Regioselective Formation of η^3-Allylic Ligands via the Reaction of Alkynes with $[\{Pd(CH(SiMe_3)C_6H_4NMe_2\text{-}2)(\mu\text{-}Cl)\}_2]$[1]

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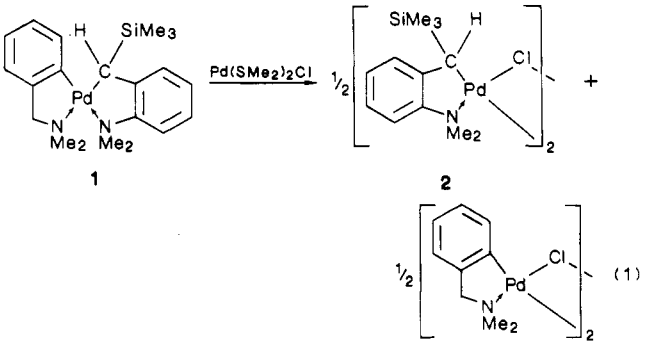
The dimeric cyclopalladated complex $[\{Pd(dmat\text{-}Si)(\mu\text{-}Cl)\}_2]$ (**2**, dmat-Si = $CH(SiMe_3)C_6H_4NMe_2$-2) was synthesized by a transmetalation reaction between the bicyclic complex [Pd(dmat-Si)(dmba)] (**1**, dmba = $C_6H_4CH_2NMe_2$-2) and $[Pd(SMe_2)_2Cl_2]$. The reactions between **2** and alkynes $R^1C{\equiv}CR^2$, substituted by at least one electron-withdrawing group, afforded η^3-allylic complexes $[Pd\{\eta^3\text{-}(CR^2(SiMe_3)\text{=}CR^1\text{=}CH)C_6H_4NMe_2\text{-}2\}Cl]$ ($R^1 = R^2 = CF_3$ (**3**) or CO_2Me (**4**); $R^1 = CO_2Et$, $R^2 = Ph$ (**5a**)) in a regioselective fashion. The structures of compounds **3–5a** have been elucidated by NMR studies, including nuclear Overhauser experiments. These studies revealed that the $SiMe_3$ group occupies an anti position in the allylic chain. Compound **5a** isomerized slowly in solution to give **5b** in which the $SiMe_3$ group was found in a syn position. A proposed mechanism for the formation of **3–5a** involves insertion of the alkyne into the Pd–C bond of **2** and subsequent intramolecular 1,3-shift of the $SiMe_3$ group onto the newly palladated carbon atom.

Introduction

We have recently described the synthesis of a variety of chiral cyclopalladated compounds in which a chiral carbon is directly σ-bonded to the metal.[2] This has been achieved by chelating two different tertiary amines, one of them being the 2-(dimethylamino)-α-(trimethylsilyl)-benzyl anion (dmat-Si), to palladium. Compared to related compounds in which a $SiMe_3$ substituent is absent, these complexes display unexpected novel reactivity toward both electrophilic and nucleophilic reagents.[2,3] Reactions of bicyclic [Pd(dmba)(dmat-Si)] (**1**, dmba = 2-[(dimethylamino)methyl]phenyl anion) with hexafluorobut-2-yne, for instance, afforded unexpected dinuclear complexes[3] instead of the anticipated insertion of this activated alkyne into the Pd–C bond as previously found for a series of cyclopalladated amines.[4] However, our previous findings indicated that halide-bridged cyclopalladated compounds compared to the corresponding bicyclic complexes[5] show an enhanced reactivity toward alkyne insertion.[6] We therefore set out a study of the reactions of alkynes with dimeric halide-bridged dmat-Si palladium complexes with a view to comparing their reactivity with that of the corresponding bicyclic complexes. The initially described synthesis of $[\{Pd(dmat\text{-}Si)(\mu\text{-}X)\}_2]$ (**2**) was performed via the reaction of **1** with benzyl bromide.[2] This route, however, afforded the halide-bridged compound in only low yields and unacceptable purity for further reactions. Herein we describe a new straightforward synthesis of **2** based on a transmetalation reaction and an investigation of the reactivity of **2** with alkynes.

Results and Discussion

Synthesis of $[\{Pd(dmat\text{-}Si)(\mu\text{-}Cl)\}_2]$ (2). We have already briefly described the transmetalation reaction between **1** and $[Pd(SR_2)_2Cl_2]$.[7] When R is Me, the expected transmetalated products, i.e. $[\{Pd(dmba)(\mu\text{-}Cl)\}_2]$ and $[\{Pd(dmat\text{-}Si)(\mu\text{-}Cl)\}_2]$ (**2**), were obtained and the two bridged dimers were easily separated by selective solvent extraction. The more soluble complex **2**, extracted with pentane, was isolated as a yellow crystalline material in 60% yield; see eq 1. It must be noted that in a similar



reaction of **1** with $[Pd(SEt_2)_2Cl_2]$ the analogous transmetalated products are also formed, but it was found that now **2** reacted further with $[Pd(SEt_2)_2Cl_2]$ to yield a novel μ-alkylidene compound.[7]

The ^1H NMR spectrum of **2** comprises four different sets of ligand resonances as previously observed for the bromide analogue $[\{Pd(dmat\text{-}Si)(\mu\text{-}Br)\}_2]$.[2] The signal of the $SiMe_3$ group, for instance, consists of four singlets indicating that **2** exists as a mixture of four isomers, i.e. cis and trans isomers which can be found as either *SS,RR* or *SR,RS*

(1) Reactivity of Cyclopalladated Compounds. 19. Part 18: Dupont, J.; Pfeffer, M.; Daran, J. C.; Gautheron, J. *J. Chem. Soc., Dalton Trans.* **1988**, 2421.

(2) Maassarani, F.; Pfeffer, M.; Le Borgne, G.; van Koten, G.; Jastrzebski, J. T. B. H. *Organometallics* **1987**, *6*, 1111.

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

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(5) (a) Bahsoun, A.; Dehand, J.; Pfeffer, M.; Zinsius, M.; Bouaoud, S.-E.; Le Borgne, G. *J. Chem. Soc., Dalton Trans.* **1979**, 547. (b) Maassarani, F.; Pfeffer, M.; Le Borgne, G. *J. Chem. Soc., Chem. Commun.* **1986**, 488. (c) Maassarani, F.; Pfeffer, M.; Le Borgne, G. *Organometallics* **1987**, *6*, 2029. (d) Maassarani, F.; Pfeffer, M.; Le Borgne, G. *Organometallics* **1987**, *6*, 2043.

(6) Only activated alkynes like hexafluorobut-2-yne and dimethyl acetylenedicarboxylate can be inserted into the Pd–C bonds of these species.[4]

(7) Maassarani, F.; Pfeffer, M.; Spek, A. L.; Schreurs, A. M. M.; van Koten, G. *J. Am. Chem. Soc.* **1986**, *108*, 4222.

(8) Note that one side of the coordination plane is screened from attack by the anti-planar positioned $SiMe_3$ group.

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diastereoisomers. The relative abundance of the four isomers varies from one preparation of **2** to another so that it is not known whether any chiral recognition occurs during the dimer formation. The reaction between the pure enantiomer [Pd{(*S*)-dmba}{(*S*)-dmat-Si}][2] ((*S*)-dmba = 2-[1-(*S*)-(dimethylamino)ethyl]phenyl, $C_6H_4CH(Me)NMe_2$-2-(*S*)) with $Pd(SMe)_2Cl_2$ afforded compound **2** as an isomeric mixture identical with that obtained in the previous reaction. Thus racemization of the *S* palladated benzylic carbon atom occurs during the transmetalation process. This result is further support for the reaction sequence proposed for the transmetalation reaction,[7] which involves attack of the "$Pd(SR_2)Cl_2$" unit either at the chiral palladated benzylic carbon atom of (*S*)-dmat-Si or at the aromatic σ-bonded carbon atom of (*S*)-dmba of [Pd(S-dmba){(*S*)-dmat-Si}]. Attack at the palladated chiral benzylic carbon center would occur with inversion of its configuration,[9] whereas attack at the aromatic carbon center would involve retention of configuration. The fact that racemization is found indicates that the transmetalation proceeds via a combination of these two modes of attack.

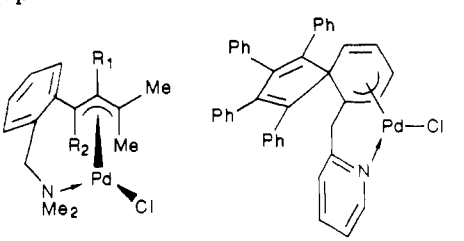
Reactions of [{Pd(dmat-Si)(μ-Cl)}$_2$] (2) with Alkynes. Treating compound **2** in CH_2Cl_2 with excess but-2-yne, diphenylacetylene, or 1-phenylprop-1-yne did not lead to any reaction even after several hours at reflux temperature. However, reaction occurs with activated alkynes that are substituted by at least one electron-withdrawing group. Reacting **2** with excess hexafluorobut-2-yne (hfb), at room temperature, afforded quantitatively a yellow product, **3**. Elemental analyses indicated that one alkyne molecule had been incorporated per palladium atom. Both ^{19}F and ^1H NMR spectra show only one resonance pattern, and therefore **3** is a single isomer. In its ^{19}F NMR spectrum two quartets are found for two inequivalent CF_3 groups cis to each other ($^5J_{F-F}$ = 12.5 Hz) indicating that insertion of a molecule of hfb into the Pd–C bond of **2** must have taken place. The chemical shifts of these two CF_3 groups (−18.8 and −21.6 ppm) are downfield of the usual range for CF_3 groups bound to olefinic units ($\delta \approx -50$ ppm, see ref 4 and 5a for examples). This strongly suggests that these CF_3 groups are bonded to a different type of skeletal unit. In the ^1H NMR spectrum ($CDCl_3$) of **3** the resonance pattern of the NMe_2 group consists of two singlets whose chemical shifts differ by only 0.01 ppm. This difference is very small when compared to data for the starting material **2** and similar compounds in which there is a coordinated NMe_2 unit and in which one alkyne has been inserted into a Pd–C bond.[4,5a,c] When the ^1H NMR spectrum is recorded in a solution of benzene-d_6, this difference increases markedly to 0.12 ppm. This could be explained by a monomeric structure for **3** with intramolecular Pd–N coordination which would render the NMe_2 methyl groups diastereotopic. An important further feature of this spectrum is the presence of a singlet at 5.37 ppm which is a characteristic position for an allylic proton.[9] No signal could be found in the region where $(SiMe_3)CH$ benzylic protons are expected to resonate (cf. for **2**, δ(CH(SiMe$_3$)) = 3.39 ppm). All these observations indicate that the insertion of the alkyne has led to the formation of a new six-electron anionic donor ligand which is coordinated to Pd through an η^3-allylic unit and most reasonably also through the NMe_2 group (see a proposed structure for **3** in the scheme). A very similar structure was found recently[9d] in complexes **6** obtained by reacting cyclopropenes with [{Pd(dmba)(μ-Cl)}$_2$].[9e] We have previously fully established the structure of compound **7** which is related to the proposed monomeric structure for **3**. In **7** an allylic unit is η^3-bonded to Pd and is stabilized by intramolecular coordination of a pyridinic nitrogen atom, the number of atoms between the allylic chain and the nitrogen atom being the same as in the compounds studied here.[5b]

Table I. Nuclear Overhauser Effects in Compound 4

signal irradiated	intensity increase, (%)				
	$SiMe_3$	NMe_a[a]	CO_2Me[c]	H allyl	C_6H_4
$SiMe_3$	...		0.1	3.7	
NMe_a[a]	0.8	...		9.0	8.9
NMe_b[b]	0.7			3.5	9.6
CO_2Me[c]	7.0		...		
H allyl	0.4	0.1		...	0.3

[a] Signal at 3.14 ppm. [b] Signal at 3.08 ppm. [c] Signal at 3.72 ppm.

The position of the $SiMe_3$ group on the η^3-allylic moiety was further established, see below, on the basis of NOE NMR spectra. For compound **3** the absence of any J_{HF} coupling constant between the allylic proton and the CF_3 groups is initial evidence for the structure proposed in which this H atom is on the carbon adjacent to the phenyl unit. Indeed, if this proton were at the terminal carbon of the allyl group, adjacent to a CF_3 unit, one would anticipate the existence of a $^3J_{HF}$ of ca. 9–11 Hz, i.e. analogous to what was found earlier for a compound in which a CF_3 and a proton are in geminal positions with respect to a vinyl group.[10]



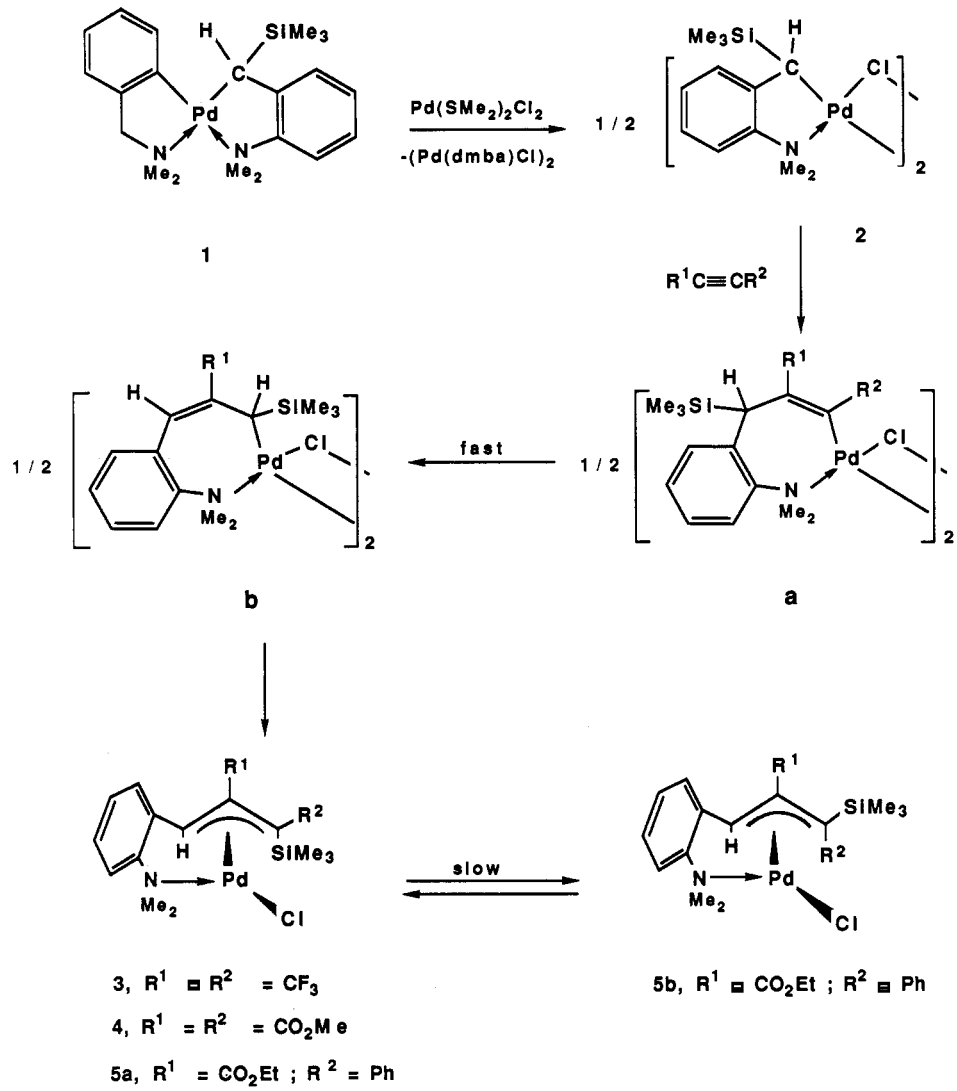
6 **7**

Complex **2** also reacts with 1 equiv of either dimethyl acetylenedicarboxylate or ethyl 3-phenylpropiolate to afford **4** and **5**, respectively (see Scheme I). Analytical and spectroscopic data suggest that these two compounds have a structure similar to that of **3**. Particularly diagnostic of the formation of the η^3-allylic group is the presence of a signal in the ^1H NMR spectra of **4** and **5a** at 5.4 and 5.2 ppm, respectively, corresponding to one allylic proton. The ^1H NMR of **5a** shows the presence of only one isomer, and it can therefore be concluded that the reaction of the ethyl 3-phenylpropiolate is regiospecific. The relative positions of the substituents with respect to the η^3-allyl chain have been established by means of nuclear Overhauser effect (NOE) NMR experiments. The results of this study, for compound **4**, are shown in Table I. From these data can be concluded that (i) the $SiMe_3$ and the allylic protons occupy anti positions, (ii) the $SiMe_3$ group must be located at a carbon atom that is also bearing a CO_2Me unit, and (iii) the allylic proton is to be found at the carbon adjacent to the phenyl ring, as in **3** (see the important NOE effect on this proton as compared to that found on the $SiMe_3$ unit

(9) (a) Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, H. *J. Am. Chem. Soc.* **1983**, *105*, 7768. (b) Dallas, B. K.; Hughes, R. P.; Shumann, K. *J. Am. Chem. Soc.* **1982**, *104*, 5380. (c) Sadownick, J. A.; Lippard, S. J. *Inorg. Chem.* **1973**, *12*, 2659. (d) Maassarani, F.; Pfeffer, M.; Le Borgne, G.; Grandjean, D. *Organometallics* **1986**, *5*, 1511. (e) **Note Added in the Proof.** The crystal structure of a compound very related to **6** was determined recently. It shows the intramolecular coordination of N to Pd: van der Schaaf, P. A.; van Koten, G.; Spek, A. L.; Pfeffer, M., unpublished results.

(10) Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1972**, *94*, 1886. Gomes de Lima, L.; Cariou, H. Scordia, H.; Kergoat, R.; Kubicki, M. M.; Guerchais, J. E. *J. Organomet. Chem.* **1985**, *290*, 321.

Scheme I. Proposed Reaction Path for the Formation of Compounds 3–5 Showing the Two Likely Intermediates a and b



when irradiating at the position of the NMe_2 resonances). Thus one can deduce from these experiments that it is the $SiMe_3$ group and not the benzylic proton of the dmat-Si moiety that has migrated upon reaction of **2** with alkynes which consequently gives rise to the proposed structure of **3** and **4** (see Scheme I).

The structure of **5a** was established accordingly. In particular irradiation at the $SiMe_3$ proton resonance induced the highest enhancement to the allylic proton (15%) and the phenyl group (7%), whereas no detectable effect was found for the protons of the CO_2Et group. This latter observation allowed us to unambiguously determine the orientation of the insertion of this unsymmetrical alkyne into the Pd–C bond of **2** (see below).

Compound **5a** is not stable in solution and in $CDCl_3$: isomerization into a new compound, **5b**, whose ^1H NMR spectrum is closely related to that of **5a**, was observed. This isomerization process is not very fast since the equilibrium situation was reached only after 13 days, the equilibrium ratio between **5a** and **5b** being 1:2. In a NOE study of **5b** no enhancement was detected for the resonance of the allylic proton when the $SiMe_3$ signal was irradiated. Significant enhancements of 2 and 1.2% were, however, observed for the signals of the CO_2Et and the phenyl groups, respectively. These observations are in agreement with a syn position of the $SiMe_3$ group with respect to the CO_2Et group, the allylic proton still being in the anti position. Thus, the isomerization of **5a** into **5b** is the result of a syn–anti isomerization of the η^3-coordinated allylic group, a process that has been well studied for related compounds containing this moiety.[11]

A likely pathway that can be drawn to explain the formation of complexes **3–5** is depicted in Scheme I. It is reasonable to assume that as initial step the alkyne inserts into the Pd–C bond of **2** to give the intermediate **a** which contains a seven-membered palladocyclic ring. This reaction is likely to occur from an intermediate in which the alkyne, after cleaving the chloride bridges of **2**, is η^2-bonded to Pd. The regioselectivity in the reaction with the unsymmetrical alkyne (ethyl 3-phenylpropiolate) is the same as that which we observed earlier in related reactions, i.e. the isomer that is formed is the one in which the phenyl group is located on the palladated carbon atom of the seven-membered ring.[5] Molecular models indicate that the benzylic carbon atom of this intermediate is sterically very congested so that it is not possible for the $SiMe_3$ group to be in an anti-planar position with respect to the C_6H_4 plane. This is a situation that has been shown to be a relatively more stable one than that with the $SiMe_3$ in the

(11) Vrieze, K.; Praat, A. P.; Cossee, P. *J. Organomet. Chem.* **1968**, *12*, 533. Faller, J. W.; Thomsen, M. E.; Mattina, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 2642.

peri-planar position in many cases.[2,3,12] In intermediate **a** the $SiMe_3$ group could therefore undergo a 1,3-sigmatropic rearrangement[13] leading to the intermediate **b** which could then rearrange to the final products. It is obvious, for steric reasons, that the anti rather than the syn position on the η^3-coordinated allylic moiety is the most accessible one, so that the observed formation of a kinetic isomer having the bulky $SiMe_3$ substituent in this position is logical. In the case of **3** and **4** this is also the thermodynamically stable isomer. However, for **5** some steric hindrance still pertains between the CO_2Et and the Ph groups so that the anti–syn isomerization occurs leading to the thermodynamically more stable isomer **5b**.

Experimental Section

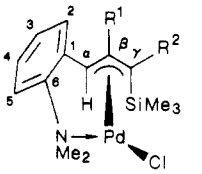
General Data. All manipulations were performed under dry oxygen-free nitrogen by using standard Schlenk techniques. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 200.00 and 50.32 MHz, respectively, on a Bruker SY200 instrument. Proton and carbon chemical shifts (δ in ppm, J in Hz) are positive downfield relative to external $SiMe_4$. The ^{19}F NMR spectra were recorded at 84.67 MHz on a Bruker WH-90 instrument, the chemical shifts being negative upfield relative to external $CFCl_3$. 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(C$_6$H$_4$CH$_2$NMe$_2$-2)(CH(SiMe$_3$)C$_6$H$_4$NMe$_2$-2)] (**1**)[3] and $[Pd(SMe_2)_2Cl_2]$[14] were prepared by published methods. All alkynes are commercially available and were used without further purification.

[{Pd(CH(SiMe$_3$)C$_6$H$_4$NMe$_2$-2)(μ-Cl)}$_2$] (2). A stoichiometric amount of $[Pd(SMe_2)_2Cl_2]$ (0.20 g, 0.67 mmol) was added to a solution of **1** (0.30 g, 0.67 mmol) in toluene and the reaction mixture heated at ca. 100 °C for 10 min. After being cooled to room temperature, the dark solution obtained was filtered through a Celite column (l = 3 cm) to remove traces of metallic Pd, affording an orange solution. The solvent was removed in vacuo to give an orange-beige solid. This was vigorously stirred in pentane (30 mL) for 2 h. The resulting suspension was filtered giving a yellow filtrate from which by evaporation of the pentane **2**, as a pale yellow solid (0.14 g, 58%), was obtained. **2** was crystallized from a CH_2Cl_2/pentane solution at −20 °C. Anal. Calcd for $C_{24.5}H_{41}Cl_3N_2Pd_2Si_2$ (**2** + 0.5CH_2Cl_2): C, 39.82; H, 5.59; N, 3.79. Found: C, 39.69; H, 5.61; N, 3.89. The same amount of CH_2Cl_2 was also found by ^1H NMR (in $CDCl_3$): δ 7.08–6.91 (m, 4 H, aromatic protons), 3.39 (m, 1 H, C–H), 3.26 (m, 3 H, N–CH_3), 3.06 (m, 3 H, N–CH_3), 0.21, 0.16, 0.13, and 0.11 (4s, 9 H, $SiMe_3$).

[Pd{η^3-(C(SiMe$_3$)(CF$_3$)=C(CF$_3$)=CH)C$_6$H$_4$NMe$_2$-2}Cl] (3). A large excess of hexafluorobut-2-yne (0.16 g, 1 mmol) was condensed at liquid-nitrogen temperature onto a frozen solution of **2** (0.14 g, 0.20 mmol) in CH_2Cl_2 (25 mL). The reaction mixture was slowly warmed to room temperature. After the solution was stirred for 24 h, the solvent was evaporated in vacuo and the residue dissolved in the minimum amount of toluene (5–10 mL). Slow diffusion of pentane into the toluene solution, at −20 °C, afforded **3a** as yellow crystals (0.17 g, 83%). Anal. Calcd for $C_{16}H_{20}ClF_6NPdSi$: C, 37.66; H, 3.95; N, 2.74. Found: C, 37.89; H, 3.95; N, 2.71. ^1H NMR ($CDCl_3$): δ 7.41–7.17 (m, 4 H, aromatic protons), 5.37 (s, 1 H, allylic proton), 3.10 and 3.09 (2s, 6 H, N–CH_3), 0.39 (s, 9 H, $SiMe_3$). ^1H NMR (C_6D_6): δ 5.06 (s, 1 H, allylic proton), 2.70 and 2.58 (2s, 6 H, N–CH_3), 0.34 (s, 9 H, $SiMe_3$). ^{19}F NMR ($CDCl_3$): δ −21.57 (q, 3 F, CF_3), −18.8 (q, 3 F, CF_3, $^5J_{F-F}$ = 12.5).

[Pd{η^3-(C(SiMe$_3$)(CO$_2$Me)=C(CO$_2$Me)=CH)C$_6$H$_4$NMe$_2$-2}Cl] (4). Dimethyl acetylenedicarboxylate (0.07 g, 0.53 mmol) was added to a solution of **2** (0.12 g, 0.17 mmol) in CH_2Cl_2 (20 mL). After this solution was stirred for 3.5 h at room temperature, the solvent was removed in vacuo. Extraction of the crude product with pentane (15 mL), followed by addition of hexane (5 mL), afforded compound **4** as yellow crystals after 4 days at −20 °C (0.07 g, 41%). Anal. Calcd for $C_{18}H_{26}ClNO_4PdSi$: C, 44.09; H, 5.34; N, 2.86. Found: C, 44.35; H, 5.10; N, 2.81. IR (KBr): $\nu_{C=O}$ 1735 (vs), 1695 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.34–7.27 (m, 4 H, aromatic protons), 5.40 (s, 1 H, allylic proton), 3.72 and 3.52 (2s, 6 H, CO_2CH_3), 3.14 and 3.08 (2s, 6 H, N–CH_3), 0.33 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 172.4, 165.2 (2 CO_2Me), 160.5 (C_6), 133.0 (C1), 129.9, 128.3, 128.2, 122.02 (C2–C5), 121.98 (C_β), 83.5 (C_α), 67.7 (C_γ), 52.6 and 49.8 ($2CO_2CH_3$), 52.9 and 52.4 ($2N-CH_3$), 1.8 ($Si(CH_3)_3$). The numbering of the carbon atoms follows that of the scheme shown below:



[Pd{η^3-(C(SiMe$_3$)(Ph)=C(CO$_2$Et)=CH)C$_6$H$_4$NMe$_2$-2}Cl] (5a,b). A twofold excess of ethyl 3-phenylpropiolate (0.14 g, 0.80 mmol) was added dropwise to a solution of **2** (0.14 g, 0.20 mmol) in CH_2Cl_2 (25 mL). The reaction mixture was stirred for 4 h at room temperature, giving an orange solution. The solvent was evaporated in vacuo, and the residue was dissolved in pentane. Complex **5a** was produced as yellow crystals (0.12 g, 57%) by slow diffusion of hexane into the pentane solution at −20 °C. Anal. Calcd for $C_{23}H_{30}ClNO_2PdSi$: C, 52.88; H, 5.79; N, 2.68. Found: C, 52.79; H, 5.92; N, 2.61. IR (KBr): $\nu_{C=O}$ 1727 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.55–7.14 (m, 9 H, aromatic protons), 5.20 (s, 1 H, allylic proton), 3.58 (m, 2 H, O–CH_2, ABX_3 spin system), 3.10 and 3.09 (2s, 6 H, N–CH_3), 0.57 (t, 3 H, CH_3), 0.23 (s, 9 H, $SiMe_3$).

Compound 5b was not isolated; it was only identified in the $CDCl_3$ solution by its ^1H NMR spectrum: δ 4.96 (s, 1 H, allylic proton), 3.96 (qd, 2 H, O–CH_2, ABX_3 spin system), 3.08 and 2.94 (2s, 6 H, N–CH_3), 0.84 (t, 3 H, CH_3), 0.19 (s, 9 H, $SiMe_3$).

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Registry No. 1, 93184-75-9; **2** (isomer 1), 119239-68-8; **2** (isomer 2), 119239-70-2; **2** (isomer 3), 119239-71-3; **2** (isomer 4), 119239-72-4; **3**, 119144-98-8; **4**, 119144-99-9; **5a**, 119145-00-5; **5b**, 119239-69-9; $Pd(SMe_2)_2Cl_2$, 14567-23-8; [Pd{(*S*)-dmba}{(*S*)-dmat-Si}], 106782-04-1; hexafluorobut-2-yne, 692-50-2; dimethyl acetylenedicarboxylate, 762-42-5; ethyl 3-phenylpropiolate, 2216-94-6.

(12) Jastrzebski, J. T. B. H.; van Koten, G.; Knapp, C. T.; Schreurs, A. M. M.; Kroon, J.; Spek, A. L. *Organometallics* **1986**, *5*, 1551. Wehman, E.; van Koten, G.; Hardeman, G.; Stam, C. H.; Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 536.

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(14) Mann, F. G.; Purdie, D. *J. Chem. Soc.* **1935**, 1549.