pentane as bright yellow crystals (**5**, 0.15 g, 31%). Anal. Calcd for $C_{22}H_{23}N_2PdSi$ (**5**): C, 58.09; H, 6.16; N, 6.16. Found: C, 58.55; H, 6.46; N, 6.04.

$\{[(S)-2-NMe_2CH(Me)C_6H_4]Pd\{[(Z)-CH(SiMe_3)C_6H_4NMe_2-2]\}$ (**6a**, **Z = R Isomer**, and **6b**, **Z = S Isomer**). To a suspension of $\{[Pd((S)-dmab)(\mu-Cl)]_2\}$ (0.87 g, 1.5 mmol) in Et_2O (50 mL) at -70 °C was added a solution of **1** (0.66, 3.12 mmol) in Et_2O (15 mL) slowly. The resulting solution was warmed up to 25 °C, and the Et_2O was removed in vacuo. The residue was extracted with toluene, and the extracts were filtered on a Celite column ($l = 5$ cm) in order to remove the metallic palladium formed during the reaction. The yellow solution thus obtained was evaporated to dryness. The residue was extracted with six portions of pentane which were combined to give three fractions: fraction α (2×10 mL), fraction β (2×15 mL), and fraction γ (2×25 mL). The remaining residue was extracted with Et_2O (2×15 mL) affording fraction δ . The volume of fraction α was concentrated (to 5 mL) from which, at -20 °C, the pure diastereomer **6a** crystallized as a white solid (~ 0.01 g, 1%). The following three fractions β , γ , and δ each contained a mixture of the two diastereomers of which the molar ratio of **6a:6b** (68:32, 56:44, and 11:89, respectively) was determined by 1H NMR.

The residue, which was also insoluble in Et_2O , was dissolved in the minimum amount of toluene. Addition of pentane to this concentrated toluene solution at -20 °C afforded the pure less soluble diastereomer **6b** as white needles (0.30 g, 22%). From the concentrated fractions β , γ , and δ a further amount of pure **6b** could be obtained, resulting in a total yield of 28%. Anal. Calcd for $C_{22}H_{34}N_2PdSi$ (**6b**): C, 57.31; H, 7.43; N, 6.08; Pd, 23.11; Si, 6.08. Found: C, 56.86; H, 7.37; N, 6.18; Pd, 23.34; Si, 5.60.

Reaction of 4 with Benzyl Bromide. A large excess of benzyl bromide (1.4 g, 8.2 mmol) was added to a solution of **4** (0.12 g, 2.26 mmol) in benzene (40 mL) and the resulting mixture stirred for 20 h at 40 °C. During this reaction period, a white solid deposited that was collected by filtration and then crystallized at -20 °C from a CH_2Cl_2 /pentane solution affording **9** as colorless crystals.

The filtrate was concentrated in vacuo, and a layer of pentane was put on top of the CH_2Cl_2 solution to give by slow diffusion of pentane at -80 °C orange-yellow crystals of **7**. Although the isolated yields of pure **7** and **9** were low due to separation problems, the actual yields appeared to be close to quantitative as was shown by the 1H NMR spectrum of the crude product. Anal. Calcd for $(C_{12.25}H_{20.5}BrCl_{0.5}NPdSi)_2$ ($7 + 0.25CH_2Cl_2$): C, 35.54; H, 4.95; N, 3.38. Found: C, 35.33; H, 4.63; N, 3.46. (The amount of CH_2Cl_2 was quantitatively determined by 1H NMR spectroscopy.) Anal. Calcd for $C_{23}H_{26}BrN$ (**9**): C, 69.71; H, 6.56; N, 3.54. Found: C, 69.51; H, 6.30; N, 3.56. **9**: 1H NMR ($CDCl_3$) δ 5.22 (s, 2 H, CH_2^b), 4.98 (s, 2 H, CH_2^a), 4.05 (s, 2 H, CH_2^c), 3.09 (s, 6

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(15) (a) The abbreviation used for the monoanionic ligands used in this paper as derived from the trivial names of their parent compounds are dmab from *N,N*-dimethylbenzylamine (dmabH), 8-mq from 8-methylquinoline (8-mqH), (S)-dmab from the *S*-enantiomer of α -methyl-substituted dmabH ((S)-dmabH), (S)-(1-(*N,N*-dimethylamino)ethyl)benzene, dmat from (dimethylamino)toluene (dmatH), and dmat-Si from α -trimethylsilyl-substituted dmatH (dmatH-Si, 2-(dimethylamino)- α -(trimethylsilyl)toluene). (b) We found that the use of freshly in situ prepared **1** afforded better yields of the bicyclic palladium compounds as compared with the reactions in which **1**¹⁴ is isolated before further reaction.

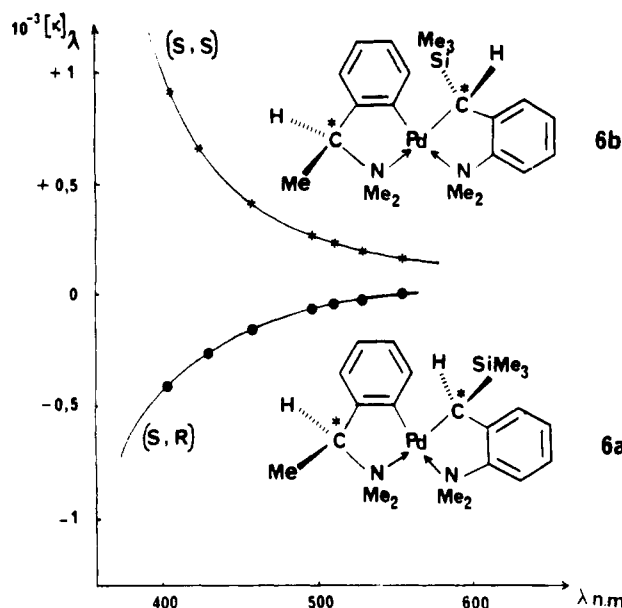
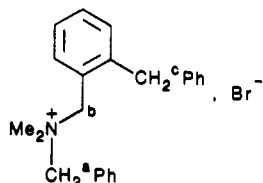


Figure 1. CD spectra of 6a and 6b (10^{-3} g/mL in toluene solutions).

H, N-CH₃). The assignment of a, b, and c to the different CH₂ groups is as follows:



Molecular Structure Determination of Compound

[(*S*)-2-NMe₂CH(Me)C₆H₄]Pd[(*S*)-CH(SiMe₃)C₆H₄NMe₂-2] (6b). X-ray Crystallographic Data. Crystals of C₂₂H₃₄N₂PdSi (*M_r* = 461.02) are colorless and air-stable well-formed parallelepipeds. Crystal data and data collection parameters are given in Table III. The unit-cell parameters were refined by using the θ angles of 25 reflections measured on an Enraf-Nonius CAD-4 automatic diffractometer.

In view of both the size of the single crystal used for the data collection and the low value of μ , absorption corrections were not performed. Corrections for Lorentz and polarization effects were applied.

Solution and Refinement of the Structure. The structure has been solved on a PDP 11/60 computer, by using the Enraf-Nonius SDP package.¹⁶ Atomic positions have been obtained from program MULTAN and subsequent Fourier difference synthesis, for the 26 independent non-hydrogen atoms of the molecule constituting the asymmetric unit.

Least-squares refinement of coordinates and thermal parameters, first isotropic and then anisotropic, of these 26 atoms led to values of $R = 0.029$ and $R_w = 0.039$.

At this stage of the refinement, the 34 independent hydrogen atoms were introduced in calculated position with isotropic thermal parameters of 5 Å². Most of them were located on a Fourier difference synthesis. Their introduction in the refinement, with fixed coordinates and thermal parameters, is significant in lowering R and R_w to the final values after two last cycles of refinement of coordinates and anisotropic thermal parameters of the 26 non-hydrogen atoms. The values of R and R_w thus calculated are 0.0211 and 0.0300 if both C1 and C14 have respectively the R configuration, these values being 0.0200 and 0.0289, respectively, if these chiral carbon atoms have the reverse S configuration.

This difference, according to Hamilton's R factor significance

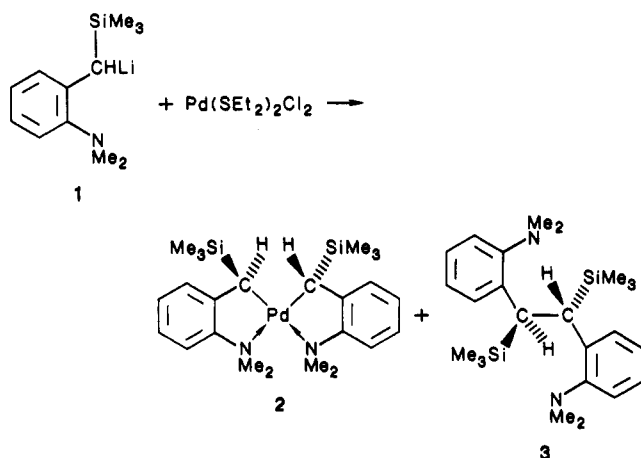
(16) "The Enraf-Nonius CAD-4 SDP", real time system for concurrent X-ray data collections and crystal structure determination in: Schenk, H.; Olthof-Hazelkamp, P.; Van Koenigsveld, H.; Bassi, G. C. *Computing in Crystallography*; Delft University Press: Holland, 1978.

test¹⁷ indicates that the second enantiomer gives the correct absolute configuration, which is S for the chiral carbon atoms C1 and C14. This is also in accordance with the known S configuration for the carbon atom C1.

The final atomic coordinates for the correct diastereomer are given in Table V. The numbering of the atoms is shown in Figure 1. Bond distances and angles are given in Table IV.

Results and Discussion

Attempted Synthesis of [Pd{CH-(SiMe₃)C₆H₄NMe₂}]₂ (2). Several studies revealed that [Pd(SEt₂)₂Cl₂] is a good starting material for the synthesis of symmetrical bicyclic compounds by reaction with lithiated ligands.⁸ However, we found that reaction of this palladium halide complex with 2 equiv of 1 led to the formation of an organopalladium compound 2 in only minor amounts (3–4% yield). Although this compound



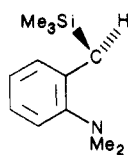
could not be obtained pure from the reaction mixture because of its high solubility in any organic solvent, it was identified by ¹H and ¹³C NMR spectroscopy as 2. The observation of the benzylic protons at 1.98 ppm, which is particularly diagnostic for a proton bonded to a metalated benzylic carbon center, and the SiMe₃ proton resonance at 0.26 ppm were specifically indicative for the nature of 2. These values are also close to those of related compounds presented in Tables I and II. Moreover, the presence of two different signals for the NMe₂ unit is a strong indication that the nitrogen atom in this species is coordinated to the Pd center, this diastereotopicity of the methyl groups being the result of the presence of the chiral carbon atom in the dmat-Si ligand.

The major product of the reaction was the organic product 3 in which two dmat-Si ligands are coupled via a C–C bond. The latter product most likely arose from a reductive elimination reaction involving 2, which is the initial product of the transmetalation reaction of [Pd-(SEt₂)₂Cl₂] with 1.

The existence of only one set of signals in the NMR spectra of 2 and 3 pointed to a high stereospecificity of the reactions by which they are formed. It is most likely that in 2 the bulky SiMe₃ groups are located on opposite sides of the Pd coordination plane rather than on the same side. Accordingly, the configuration of the chiral carbon atoms in 2 should be SS,RR rather than SR,RS . As a result the reductive elimination process will produce 3 as only one pair of enantiomers.

Synthesis of [(NMe₂CH₂C₆H₄)Pd{CH-(SiMe₃)C₆H₄NMe₂}] (4) and [(NMe₂CH₂)Pd{CH-

(17) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England 1974; Vol. IV, p 288.

Table I. Relevant ^1H NMR Data of the Compounds Containing the Following Moiety^a

	NMe ₂	CH	SiMe ₃	C ¹³ N	
	3.09/2.89	1.98	0.26		
	2.69	3.41	-0.37		
	3.03/2.97 ^b	2.32	-0.16	{ 2.76/2.38 ^b 4.29/3.21 ^c	{ NMe ₂ CH ₂ } dmba
	2.52/2.39	<i>e</i>	+0.06	{ 2.06/1.87 4.02/2.72 ^c	{ NMe ₂ CH ₂ } dmba
	2.61	2.51	+0.02	{ 2.23/1.99 4.08/2.85	{ NMe ₂ CH ₂ } dmba
	3.12/3.00	2.23	0.04	2.91/2.77 ^f	CH ₂ 8-mq
	3.00/2.96	2.28	-0.19	{ 3.23 ^h 2.64/2.43 1.83 ^h	{ CH NMe ₂ C-Me } (S)-dmba
	3.04/2.95	<i>e</i>	-0.16	{ 4.09 ⁱ 2.82/2.28 1.39 ⁱ	{ CH NMe ₂ C-Me } (S)-dmba
	2.52/2.46	<i>e</i>	+0.10	{ 3.91 2.23/1.78 1.05	{ CH NMe ₂ C-Me } (S)-dmba
	2.64	2.50	+0.05	{ 3.90 2.41/1.91 1.12	{ CH NMe ₂ C-Me } (S)-dmba
	{ 3.33/3.09 3.29/3.10	{ 3.54 3.53/3.47	{ 0.17/0.14 0.21/0.15		
	3.26/3.12	2.77	-0.36		

^aAll spectra recorded in CDCl₃ solvent, at room temperature, unless otherwise stated. Chemical shifts in ppm. ^bAssignment were based on 2D NMR measurements; see Experimental Section. ^c²J_{HA-HB} = 12.6 Hz. ^dRecorded in C₇D₈ at room temperature. ^eObscured by NMe₂ resonances. ^fRecorded in C₇D₈ at 100 °C; coalescence temperature for the NMe₂ signal of the dmat-Si chelate: 95 °C. ^g²J_{HA-HB} = 14.6 Hz. ^h³J_{H-H} = 6.4 Hz. ⁱ³J_{H-H} = 6.6 Hz. ^jRecorded in C₇D₈ at 100 °C; coalescence temperature for the NMe₂ signal of the dmat-Si chelate: 53 °C.

(SiMe₃)C₆H₄NMe₂] (5). In previous studies we, and others, showed that cyclometalated Pd complexes with two different chelates are often much less prone to reductive elimination than the corresponding complexes with two equal chelates (cf. the preparation of [Pd(2-

Me₂NC₆H₄CH₂)₂] (1.5% yield) with that of Pd(2-Me₂NC₆H₄CH₂)(dmba) (ca. 50% yield).^{8d} For this reason 1 was reacted with chloride-bridged cyclopalladated dimers as starting compounds (cf. ref 8b,d).

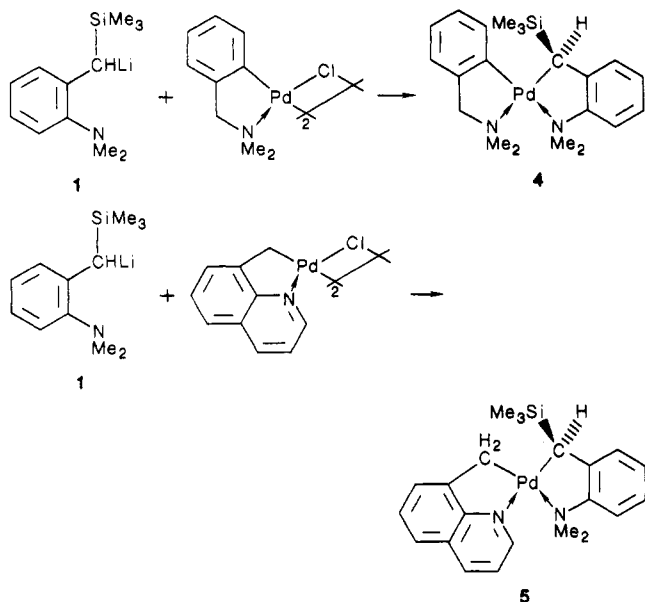
Treating [[Pd(dmba)(μ-Cl)]₂] and [[Pd(8-mq)(μ-Cl)]₂]

Table II. Relevant ^{13}C NMR Data of the Bicyclic Pd Compounds^a

N(CH ₃) ₂	CH	Si(CH ₃) ₃	C ^b N		
2	52.3/50.2 ^b	22.7	2.1		
4	51.1/50.6	31.2	2.6	{ 71.9 50.4/47.9	{ CH ₂ N(CH ₃) ₂ } dmbs
5	52.2/50.6	20.7	2.3	15.8	CH ₂ -Pd 8-mq
1a	51.6/50.3	32.1	2.2	{ 74.9 50.2/46.7 24.3	{ CH(CH ₃) N(CH ₃) ₂ CH(CH ₃) } (S)-dmbs
6b	51.1/50.2	31.7	2.4	{ 70.4 48.3/42.0 13.0	{ CH(CH ₃) N(CH ₃) ₂ CH(CH ₃) }

^aAll spectra recorded in CDCl₃ at room temperature. Chemical shifts in ppm. ^bBroad signals.

with 1 equiv of Li(dmat-Si) (1) per palladium atom afforded compounds 4 and 5, respectively (cf. ref 15a for the abbreviations used). The yield of 4 was quite high (up to 60%), whereas 5 could be obtained in a crystalline form in 30% yield. These results are to be compared with those obtained by using Li(dmat) as the anionic ligand^{8d} when [Pd(dmat)(dmbs)] was formed but could not be isolated pure while the compound with the 8-mq chelate was not obtained at all. This suggests that the presence of the SiMe₃ grouping at the benzylic carbon of the dmat chelate has a strong influence on the stability of the organometallic products.

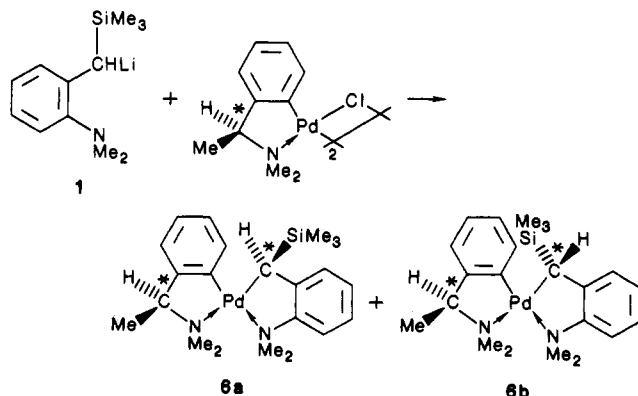


The characterization of the new compounds is based on their elemental analyses and ^1H and ^{13}C NMR spectra, which have as a notable feature the diastereotopicity of the NMe₂ and the CH₂ groups. On the basis of the results of a 2D NMR spectrum (see Experimental Section) of 4, the assignment of the NMe₂ resonances to either the dmat-Si or the dmbs ligand was possible. This also enabled us to assign the resonance patterns of 6b with reasonable certainty (vide infra).

Synthesis of the Optically Active Compounds

[(S)-2-NMe₂CH(Me)C₆H₄]₂Pd[(Z)-CH(SiMe₃)C₆H₄NMe₂] (6, Z = R or S). Reaction of the cyclopalladated dimer containing the (S)-dmbs^{15a} chelate with Li(dmat-Si) led to the formation of compound 6a and 6b.

The ^1H NMR spectrum of the crude reaction product showed two resonance patterns for each set of protons which directly indicated that 6 was present as two stable



isomeric forms which could arise from either cis or trans arrangement of the C^bN chelates. However, since the usual stable configuration for these square-planar complexes is the cis arrangement, we anticipated that both 6a and 6b were two diastereomers resulting from the different configurations of the dmat-Si benzylic carbon atom.

Isomer 6a is by far the more soluble, and it dissolves even in pentane. This hampered its isolation in a pure form (as determined by ^1H NMR spectroscopy), in yields better than 1%.¹⁸ The second isomer 6b, however, could be obtained pure in reasonable yields. The CD spectra of both compounds have been recorded (see Figure 1), and its asymmetry confirmed that 6a and 6b are diastereomers and not enantiomers.

An X-ray structure determination of 6b revealed the absolute configuration of the chiral benzylic center of the dmat-Si chelate in 6b as S. This assignment emerged from the application of Hamilton's R factor significance test (see Experimental Section). The configuration of the benzylic carbon centers of the [Pd(dmat-Si)(dmbs)] (4) and [Pd(dmat-Si)(8-mq)] (5) complexes is stable as is indicated by the fact that the two diastereomers of [Pd(dmat-Si)-((S)-dmbs)] (6a,b) could be separated and did not epimerize. For example, a solution of 6b in CDCl₃ was stable for several months. This observation is noteworthy because of the fact that the NMe₂ grouping of the dmat-Si ligand in 6a and 6b became enantiotopic above 95 and 53 °C, respectively. Above these temperatures only one resonance was observed for these NMe₂ protons, which points to the occurrence of a process involving Pd←N bond dissociation-association and concomitant pyramidal inversion of configuration at the noncoordinated N center of the dmat-Si ligand. Interestingly no coalescence could be observed (up to 120 °C) for the NMe₂ protons of the dmbs or the (S)-dmbs signals in compounds 4 and 6b, respectively. Indeed, if a process similar to that described above for the dmat-Si chelate would have taken place for these NMe₂ groupings, the corresponding calculated coalescence temperature is of the order of 105 and 79 °C for 4 and 6b, respectively. Accordingly this suggests that the N → Pd bonds of the dmbs and (S)-dmbs chelates are significantly stronger than those of the dmat-Si ligand.

Molecular Geometry of [(S)-2-NMe₂CH-(Me)C₆H₄]₂Pd[(S)-CH(SiMe₃)C₆H₄NMe₂-2] (6b). The molecular geometry of 6b is shown in an ORTEP drawing (Figure 2) while selected bond lengths and angles as well as least-squares planes are listed in Tables IV and VI,²⁹ respectively.

(18) We could not check whether the transmetalation reaction involved any extent of chiral recognition. The usual workup of the reaction involved a washing with pentane in order to eliminate the dmat-Si arene formed which always led to the loss of some 6a because of its solubility in this solvent.

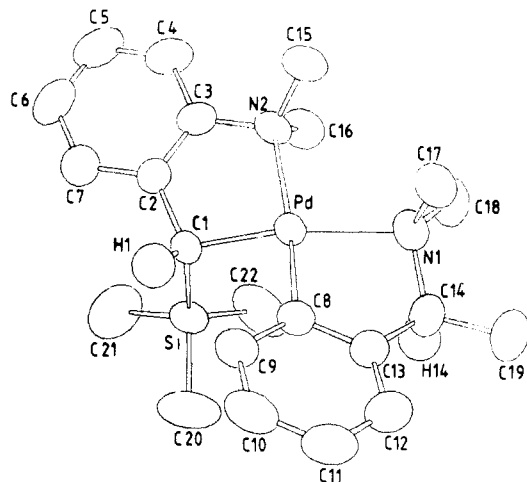


Figure 2. ORTEP of view of $[(S)-2-NMe_2CH(Me)C_6H_4]Pd[(S)-CH(SiMe_3)C_6H_4NMe_2-2]$ (**6b**).

Table III. Summary of Crystal Data and Data Collection Parameters of Compound **6b**

formula	$C_{22}H_{34}N_2PdSi$
fw	461.02
<i>a</i> , Å	10.027 (2)
<i>b</i> , Å	11.481 (4)
<i>c</i> , Å	10.833 (2)
β , deg	115.08 (2)
<i>V</i> , Å ³	1129.5
<i>Z</i>	2
ρ (calcd), g cm ⁻³	1.355
space group	$P2_1$ (monoclinic)
crystal dimens, mm	0.24 × 0.18 × 0.15
radiatn	MoK α (graphite-monochromated)
μ , cm ⁻¹	8.7
scan mode	$\omega-2\theta$
scan angle, deg	1.00 + 0.35 tan
detector aperture, mm	2.40 + 0.50 tan
θ limits, deg	2–25
total measurements	2330
unique data used ($I > \sigma(I)$)	1843
$R = \sum F_o - F_c / \sum F_o $	0.0200
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.0289

Table IV. Selected Bond Distances (Å) and Angles (deg) for **6b**

Bond Distances			
Pd–N1	2.213 (4)	N2–C16	1.486 (7)
Pd–N2	2.234 (4)	C8–C13	1.385 (7)
Pd–C1	2.024 (5)	C13–C14	1.503 (9)
Pd–C8	1.990 (4)	C14–C19	1.527 (8)
C1–Si	1.873 (5)	C14–N1	1.515 (6)
C1–C2	1.499 (6)	N1–C17	1.477 (7)
C2–C3	1.383 (6)	N1–C18	1.490 (7)
C3–N2	1.472 (6)	Si–C20	1.835 (6)
N2–C15	1.485 (7)		
Bond Angles			
N1–Pd–C8	80.2 (2)	Pd–N1–C18	113.9 (3)
C8–Pd–C1	94.7 (2)	Pd–N1–C14	101.9 (3)
N1–Pd–C1	169.9 (2)	Pd–N1–C17	101.9 (3)
C1–Pd–N2	82.8 (2)	C17–N1–C18	109.3 (4)
C8–Pd–N2	169.2 (2)	N1–C14–C19	114.3 (5)
Pd–N1–C17	111.4 (3)		

The palladium atom has a slightly distorted square-planar coordination geometry. The two palladated carbon atoms are cis to each other. This cis configuration has been found in almost all the metallobicyclic complexes in which two three-electron chelates $C^{\wedge}N$ are bound to a Pd(II) center.⁸ Notable exceptions were published by Newkome et al., who described the syntheses and molecular structures of bicyclic complexes derived from the palladation

Table V. Positional Parameters and Their Estimated Standard Deviations

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Pd	−0.02434 (3)	0.000	0.10878 (2)	2.735 (5)
Si	−0.0089 (1)	0.0734 (1)	0.3927 (1)	3.81 (3)
N1	−0.1323 (4)	0.0687 (3)	−0.1016 (3)	3.52 (8)
N2	0.2146 (3)	0.0351 (3)	0.1706 (3)	3.46 (8)
C1	0.0476 (4)	−0.0460 (4)	0.3070 (4)	3.04 (9)
C2	0.2097 (5)	−0.0703 (4)	0.3639 (4)	3.2 (1)
C3	0.2932 (4)	−0.0276 (4)	0.3000 (4)	3.6 (1)
C4	0.4443 (5)	−0.0452 (5)	0.3542 (6)	5.0 (1)
C5	0.5131 (6)	−0.1107 (7)	0.4706 (6)	6.0 (2)
C6	0.4308 (6)	−0.1562 (6)	0.5338 (6)	5.6 (2)
C7	0.2823 (6)	−0.1365 (5)	0.4824 (5)	4.4 (1)
C8	−0.2266 (4)	−0.0624 (4)	0.0541 (4)	2.99 (9)
C9	−0.2675 (5)	−0.1618 (5)	0.1054 (5)	4.0 (1)
C10	−0.4111 (5)	−0.2047 (6)	0.0434 (5)	4.9 (1)
C11	−0.5143 (5)	−0.1496 (6)	−0.0693 (6)	5.2 (1)
C12	−0.4773 (5)	−0.0521 (7)	−0.1212 (5)	4.9 (1)
C13	−0.3333 (4)	−0.0101 (5)	−0.0604 (4)	3.52 (8)
C14	−0.2863 (5)	0.0943 (5)	−0.1158 (5)	4.0 (1)
C15	0.2534 (5)	−0.0161 (6)	0.0642 (5)	4.8 (1)
C16	0.2630 (5)	0.1587 (5)	0.1883 (6)	5.0 (1)
C17	−0.1366 (5)	−0.0197 (4)	−0.2023 (4)	4.2 (1)
C18	−0.0639 (7)	0.1774 (5)	0.1234 (6)	5.2 (1)
C19	−0.3929 (7)	0.1358 (6)	−0.2573 (6)	5.7 (2)
C20	−0.1989 (6)	0.0488 (7)	0.3699 (6)	7.2 (2)
C21	0.1077 (9)	0.0779 (9)	0.5783 (7)	8.9 (2)
C22	0.0013 (0)	0.2230 (7)	0.3347 (8)	9.3 (2)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(1/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + AC(\cos \beta)B(1,3) + BC(\cos \alpha)B(2,3)]$.

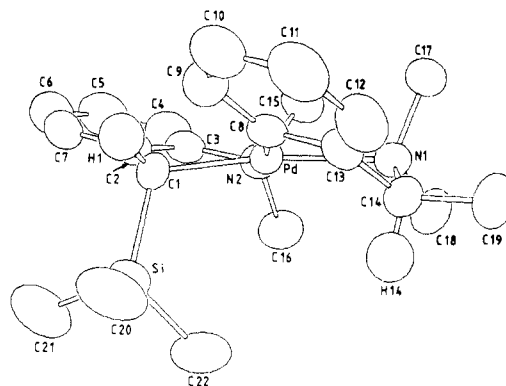


Figure 3. ORTEP view of **6b** showing the relative orientation of the Si and C19 atoms at the two chiral centers.

of 2-substituted pyridines.¹⁹ In these compounds the palladated carbon centers are linked trans across the palladium atom as a result of the chelate ligand stereochemistry.

An other view of **6b** is given in Figure 3 that clearly shows the mutual orientation of the SiMe₃ and Me substituents of the chiral centers.^{20c} The absolute configuration of the benzylic carbon atom C1 in **6b** is *S*. Figure 3 shows that the puckering of the (*S*)-dmba ring is such that its phenyl unit is oriented opposite to the bulky SiMe₃ group. As a consequence the methyl substituent on the benzylic carbon atom of the (*S*)-dmba is almost in an in-plane position with respect to the (*S*)-dmba phenyl ring. It is interesting to note that the opposite ring puckering of the Pd[(*S*)-dmba] chelate ring would place this Me substituent in a more favorable perpendicular position, and this conformation has been found to be the most stable one for two other related metal complexes containing the

(19) Newkome, G. R.; Gupta, V. K.; Fronczek, F. R. *Organometallics* 1982, 1, 9; 1983, 2, 785.

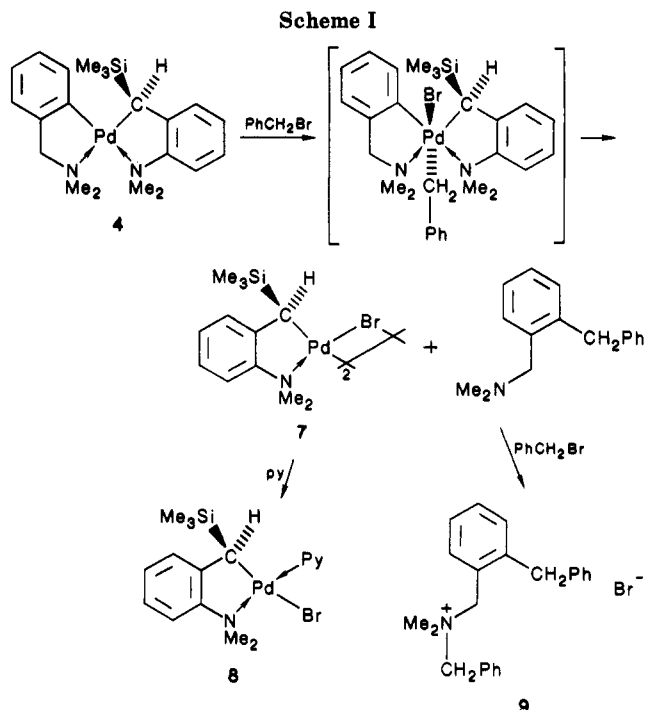
chiral CH(Me) unit.^{20a,b} However, in the case of **6b** this favorable ring puckering would require the opposite ring puckering in the Pd(dmat-Si) chelate ring that would place the SiMe₃ group in an in-plane position with the aryl group. Since the SiMe₃ substituent is bulkier than the Me group, this combination of ring puckering of the two chelate rings is expected to be less stable than the actual combination found in the X-ray crystal structure of **6b**.

From this molecular structure determination, a possible configuration for the other diastereomer **6a** can be proposed. The SiMe₃ grouping on the benzylic center in **6a** that has now the *R* configuration should also be found in an axial position with respect to the phenyl ring of the dmat-Si ligand. This conformation would then combine with a puckering of the (*S*)-dmba chelate ring that has the methyl C19 in an axial position.

The main structural data, Pd-C and Pd-N distances and angles within the metallocyclic units, compare well with those of related compounds^{8d,21,29} with the exception of the compound [Pd{3,3'-[C(CO₂Et)₂CH₂]₂,2,2'-bipyridyl}] reported by Newkome et al.^{21c} Surprisingly in this latter complex the Pd-C distances are markedly longer (by ca. 0.15 Å) than those of the other compounds whereas the Pd-N distances follow exactly the opposite trend.²² This difference may be due either to the four bulky CO₂Et substituents on the palladated carbon atoms or to the fact that the dimetalated ligand is not ideally suited to spanning all four square planar sites.

Reactivity of the Pd-C Bonds of Compounds 4. Insertion of alkynes (dimethyl acetylenedicarboxylate, diphenylacetylene, and hexafluorobut-2-yne) into the Pd-C bonds of **4** and **5** was not observed. This result is in marked contrast to the successful insertion reactions found for related cyclopalladated compounds (e.g. [Pd(dmba)-(8-mq)], [Pd(dmba)₂], etc.).^{8d} For example, we showed recently that compounds **4** and **5** when treated with an excess of hexafluorobut-2-yne²³ lead to an unexpected dimerization of the alkyne between two different palladium centers.

We have also treated compound **4** with other reagents (both nucleophilic and electrophilic) that are well-known to form cross-coupled products with cyclopalladated compounds. However, no reaction occurred with methyl vinyl ketone although this activated olefin has been successfully used in many reactions with palladated amines.^{24,25} Using



acyl chlorides²⁶ gave an insoluble red material, the workup of which²⁷ afforded the free protonated amines (dmbaH and dmatH-Si), but a functionalized ligand could not be detected.

Recent studies showed that benzyl bromide reacts with dialkylpalladium complexes to give the corresponding benzyl alkyl cross-coupled products.²⁸ Consequently **4**, which can be considered to be an alkylpalladium compound, should be an excellent candidate for this reaction. However, when **4** was treated with an excess of PhCH₂Br the expected C-C bond formation between the benzyl and the dmat-Si groups did not take place. Surprisingly, the Pd(dmat-Si) unit was found back after the reaction as the bromide-bridged dimer **7**, whereas the dmba monoanion was quantitatively cleaved from the Pd center and converted into the cross-coupled product **9** (see Scheme I).

Since halide-bridged dimers like **7** exist as a mixture of *cis* and *trans* isomers and moreover as a result of the configuration at the benzylic carbon atom, these isomers also exist as a mixture of *SS,RR* and *SR,RS* diastereomers, the ¹H NMR spectrum for **7** is very complex. Four signals for each set of protons are observed. When **7** is reacted with pyridine, this ¹H NMR spectrum became much simpler and the NMR data indicated that the pyridine ligand has cleaved the bromide bridges in **7** to give **8**. In the latter mononuclear complex the pyridine ligand is most probably located in the position *trans* to the nitrogen atom of the dmat-Si chelate. It has been well-established now that reactions of electrophiles with Pd(II) compounds proceed via an oxidation addition on the metal followed by a reductive elimination. In the case of the present reaction this would lead to the reaction sequence shown in Scheme I.

(25) [Pd(dmba)₂] reacts with MVK to afford good yields of the known dmba MVK product.²⁴

(26) Holton, R. A.; Natalie, K. J. *Tetrahedron Lett.* 1981, 22, 267. Clark, P. W.; Dyke, H. J.; Dyke, S. F.; Perry, G. J. *Organomet. Chem.* 1983, 253, 399.

(27) We used the same workup than the one described in ref 26.

(28) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* 1979, 101, 4981. Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* 1980, 102, 4933. Diversi, P.; Fasce, D.; Santini, R. *J. Organomet. Chem.* 1984, 269, 285.

(29) These data are included in the supplementary material to this paper.

(20) (a) Tani, K.; Brown, L. D.; Ahmed, J.; Ibers, J. A.; Yokota, M.; Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* 1977, 99, 7876. (b) Van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Pontenagel, W. M. G. F.; Kroon, J.; Spek, A. L. *J. Am. Chem. Soc.* 1978, 100, 5021. (c) The following torsion angles give additional evidence for the axial position of the SiMe₃ group and the equatorial position of C19 with respect to the dmat-Si and S-dmba chelate rings, respectively: Si-C1-C2-C3 = 100.5 (4)°; Si-C1-C2-C7 = 79.6 (5)°; C8-C13-C14-C19 = 167.4 (5)°; C12-C13-C14-C19 = 12.7 (8)°.

(21) (a) Dehand, J.; Mauro, A.; Osson, H.; Pfeffer, M.; De A. Santos, R. H.; Lechat, J. R. *J. Organomet. Chem.* 1983, 250, 537. (b) Russel, D. R.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* 1975, 1743. (c) Newkome, G. R.; Puckett, W. E.; Kiefer, G. E.; Gupta, V. K.; Fronczek, F. R.; Pantaleo, D. C.; McClure, G. L.; Simpson, J. B.; Deutsch, W. A. *Inorg. Chem.* 1985, 24, 811. (d) Janecki, T.; Jeffreys, J. A. D.; McCullough, K. J.; Pauson, P. L.; Pietrzykowski, A., unpublished results. (e) Newkome, G. R.; Kiefer, G. E.; Frere, Y. A.; Onishi, M.; Gupta, V. K.; Fronczek, F. R. *Organometallics* 1986, 5, 348.

(22) This behavior is in fact opposite to what is usually observed, the larger *trans* influence of the σ -bonded carbon compared to coordinated nitrogen leading to longer Pd-N than Pd-C distances.

(23) Maassarani, F.; Pfeffer, M.; Le Borgne, G.; Wehman, E.; Van Koten, G. *J. Am. Chem. Soc.* 1984, 106, 8002.

(24) Brisdon, B. J.; Nair, P.; Dyke, S. F. *Tetrahedron* 1981, 37, 173. Barr, N.; Dyke, S. F.; Quessy, S. N. *J. Organomet. Chem.* 1983, 253, 391. Kasahara, A.; Izumi, T.; Watabe, H. *Bull. Chem. Soc. Jpn.* 1979, 52, 957. Holton, R. A.; Kjonas, R. A. *J. Am. Chem. Soc.* 1977, 99, 4177. Holton, R. A.; Kjonas, R. A. *J. Organomet. Chem.* 1977, 133, C5. Holton, R. A. *Tetrahedron Lett.* 1977, 35, 55.

The most important feature of this reaction is then that the reductive elimination of the benzyl group in the Pd(IV) intermediate comprises attack of the benzyl carbon atom on the aromatic carbon atom of the dmba and not, as predicted, on the benzylic carbon atom of the dmat-Si. Very likely, the isolation of **9** as an ammonium salt resulted from a subsequent reaction of the initially formed cross-coupled product with an excess of benzyl bromide.

Registry No. 1, 93184-81-7; 2, 93184-81-7; 3, 106799-29-5; 4, 93184-75-9; 5, 93184-76-0; 6a, 106861-78-3; 6b, 106782-04-1; 7,

106782-01-8; 8, 106782-02-9; 9, 106782-03-0; Pd(SEt₂)₂Cl₂, 14873-91-7; [Pd(dmba)(μ-Cl)]₂, 18987-59-2; [Pd(8-mg)(μ-Cl)]₂, 28377-73-3; [Pd((S)-dmba)(μ-Cl)]₂, 34424-15-2; benzyl bromide, 100-39-0.

Supplementary Material Available: Listings of positional parameters for hydrogen atoms, thermal parameters, and least-squares planes (Table VI) for **6b** and a table reporting selected structural data in various palladabicyclic compounds (Table VII) (7 pages); a listing of structure factors for **6b** (11 pages). Ordering information is given on any current masthead page.

Preferential Activation of a *tert*-Butyl Group over a Cyclopropyl Group in the Intramolecular Reaction of *trans*-Dichlorobis(di-*tert*-butylcyclopropylphosphine)platinum(II) To Form a Platinaphosphacyclobutane. Synthesis and Structure of PtCl₂[P(*t*-Bu)₂CHCH₂CH₂]₂ and Its Derivatives

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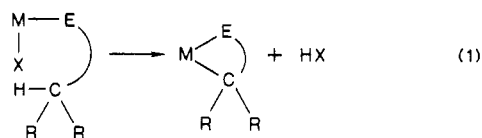
The complex PtCl[P(*t*-Bu)(CMe₂CH₂)(CHCH₂CH₂)](P(*t*-Bu)₂CHCH₂CH₂) (**2**) has been obtained by the elution of *trans*-PtCl₂(P(*t*-Bu)₂CHCH₂CH₂)₂ (**1**) on silica or Florisil supports and by the reaction of **1** with thallium(I) acetate. The complex *trans*-PtHCl(P(*t*-Bu)₂CHCH₂CH₂)₂ (**3**) is a byproduct of the Florisil-assisted reaction. Complex **3** has also been synthesized by reduction of **1** with hydrazine hydrate. The dimer [PtCl(P(*t*-Bu)₂CHCH₂CH₂)₂(μ-Cl)]₂ (**4**) forms from **1** in dioxane or toluene/acetic acid solvent. Complexes **1**–**3** have been characterized by means of elemental analysis and IR and NMR spectroscopy. The structures of **1**–**4** have been determined by X-ray methods.

Introduction

Sterically assisted intramolecular activation that leads to metallacycles has been observed for numerous transition-metal complexes.¹ A common reaction sequence is shown in Scheme I where E can be almost any donor group and the metallacyclic ring may contain as few as three or as many as six atoms. Systems where E(CR₂H) is a bulky tertiary phosphine ligand have been extensively investigated.^{1b–e}

Although electronic factors become important with ligands of like steric bulk,^{1d} certain steric factors, such as large phosphorus cone angle, halide ion (I > Br > Cl), and ring size (5 > 4 > 6), optimize conditions.^{1b,d,f} The phosphine P(*t*-Bu)₃ forms four-membered metallacycles in its complexes with Pt(II) much more easily than does P(*t*-Bu)₂Ph because of the larger contribution of *t*-Bu relative to Ph to the phosphorus cone angle.^{1f} The less sterically congested complex PtCl₂(P(*t*-Bu)Ph)₂ undergoes very little ortho-metalation after prolonged periods at reflux in 2-methoxyethanol, but with the addition of LiBr to the reaction mixture the internally metalated complex PtBr(P(*t*-Bu)C₆H₄Ph)(P(*t*-Bu)Ph)₂ is formed after 48 h at reflux. The complex *trans*-PtCl₂(P(*t*-Bu)₂(*o*-Tol))₂ (Tol = tolyl) undergoes internal metalation more readily than the cor-

Scheme I



responding P(*t*-Bu)₂Ph complexes since the resulting metallacycle contains five atoms. Still, Pt(II) complexes of the extremely bulky P(*t*-Bu)₃ ligand are more reactive with respect to internal metalation than are those of P(*t*-Bu)₂(*o*-Tol).

In complexes exhibiting similar steric congestion, aromatic substituents on phosphorus are metalated more easily than are aliphatic ones despite larger aryl C–H bond energies. The π-electron cloud of the aryl group is more readily attacked by an electrophilic metal atom.² Cyclopropane should be similarly more reactive, as electron density located in relatively high s-character orbitals away

(1) (a) Collman, J. P.; Hegedus, L. J. *Principles and Applications of Organo-transition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. (b) Shaw, B. L. *J. Organomet. Chem.* 1980, 200, 307 and references therein. (c) Goel, R. G.; Montemayor, R. G. *Inorg. Chem.* 1977, 16, 2183. (d) Cheney, A. J.; Mann, B. E.; Shaw, B. L.; Slade, R. M. *J. Chem. Soc. A* 1971, 3833. (e) Werner, H.; Kraus, H. *J. Organomet. Chem.* 1981, 204, 415. (f) Tolman, C. A. *Chem. Rev.* 1977, 77, 313.

(2) A notable exception is [PdCH₂CMe₂P(*t*-Bu)Ph]₂(μ-Cl)₂ prepared by reaction of PdCl₂P(*t*-Bu)₂Ph with AgOAc. See ref 1e.

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