Insertion Reactions into Palladium–Carbon Bonds of Complexes Containing Terdentate Nitrogen Ligands; Experimental and Ab initio MO Studies[+]

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Received January 26, 1998

Keywords: Insertion / N ligands / Terdentate ligands / Rigid ligands / Palladium

Novel methyl complexes [Pd(Me)(N-N-N)]X (N-N-N = flexible or rigid terdentate nitrogen ligand, X = Cl, SO_3CF_3, BAr'_4) have been synthesized and fully characterized. All complexes readily underwent insertion of carbon monoxide resulting in the quantitative formation of complexes [Pd{C(O)Me}(N-N-N)]X [X = Cl (**1d–6d**), BAr'_4 (**1e–6e**)]. Subsequently, complexes **2e–6e** underwent quantitative insertion of norbornadiene, resulting in complexes [Pd{C_7H_8C(O)Me}(N-N-N)]BAr'_4 (**2f–6f**). Unexpectedly, these complexes, including even those containing rigid terdentate nitrogen ligands, possess a structure in which the nitrogen ligand is coordinated in a bidentate fashion. A kinetic study of the reaction of norbornadiene with complexes **1e–6e** revealed that the reactivity of complexes **1e–6e** toward norbornadiene increases with increasing rigidity of the terdentate ligand, i.e. with increasing strain in the PdN_3 moiety, which indicates that insertion very likely occurs via a mechanism involving nitrogen dissociation. This is fully supported by ab initio MO calculations on CO and ethylene insertion into carbon–palladium bonds of cationic model systems containing a rigid terdentate nitrogen ligand, which showed that the lowest-energy pathway for both insertion reactions consists of substitution of one of the distal nitrogen atoms of the rigid terdentate nitrogen ligand by the substrate, followed by a rate-determining migratory insertion of the substrate into the carbon–palladium bond.

In many transition-metal-catalyzed reactions the insertion of an unsaturated molecule into a carbon−metal bond is a key step.[1][2] A recent example is the palladium-catalyzed copolymerization of carbon monoxide and alkenes, leading to the formation of polyketones, which process involves the perfectly alternating insertion of CO and alkenes into carbon−palladium bonds.[3][4][5][6][7] We[8][9][10][11][12][13][14][15] and others[16][17][18][19][20][21][22][23][24] have extensively studied CO and alkene insertion reactions in model complexes of the type Pd(R)X(L-L) {R = Me, C(O)Me; X = Cl, Br, I, SO_3CF_3, BF_4, [3,5-$(CF_3)_2C_6H_3)_4$B]; L-L = P-P, P-N, N-N} mimicking the intimate steps of the catalytic cycle of polyketone formation.[25] From these studies it is clear that the mechanism of CO and alkene insertion reactions is highly dependent on the nature of the ligands. In the case of ionic complexes [Pd(R)(solv)(L-L)]X {R = Me, C(O)Me; solv = Et_2O, MeCN; L-L = P-P, P-N, N-N; X = SO_3CF_3, BF_4, [3,5-$(CF_3)_2C_6H_3)_4$B} it has been shown that precoordination of CO and alkenes occurs via dissociation of the weakly coordinated solvent molecule. Both CO and alkene precoordinated complexes of the type [Pd(Me)(CO)(L-L)]X[10][19][23] and [Pd{C(O)Me}(η^2-alkene)(N-N)]X[23], respectively, have been characterized as intermediates. Studies of the insertion reactions of CO into the methyl−palladium bond of complexes Pd(Me)X(P-P) (X = Cl, PPh_3, MeCN; P-P = bidentate phosphorus ligand) showed that the reactions were enhanced by flexible bidentate phosphorus ligands, which are able to coordinate with a large bite angle, thereby lowering the energy of the transition state.[8] Furthermore, the reactions were strongly dependent on the coordinating capability of the X ligand, which indicates that insertion occurs mainly by X dissociation. Unexpectedly, insertion reactions in complexes containing flexible and rigid bidentate nitrogen ligands with a small bite angle were much faster than those in complexes containing

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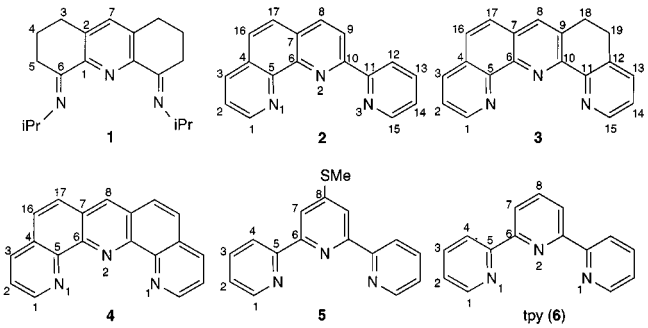
bidentate phosphorus ligands.[11][12][26] Mechanistic studies provided strong evidence that insertion reactions in neutral complexes containing bidentate nitrogen ligands occur via intermediates in which these ligands are coordinated in a unidentate fashion.[12][13][14][15]

Although most experimental studies indicate that insertion by a mechanism involving four-coordinate intermediates is more favorable than insertion by a mechanism involving five-coordinate intermediates, for a few insertion reactions a mechanism involving five-coordinate species has been suggested. For example, both intra-[27] and intermolecular[28] alkene insertions into hydride−platinum bonds and also CO insertions into aryl−[29] and alkyl−palladium[30] bonds have been proposed to occur from five-coordinate intermediates. Recently, we reported the high reactivity toward CO of the ionic complex [Pd(Me)(tpy)]Cl, containing a terdentate 2,2′:6′,2′′-terpyridine ligand.[31][32] At first, insertion was proposed to occur via five-coordinate species, as creation of a free coordination site was assumed to be rather difficult due to the favorable terdentate coordination of the tpy ligand.[31] However, Orrell et al.[33][34][35][36][37] and also others[38][39][40][41][42][43] have reported on the ability of tpy to coordinate in a bidentate fashion, which suggests that the CO insertion reaction in [Pd(Me)(tpy)]Cl may occur by a mechanism involving four-coordinate intermediates, which contain a bidentate coordinated tpy ligand. Therefore, we turned our attention to complexes containing rigid terdentate nitrogen ligands, in which dissociation of one of the distal nitrogen atoms was expected to be unlikely. We have used the novel rigid ligand **1** and the known ligands **2**[44], **3**[45], **4**[45], **5**[46], and **6** (Figure 1). In this series ligands **3** and **4** can be considered as rigid analogs of **5** and tpy (**6**).

Figure 1. Terdentate nitrogen ligands **1**−**6** with the adopted numbering schemes

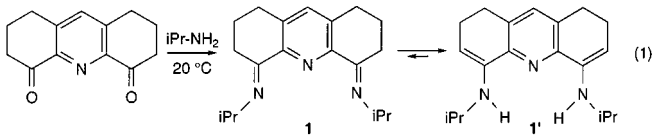


We report here the results of our study of the palladium coordination chemistry of ligands **1**−**6**. Furthermore, we present the results of an extensive kinetic study of the norbornadiene insertion in acetylpalladium complexes containing the ligands **1**−**6** and the results of ab initio MO calculations of CO and ethylene insertion reactions into carbon−palladium bonds of model complexes containing a rigid terdentate nitrogen ligand, which lead to a novel view of the role and behavior of rigid terdentate ligands in CO and alkene insertion reactions.

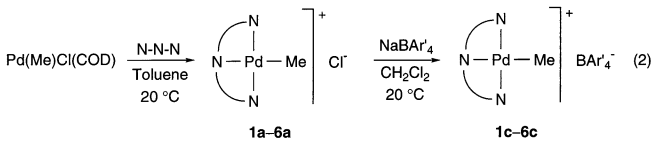
Results and Discussion

Synthesis and Characterization of Compound 1 and Methylpalladium Complexes 1a−5a, 1b, and 1c−6c

The novel compound 4,5-bis(isopropylimino)-1,2,3,4,5,6,7,8-octahydroacridine (**1**) was synthesized by a condensation reaction of 1,2,3,4,5,6,7,8-octahydroacridine-4,5-dione with isopropylamine in the presence of an excess $MgSO_4$ and a catalytic amount of formic acid (Equation 1). Compound **1** was obtained as a yellow oil. In this form or in solution at 20°C, compound **1** is rather unstable and decomposes into several uncharacterized products within a few hours. At −80°C compound **1** can be stored for several days without decomposition. As reported for 1,2-bis(isopropylimino)cyclohexane[47], (5,6-dihydro[1]pyrindin-7-ylidene)isopropylamine[15], and isopropyl-(5*H*-[1]pyrindin-7-yl)amine[15], compound **1** exists predominantly in the tautomeric form **1′**. Formation of this tautomer was revealed by NMR where a two-proton resonance at δ = 4.85 in the ^{1}H-NMR spectrum and a resonance at δ = 74.7 in the ^{13}C-NMR spectrum were observed, both characteristic of a = CH fragment. Furthermore, the IR spectrum of **1** revealed an NH stretching frequency at 3390 cm^{-1}. The instantaneous disappearance of the 5-H NMR resonance upon addition of a drop of D_2O to a solution of **1** in $CDCl_3$ indicates the presence of a rapid equilibrium between enamine and imine forms.



The chloro(methyl)palladium complexes **1a**−**5a** were synthesized by substitution of COD (= 1,5-cyclooctadiene) in Pd(Me)Cl(COD) by ligands **1**−**5** (Equation 2), similar to what is reported for methylpalladium complexes containing bidentate N-N,[11][12] N-S[48][49], P-N[10], P-P[8], and terdentate N-N-N[31][32], P-N-N[50], P-N-S[51], and N-N-S[51] ligands. Analogously to [Pd(Me)(**6**)]Cl (**6a**)[32], complexes **2a**−**5a** were obtained as yellow, air-stable solids, which are only moderately soluble in polar solvents such as methanol, ethanol, and water. In contrast, complex **1a** readily dissolves in dichloromethane and chloroform.



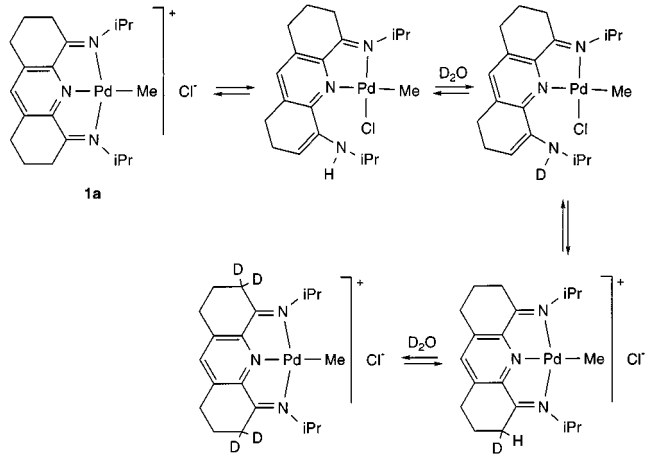
The complexes of the type [Pd(N-N-N)(Me)]X [N-N-N = terdentate nitrogen ligands **1**−**6**; X = SO_3CF_3 (**b**), BAr'_4 (**c**)] were obtained by the reaction the complexes **1a**−**6a** with silver trifluoromethanesulfonate and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Equation 2). Complexes **1b**−**6b**, however, except for **1b**, are insoluble in

common solvents and could not be characterized. In contrast, complexes **1c**−**6c** are soluble in dichloromethane, chloroform, and even in diethyl ether. Complexes **1a**,**c**−**6a**,**c** and **1b** were isolated and fully characterized. Crystals of **1b** and **4c**, suitable for X-ray analyses, were obtained by recrystallization from dichloromethane/hexane at 4°C (vide infra).

All methylpalladium complexes show a characteristic *Me*−Pd resonance at $\delta \approx 1$ in the ^{1}H-NMR spectra and at $\delta \approx 0$ in the ^{13}C-NMR spectra.[11][12][15][32][52][53][54] At 20°C, as well as at −60°C, the ^{1}H-NMR spectra of complexes **1a**, **4a**, and **5a**, show a symmetrically bonded nitrogen ligand, indicating that these ligands are coordinated in the expected terdentate fashion to the palladium center and that the chloride is present as a counter anion. The observed high equivalent conductivities for **1a**−**5a** in methanol at 20°C of 51−70 Ω^{-1} cm^2 mol^{-1} are also in agreement with an ionic complex, whereas that of the neutral precursor Pd(Me)Cl(COD) is 2.3 Ω^{-1} cm^2 mol^{-1}.

Interestingly, addition of a drop of D_2O to a solution of **1a** in $CDCl_3$ led to a complete disappearance of the 5-H NMR resonance due to H/D exchange. This result can be explained by dissociation of one of the distal nitrogen atoms of the ligand, caused by coordination of the chloride (Scheme 1). This mechanism is supported by the absence of H/D exchange for **1a** in CD_3OD, which efficiently solvates the chloride ion, hereby preventing chloride-initiated dissociation of one of the distal nitrogen atoms. Furthermore, it is in agreement with the absence of H/D exchange for **1b** and **1c**, which contain weakly coordinating anions.

Scheme 1



1a

In order to investigate the relative coordinating capabilities of the terdentate nitrogen ligands **2**−**6**, competition experiments were carried out. Addition of an equimolar amount of free **6** to a solution of complex **5c** in $CDCl_3$ at 20°C resulted in a mixture of complexes **5c** and **6c** and the free ligands **5** and **6** in a ratio **5c**/**6c** (= **6**/**5**) = 1:2. A mixture with the same **5c**/**6c** ratio was obtained upon addition of an equimolar amount of free **6** to a solution of complex **5**. These experiments and similar competition experiments with the other nitrogen ligands show that the coordinating capabilities of **2**, **3**, **4**, and **6** are comparable, but higher than that of **5**.

Molecular Structures of [Pd(Me)(1)]SO_3CF_3 (1b) and [Pd(Me)(4)]BAr'_4 (4c)

The molecular structures of **1b** and **4c** are shown in Figures 2 and 3. Selected bond lengths and bond angles of the non-hydrogen atoms are listed in Tables 1 and 2. The molecular structures of **1b** and **4c** both show a square-planar geometry with the three nitrogen atoms of the terdentate nitrogen ligand and a methyl ligand coordinated to the palladium(II) center. The relatively short Pd−N(2) bond lengths of 1.959(5) A for **1b** and 1.993(3) A for **4c** and the small *trans*-N(1)−Pd−N(3) bond angles of 155.50(19)° for **1b** and 156.95(11)° for **4c** have been observed also for **6a**[32] and for other palladium complexes containing comparable symmetric terdentate nitrogen ligands.[43][55][56][57][58][59][60][61] Interestingly, the Pd−N(1) and Pd−N(3) bond lengths in **4c** [2.103(4) and 2.116(4) A, respectively] are longer than those in [Pd(Me)(**6**)]Cl (**6a**) [Pd−N(1) = 2.048(9) A; Pd−N(3) = 2.057(8) A][32] and the angles Pd−N(1)−C(1) and Pd−N(3)−C(19) in **4c** [132.4(3) and 132.1(3)°] show a larger deviation from the ideal 120° than to those in **6a** [Pd−N(1)−C(1) = 128.8(7)°; Pd−N(3)−C(19) = 128.4(7)°].[32] These data indicate that the more rigid terdentate ligand **4** coordinates less strongly to the palladium center than the more flexible tpy ligand **6**. Whereas the four donor atoms and the palladium atom are confined to one plane in **4c** [maximum deviation from the least-squares plane is 0.005(3) A], the methyl ligand in complex **1b** is bent out of the coordination plane with an angle of 12.4(3)° between the methyl−palladium bond and the plane defined by N(1), N(2), and N(3). As a result, the methyl−palladium bond length of 2.189(4) A is large as compared to those of other palladium complexes containing a methyl ligand *trans*-positioned to a nitrogen atom (2.00−2.09 A).[10][11][12][32][47][48][50][52][53][54][58][61][62][63][65][66] The distances between C20 and the nearest hydrogen atoms on C15 and C18 of 2.67 A and 2.59 A, which are 0.23 A and 0.31 A shorter than the sum of the Van der Waals radii, clearly show that the distortion from planarity in **1b** is caused by steric interaction between the methyl ligand and the isopropyl groups. Recently, a similar observation has been made for a series of chlororhodium(I) complexes containing a terdentate nitrogen ligand. In these complexes, substituents on the side arms of the terdentate nitrogen ligand were found to force the chloride ligand out of the coordination plane.[61]

Carbon Monoxide Insertion

The methylpalladium complexes **1a**−**5a** and **1c**−**6c** reacted within 1 minute with carbon monoxide to give the corresponding acetylpalladium complexes **1d**−**5d** and **1e**−**6e**, respectively (Equation 3).

The acetylpalladium complexes **1e**−**6e** were isolated and characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. In contrast, complexes **1d**−**5d** could not be iso-

Figure 2. ORTEP drawing (50% probability level) and adopted numbering scheme of [Pd(Me)(**1**)]SO_3CF_3 (**1b**); hydrogen atoms and SO_3CF_3 anion have been omitted for clarity

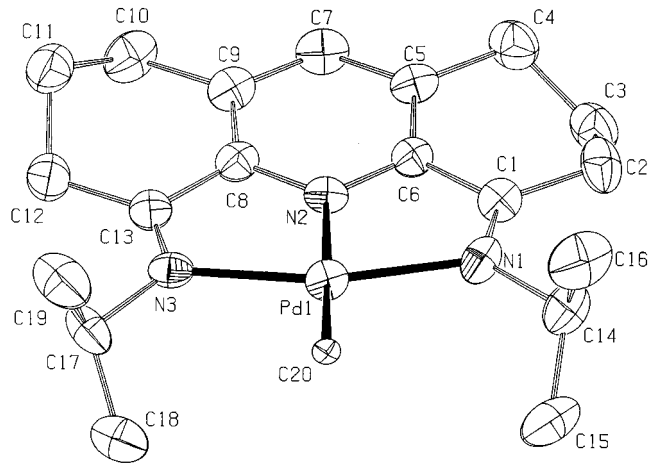


Figure 3. ORTEP drawing (50% probability level) and adopted numbering scheme of [Pd(Me)(**4**)]SO_3CF_3 (**4c**); hydrogen atoms and BAr'_4 anion have been omitted for clarity

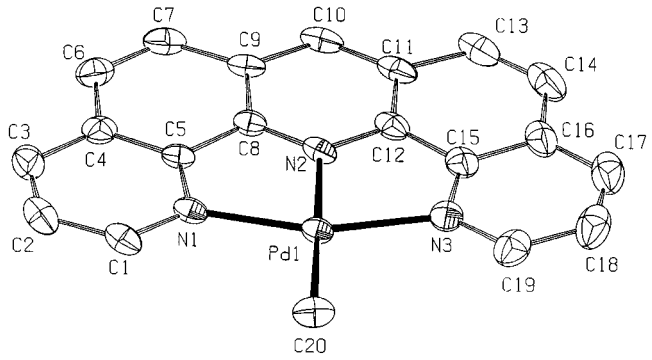


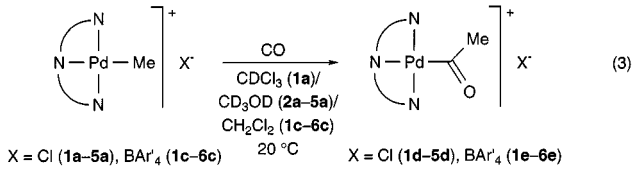
Table 1. Selected bond lengths [A] and angles [°] for [Pd(Me)(**1**)]SO_3CF_3 (**1b**) (with esd's in parentheses)

Bond lengths			
Pd(1)−N(1)	2.111(6)	N(2)−C(6)	1.333(8)
Pd(1)−N(2)	1.959(5)	N(2)−C(8)	1.341(9)
Pd(1)−N(3)	2.116(6)	N(3)−C(13)	1.262(9)
Pd(1)−C(20)	2.189(4)	N(3)−C(17)	1.490(9)
N(1)−C(1)	1.285(9)	C(1)−C(6)	1.474(9)
N(1)−C(14)	1.485(9)	C(8)−C(13)	1.488(9)
Bond angles			
N(1)−Pd(1)−N(2)	78.1(2)	Pd(1)−N(1)−C(1)	113.5(5)
N(1)−Pd(1)−N(3)	155.50(19)	Pd(1)−N(1)−C(14)	127.7(4)
N(1)−Pd(1)−C(20)	102.2(2)	Pd(1)−N(2)−C(6)	118.6(4)
N(2)−Pd(1)−N(3)	77.7(2)	Pd(1)−N(2)−C(8)	118.8(4)
N(2)−Pd(1)−C(20)	170.28(18)	Pd(1)−N(3)−C(13)	114.0(5)
N(3)−Pd(1)−C(20)	102.30(19)	Pd(1)−N(3)−C(17)	127.0(4)

lated, since these complexes, except for **1d**, are only soluble in alcohols, in which decomposition occurs within a few minutes, resulting in palladium black and an organic compound. This organic product was analyzed for **4d** and **6d** by ^{1}H NMR and GC-MS, and proved to be methyl acetate, methyl [D_3]acetate, ethyl acetate, and ethyl [D_5]acetate for decomposition in methanol, [D_4]methanol, ethanol, and

Table 2. Selected bond lengths [A] and angles [°] for [Pd(Me)(**4**)]BAr'_4 (**4c**) (with esd's in parentheses)

Bond lengths			
Pd(1)−N(1)	2.103(4)	N(2)−C(8)	1.309(5)
Pd(1)−N(2)	1.993(3)	N(2)−C(12)	1.323(6)
Pd(1)−N(3)	2.116(4)	N(3)−C(15)	1.373(5)
Pd(1)−C(20)	2.025(4)	N(3)−C(19)	1.334(5)
N(1)−C(1)	1.320(6)	C(5)−C(8)	1.431(5)
N(1)−C(5)	1.379(4)	C(12)−C(15)	1.429(6)
Bond angles			
N(1)−Pd(1)−N(2)	78.68(13)	Pd(1)−N(1)−C(1)	132.4(3)
N(1)−Pd(1)−N(3)	156.95(11)	Pd(1)−N(1)−C(5)	110.9(3)
N(1)−Pd(1)−C(20)	100.50(16)	Pd(1)−N(2)−C(8)	119.1(3)
N(2)−Pd(1)−N(3)	78.28(13)	Pd(1)−N(2)−C(12)	119.3(3)
N(2)−Pd(1)−C(20)	179.18(17)	Pd(1)−N(3)−C(15)	111.2(3)
N(3)−Pd(1)−C(20)	102.54(16)	Pd(1)−N(3)−C(19)	132.1(3)



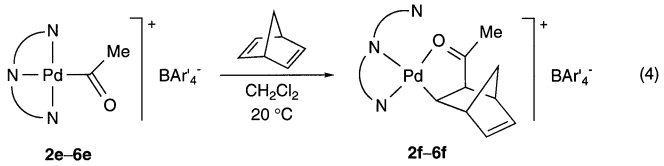
[D_6]ethanol respectively, indicating that the instability of complexes **1d**−**5d** in alcohols is caused by alcoholysis of the acetyl−palladium bond. A mechanism of this degradation process might involve dissociation of one of the distal nitrogen atoms of the terdentate ligand caused by coordination of the chloride counter anion,[67][68] followed by methanol coordination and reductive elimination of methyl acetate. This mechanism is supported by the observation that decomposition in alcohols proceeds much more slowly for complexes **2e**−**6e**, which contain the weakly coordinating tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion.[69]

The insertion of CO into the methyl−palladium bond of **1c**−**6c** is a reversible reaction. In solution decarbonylation of **1e**−**6e** occurs, resulting in reformation of the methylpalladium complexes **1c**−**6c**, without formation of any palladium black. For example, after 1 h of bubbling N_2 through a solution of **4e** in dichloromethane, 80% of decarbonylated [Pd(Me)(**4**)]BAr'_4 (**4c**) and 20% unreacted **4e** were present, whereas complete decarbonylation took place within 1 h in refluxing dichloromethane. Interestingly, complexes **1e**−**6e** also undergo decarbonylation in the solid state. Drying in vacuo for several hours or storage at 20°C for several days resulted in formation of the methylpalladium complexes **1c**−**6c**, without any other decomposition.

Alkene Insertion

(a) *Synthesis and Characterization of Alkylpalladium Complexes* **1f**−**6f**: Whereas insertion of ethylene, styrene, maleic anhydride, and cyclopentene does not occur, the acetylpalladium complexes **2e**−**6e**, but not **1e**, do react with the strained alkenes norbornene, norbornadiene, and dicyclopentadiene. Because of their complex NMR spectra, the products obtained after insertion of norbornene and dicyclopentadiene were difficult to characterize. However, the insertion of norbornadiene into the acetyl−palladium bond

of complexes **2e**−**6e** yielded the novel characterizable alkylpalladium complexes [Pd{$C_7H_8C(O)Me$}(N-N-N)]BAr'_4 (**2f**−**6f**) (Equation 4).



2e–6e **2f–6f** (4)

The reactions were completed within 30 minutes for **2e**−**6e** showing rates comparable to those found for the neutral complexes Pd{C(O)Me}Cl(Ar-BIAN) containing the rigid bidentate nitrogen ligands bis(arylimino)acenaphthene,[11][13] but the rates were slower than those observed for the ionic complexes [Pd{C(O)Me}(solv)(N-N)]SO_3CF_3 (solv = solvent; N-N = Ar-BIAN, bpy).[11][22] Complexes **2f**−**6f** were isolated and characterized by spectroscopic techniques. The ^{1}H-NMR spectra of **2f**−**6f** show the typical pattern of an inserted norbornadiene moiety and a coupling constant between the former olefinic protons of about 6 Hz, which indicates the expected *cis* addition of the carbon−palladium bond to the *exo* face of the norbornadiene.[9][11][13][16][22][32][70] Furthermore, the spectral data of **2f**−**6f** show the following interesting features: (i) In the IR spectra a low CO stretching frequency at ca. 1600 cm^{-1} is observed; (ii) In the ^{13}C-NMR spectra a low-field CO resonance appears at $\delta \approx 235$; (iii) In the ^{1}H-NMR spectra of **4f**−**6f** at −70°C separate signals for the two arms of the nitrogen ligands are observed; (iv) In the ^{15}N-NMR spectra of **2f**, **4f**, and **6f**, which will be discussed in detail separately,[71] a signal representing one distal nitrogen atom appears at $\delta \approx -150$, which is characteristic of a coordinated pyridine nitrogen atom.[72] In the case of **2f**, the signal of the other distal nitrogen atom is observed at $\delta = -68$, which is characteristic of a noncoordinated pyridine moiety[72] and can be compared to the distal nitrogen resonances of $\delta \approx -75$ for the free ligands **2**, **4**, and **6**.[71] Unfortunately, in the case of **4f** and **6f**, the signal of the noncoordinated nitrogen atom could not be observed, most probably due to the absence of a sufficiently large N-H coupling constant.

From these spectroscopic data, we conclude that the acyl oxygen atom is coordinated to the palladium center forming a C,O chelate and that, unexpectedly, the nitrogen ligand is coordinated in a bidentate fashion. In the case of flexible terdentate ligands such as **5** and **6**, the noncoordinated pyridyl moiety is most probably in a position perpendicular with regard to the palladium coordination plane, as observed in molecular structures of $Pd(C_6F_5)_2$(tpy)[36] and [Pd(η^3-C_3H_5)(tpy)]ClO_4[43], which contain a bidentate tpy ligand. In the case of rigid terdentate nitrogen ligands such as **4**, an asymmetrically bidentate coordination mode of the nitrogen ligand, i.e. with a relatively long Pd−N(central) bond and a relatively short Pd−N(distal) bond, may result in a long distance between palladium and the dissociated nitrogen atom (ca. 3.5 A, vide infra), which enables C,O chelate formation.

Complexes **4f**−**6f** show fluxional behavior on the ^{1}H-NMR time scale, as both sides of the terdentate ligand become magnetically equivalent in the temperature range of −50 to 20°C. The mechanism probably proceeds by site exchange of the distal nitrogen atoms involving a species in which the nitrogen ligand is coordinated in a terdentate fashion.

(b) *Kinetic Study of Norbornadiene Insertion:* To study the kinetics of the norbornadiene insertion into the carbon−palladium bond of complexes **1e**−**6e**, the reactions were carried out under pseudo-first-order conditions and were recorded by means of UV/Vis spectroscopy. In all cases, plotting the observed rate constants k_{obsd} versus time led to straight lines with a zero intercept, within experimental error, indicating that the rate law $k_{obsd} = k_2$[nbd] is obeyed. The experimental values of k_2 are independent of the presence of free terdentate nitrogen ligand and are listed with the respective activation parameters in Table 3.

Table 3. Rate constants k_2 and the enthalpy and entropy of activation of the reaction of complexes **1e**, **2e**, **4e**−**6e**, and **5d** with norbornadiene (standard deviations in parentheses)[a]

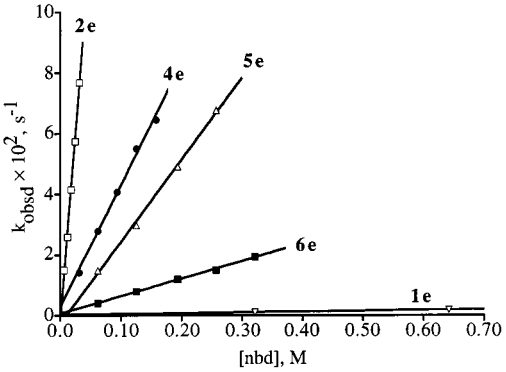
Compound	T [°C]	$10^2 k_2$ [s^{-1} м$^{-1}$]	$\Delta H^{\neq}$ [kJ mol^{-1}]	$\Delta S^{\neq}$ [J mol^{-1} K^{-1}]
1e	10.0(5)	0.11(1)	58(4)	−96(13)
	20.5(5)	0.24(1)		
	31.0(5)	0.65(1)		
2e	6.0(5)	120(5)	31(1)	−132(5)
	11.0(5)	150(6)		
	20.5(5)	251(12)		
	29.0(5)	350(9)		
4e	6.0(5)	17.7(3)	39(2)	−119(7)
	13.0(5)	25.1(4)		
	20.5(5)	40(2)		
	30.0(5)	72(3)		
5d	7.5(5)	655(28)		
5e	7.5(5)	16(1)	32(2)	−144(8)
	13.5(5)	25(1)		
	20.5(5)	33(2)		
	30.5(5)	52(2)		
6e	6.0(5)	1.86(3)	51(1)	−95(1)
	13.0(5)	3.22(3)		
	20.5(5)	5.8(1)		
	30.0(5)	11.5(3)		

[a] Conditions: dichloromethane as solvent, [Pd] = 0.19 мм.

The activation enthalpy (31−58 kJ mol^{-1}) and the large negative activation entropy (−144 to −95 J mol^{-1} K^{-1}) are comparable with those of the k_2 pathway of reaction of norbornadiene with Pd{C(O)Me}Cl(*p*-An-BIAN) containing the rigid bidentate nitrogen ligand bis(*p*-anisylimino)acenaphthene ($\Delta H^{\neq}$ = 48.4(18) kJ mol^{-1}; $\Delta S^{\neq}$ = −126(6) J mol^{-1} K^{-1}).[13] The rate constant k_2 is highly dependent on the terdentate nitrogen ligand in [Pd{C(O)Me}(N-N-N)]BAr'_4 (**1e**−**6e**) and increases in the order N-N-N = **1** << **6** << **5** < **4** << **2** (Figure 4). The reaction of norbornadiene with **1e** proceeded very slowly and an extremely large excess of norbornadiene (800−4000 equiv.) was required in order to ensure relatively fast norbornadiene insertion as compared to decarbonylation. Due to the absence of isosbestic points for the reaction of **3e**

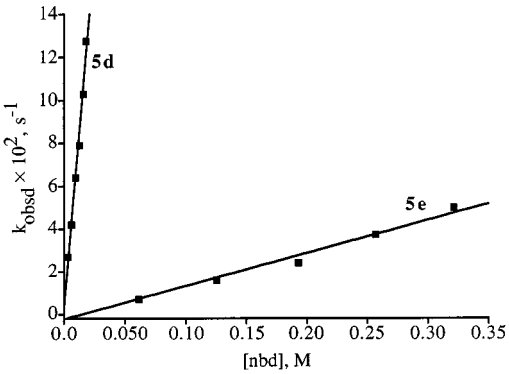
with norbornadiene, no rate constants were determined for this reaction.

Figure 4. Pseudo-first-order rate constants (k_{obsd}) of the reaction of [Pd{C(O)Me}(N-N-N)]BAr'_4 (**1e**, **2e**, and **4e**−**6e**) with nbd as a function of the concentration of nbd; conditions: dichloromethane as solvent, 20.5°C, [Pd] = 0.19 mM



The influence of the counter anion X of [Pd{C(O)Me}(N-N-N)]X on the reaction with nbd was studied for the rigid ligand **4** and the flexible ligands **5** and **6**. In order to prevent decomposition of the unstable acetylchloropalladium complexes **4d**−**6d**, the reactions were carried out at 7.5°C. Unfortunately, a rate constant could be determined only in the case of **5d**, as isosbestic points were not obtained for **4d** or **6d**. From Figure 5 it is clear that the k_2 value of the reaction of [Pd{C(O)Me}(**5**)]X [X = Cl (**5d**), BAr'_4 (**5e**)] with nbd is highly dependent on the nature of the counter anion X; the k_2 rate constant increases from 0.16(1) s^{-1} M^{-1} for **5e** to 6.55(28) s^{-1} M^{-1} for **5d**.

Figure 5. Pseudo-first-order rate constants (k_{obsd}) of the reaction of [Pd{C(O)Me}(**5**)]X [X = Cl (**5d**), BAr'_4 (**5e**)] with nbd as a function of the concentration of nbd; conditions: dichloromethane as solvent, 7.5°C, [Pd] = 0.19 mM



Ab Initio MO Calculations

To obtain more insight into the mechanism of insertion reactions of CO and alkenes into the carbon−palladium bond of complexes containing rigid terdentate nitrogen ligands, we have carried out for the first time ab initio MO calculations of the cationic model systems [Pd(Me)(N-N-N)]$^+$ (**I**) + CO and [Pd{C(O)Me}(N-N-N)]$^+$ + ethylene.

(a) *Carbon Monoxide Insertion:* The optimized geometries and selected bond lengths and bond angles of the starting methylpalladium complex **I**, the intermediate **III**, the transition states **II** and **IV**, and the acetylpalladium product **V** are shown in Scheme 2. The relative RHF and MP2 energies have been collected in Table 4 and the potential energy profile at the MP2 level is shown in Figure 6. The calculated bond angles N(1)−Pd−N(2) and N(2)−Pd−N(3) and nitrogen−palladium bond lengths for starting complex **I** and product **V** are in good agreement with those observed experimentally for the terdentate nitrogen ligand containing methylpalladium complexes **1b** (vide supra), **4c** (vide supra), and **6a**.[32] The calculated carbon−palladium distances in structures **I** (2.05 A) and **V** (1.97 A) are as expected for methyl-[12][32][47][50][52][53][62][73][74] and acetylpalladium[12][15][23][50][52][53][75] complexes, respectively. The Pd−CO bond lengths in CO-coordination transition state **II** (2.10 A) and CO-containing complex **III** (2.10 A) are very close to that calculated for *cis*-[Pd(Me)$(NH_3)_2$(CO)]$^+$ (2.106 A)[59], but somewhat longer than that calculated for [Pd(Me)$(NH_2CH_2CH_2NH_2)$(CO)]$^+$ (1.922 A)[76] and that experimentally observed for [Pd{C(O)Me}(phen)(CO)]BAr'_4 [1.922(11) A].[23] The geometry of the CO-containing species **III** can be considered to be square-planar, in which the four coordination sites are occupied by two nitrogen atoms of the terdentate nitrogen ligand, a CO and a methyl group. At the RHF level there is a small barrier (E_a = +13 kJ mol^{-1}) for formation of species **III**, but at the MP2 level formation of species **III** appears to be barrierless (E_a = −3 kJ mol^{-1}). The formation of species **III** is much less exothermic (−64 kJ mol^{-1}, MP2 value), however, than in the case of [Pd(Me)(**8**)]$^+$ containing the rigid bidentate model ligand HN=$CHCH_2$N=CH_2 (**8**) (−170 kJ mol^{-1}, MP2 value), as expected. The CO insertion is found to proceed via a three-centered insertion transition state **IV**, which is rather close to those reported for CO insertion into the carbon−palladium bond of the complexes Pd(Me)H(PH_3)(CO)[77], *cis*-[Pd(Me)$(NH_3)_2$(CO)]$^+$[59], and [Pd(Me)$(NH_2CH_2CH_2NH_2)$(CO)]$^+$[76]. The geometry of the acetyl species **V** suggests that the reaction occurs by CO insertion into the carbon−palladium bond. The geometry of species **IV**, however, clearly shows that it is the methyl group, not the carbonyl group, that migrates during the reaction, as experimentally demonstrated for platinum and palladium complexes with bidentate phosphorus ligands by van Leeuwen et al.[20][21] The formation of the transition state for CO insertion, **IV**, appears to be the rate-determining step for acetyl formation. The transition state **IV** lies 48 kJ mol^{-1} (MP2 value) above **III**. This activation barrier is slightly lower than those found for systems containing the bidentate ligands **8** (+59 kJ mol^{-1}, MP2 value) and $NH_2CH_2CH_2NH_2$ (+62 kJ mol^{-1}, B3LYP/I value)[76], presumably because of the stronger steric repulsion in the case of species **III**. The energy of the acetyl species **V** lies only 10 kJ mol^{-1} below that of **III**, which is completely in agreement with the experimentally observed reversibility of the CO insertion in complexes **1c**−**6c** (vide supra).

Scheme 2

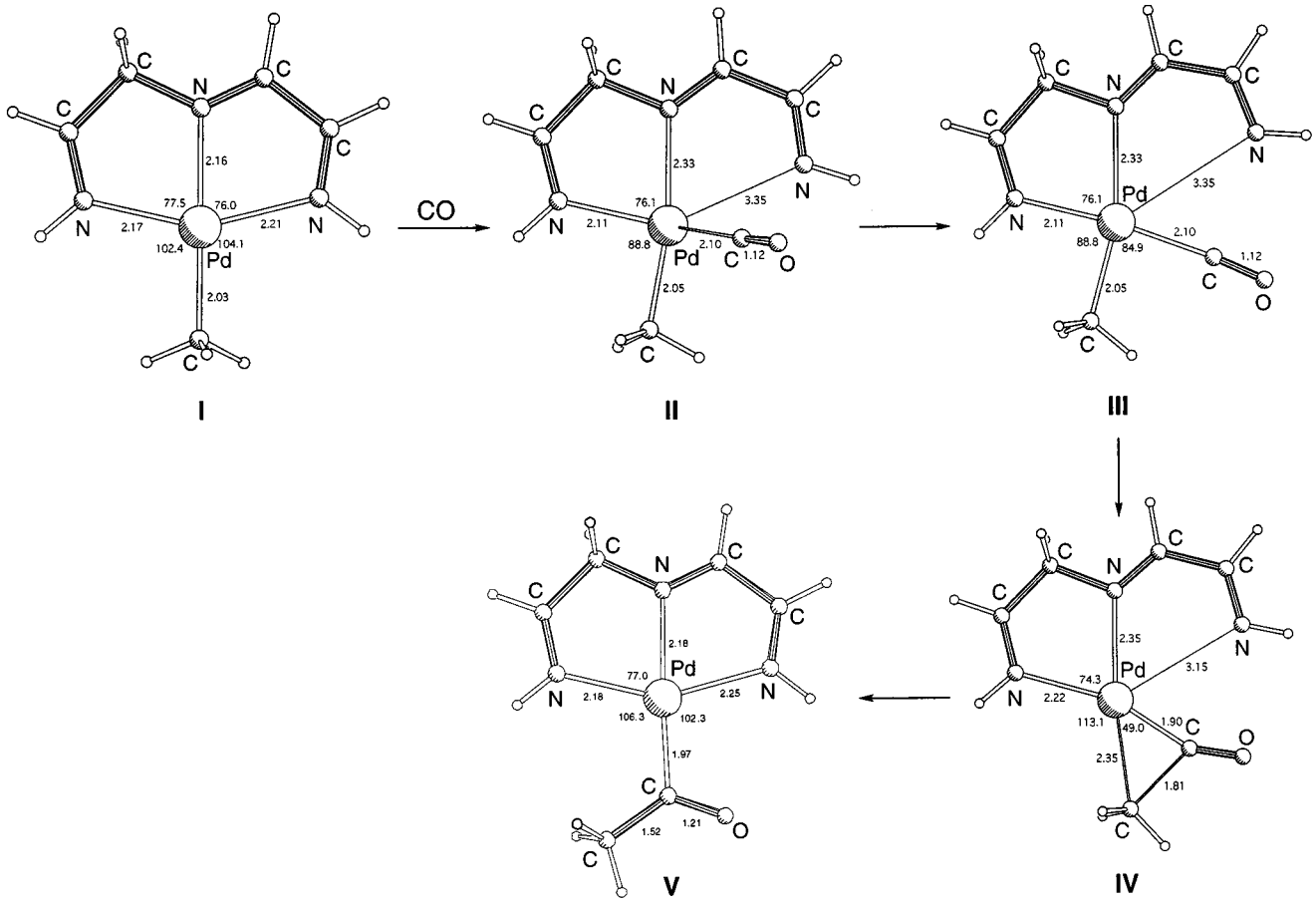
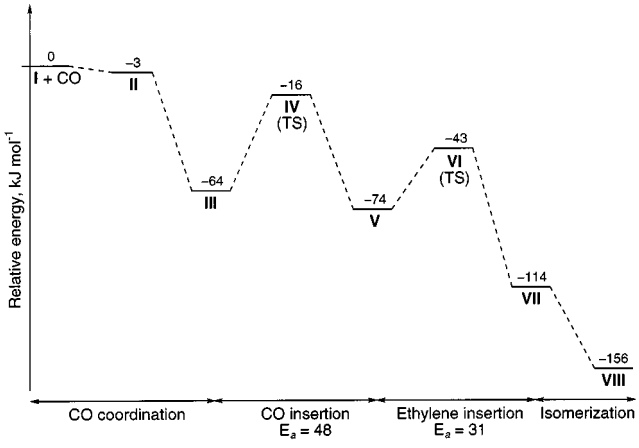


Table 4. Relative energies [kJ mol^{-1}] for stages of the CO and ethylene insertion in model systems with the ter- and bidentate nitrogen ligands **7** and **8**, respectively

Species[a]	L = **7** RHF	L = **7** MP2	L = **8** RHF	L = **8** MP2
$[Pd(Me)(L)]^+$ (**I**)	0.0	0.0	−0.0	3
CO coordination TS (**II**)	13	−3	[b]	[b]
$[Pd(Me)(CO)(L)]^+$ (**III**)	−16	−64	−93	−167
CO insertion TS (**IV**)	107	−16	15	−108
$[Pd\{C(O)Me\}(L)]^+$ (**V**)	−34	−74	−72	−137
$[Pd\{C(O)Me\}(C_2H_4)(L)]^+$	[c]	[c]	−110	−220
C_2H_4 insertion TS (**VI**)	77	−43	−34	−174
$[Pd\{\kappa^2\text{-}CH_2CH_2C(O)Me\}(L)]^+$ (**VII**)	−122	−114	−260	−278
$[Pd\{\kappa^1\text{-}CH_2CH_2C(O)Me\}(L)]^+$ (**VIII**)	−148	−156	[c]	[c]
$[Pd\{\kappa^2\text{-}CH_2CH_2C(O)Me\}(L)]^+$ (**IX**)	−149	−150	–	–

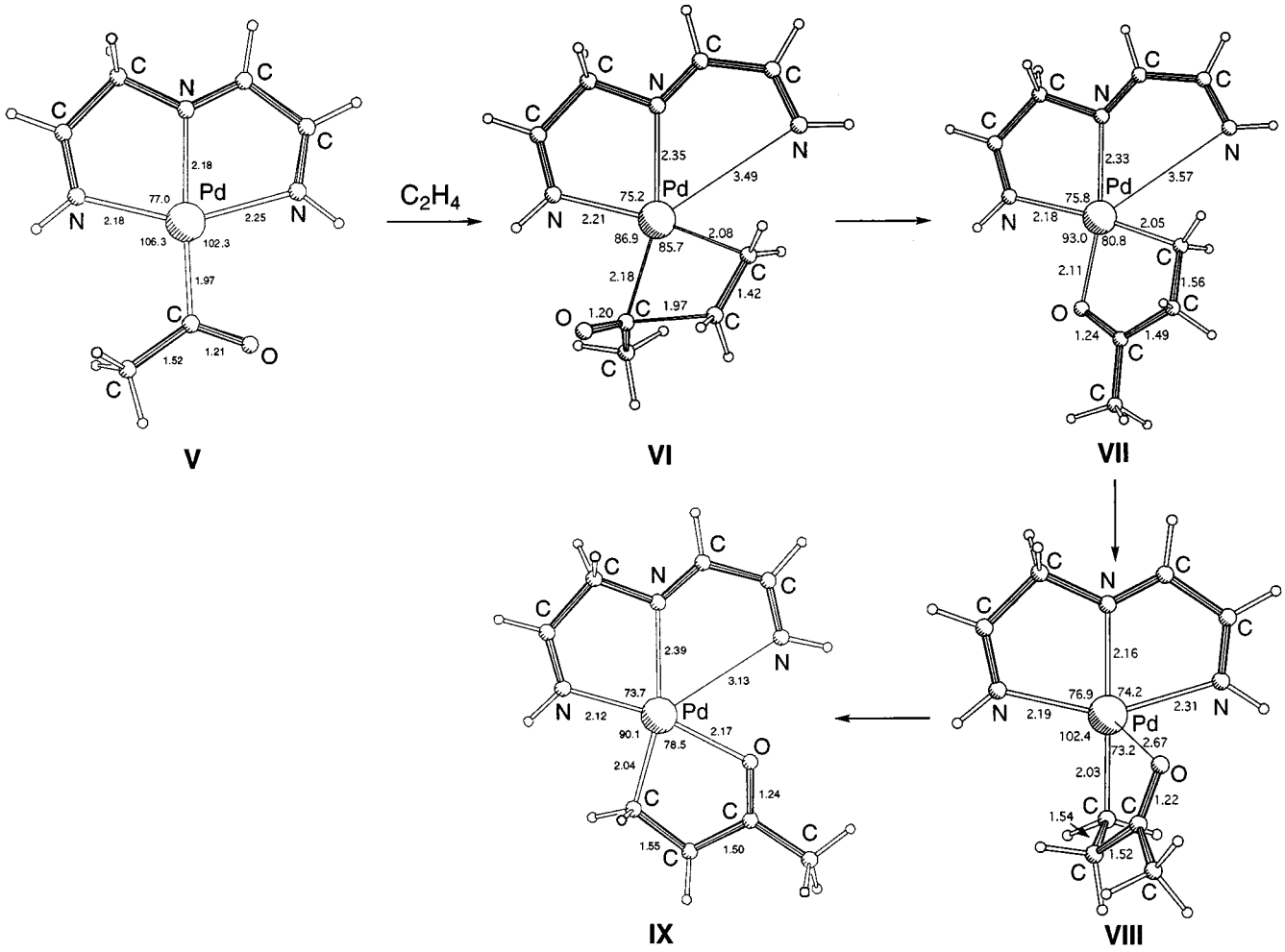
[a] Numbers of species with L = **7** are given in parentheses. – [b] Formation of $[Pd(Me)(CO)(\mathbf{8})]^+$ from $[Pd(Me)(\mathbf{8})]^+$ and CO appears to be barrierless. – [c] No minimum was found for this structure.

Figure 6. Potential-energy profile of CO and subsequent ethylene insertion in $[Pd(Me)(\mathbf{7})]^+$ (**I**), in kJ mol^{-1} at the MP2 level, relative to **I** + CO



(b) *Ethylene Insertion:* The optimized geometries and selected bond lengths and bond angles of the starting complex, the transition state, and the initial and final product are shown in Scheme 3. The relative RHF and MP2 energies have been collected in Table 4 and the potential energy profile at the MP2 level is shown in Figure 6. Analogously to the CO insertion reaction in $[Pd(Me)(\mathbf{7})]^+$, the ethylene insertion into the acetyl−palladium bond of $[Pd\{C(O)Me\}(\mathbf{7})]^+$ is found to proceed via a four-coordinate transition state (species **VI**), in which two nitrogen atoms, the inserting ethylene molecule and the acetyl ligand occupy the four coordination sites. The ethylene insertion is found to pass through a four-centered transition state, similar to those found by others in systems which contain

Scheme 3



a bidentate ligand.[76][78][79][80] At the RHF level, we did not find a minimum for a structure containing a coordinated alkene and a nitrogen ligand coordinated in a bidentate fashion; therefore, the activation energy has been calculated relative to the acetyl species and free ethylene. Since complexation energies are much higher at the MP2 level, there might be a shallow local minimum at this level, which would result in a slightly higher activation energy. In any case, the calculated activation energy of 31 kJ mol^{-1} (MP2 value) is fairly low and comparable to that of the system, which contains the bidentate ligand **8** (E_a = 37 kJ mol^{-1} at MP2 level), despite the obvious crowding in structure **VI**. In the structure of the initial product **VII**, the acyl oxygen atom interacts strongly with the palladium center, which results in a relatively long C−O bond of 1.24 A and a short Pd−O distance of 2.11 A. These values agree well with that theoretically observed in [Pd{$C_2H_4C(O)Me$}($NH_2CH_2CH_2NH_2$)]$^+$ (C−O = 1.28 A; Pd−O = 2.07 A)[76] and those experimentally observed for [Pd{$C_7H_{10}C(O)Me$}(PPh_3)$_2$]BF_4[16] (C−O = 1.240(10) A; Pd−O = 2.114(6) A) and [Pd{$C_{10}H_{12}C(O)Me$}(bpy)]SO_3CF_3[22] (C−O = 1.249(6) A; Pd−O = 2.026(3) A). In the calculations, the chelate structure **VII** isomerizes to species **VIII**, in which the nitrogen ligand is coordinated in a terdentate fashion. The carbonyl group now occupies an apical position, as theoretically observed in [Pd($C_2H_4C(O)Et$)(PH_2CH=$CHPH_2$)(CO)]$^+$[79]. Our experiments show that for complexes **2f**−**6f**, obtained after norbornadiene insertion, species **IX** is more stable than structure **VIII**. On both the RHF and MP2 level, the energies of species **IX** and **VIII** are similar. This is completely in agreement with the experimentally observed fluxional behavior on the ^{1}H-NMR time scale for complexes **4f**−**6f**, which process is proposed to proceed via species of type **VIII**.

Comparison Between Theoretical and Experimental Results

The results of the ab initio MO calculations are fully in agreement with our experimental results. The observed H/D exchange in **1a** in the presence of D_2O, the fast alcoholysis of the acetylchloropalladium complexes **1d**−**6d**, and the structure of complexes **1f**−**6f** show the ability of ligands **1**−**6** to coordinate in a bidentate fashion. Furthermore, a mechanism by substitution of one of the distal nitrogen donor atoms by the substrate followed by rate-determining migratory insertion explains the following observations.

(i) Strained alkenes undergo facile insertion in complexes **2e**−**6e**, whereas simple unstrained alkenes failed to react. Strained alkenes are known to coordinate more strongly to palladium than unstrained alkenes[9][32], so it seems reasonable to assume that unstrained alkenes are unable to compete with the distal nitrogen atoms of the nitrogen ligand for coordination to the palladium.

(ii) Complex **1e** reacts very slowly with nbd, as the two bulky isopropyl groups in **1e** will hinder alkene association significantly.

(iii) The nbd insertion rate increases in the order **6e** < **5e**, with decreasing coordinating capability of the nitrogen ligand (vide supra).[81] Consequently, the distal nitrogen atoms will dissociate more easily, resulting in a more facile substitution by the alkene.

(iv) The nbd insertion rate increases in the order **5e** << **5d**. The chloride counter anion in **5d** may initiate nitrogen dissociation by coordination to the palladium.[32][67][68]

Interestingly, the nbd insertion rate increases in the order **6e** < **4e** < **2e**, whereas on the basis of the rigidity of nitrogen ligands **2**, **4**, and **6** an insertion rate for **2e** in between those of **4e** and **6e** would be expected. Both from calculations and from the molecular structures of **1b**, **4c**, and **6a**[32], it appears that considerable deformations of the ligand skeleton are needed to achieve terdentate coordination with acceptable nitrogen−palladium distances.[82] Even so, the coordination environment is distorted, with *trans* N−Pd−N angles deviating significantly from the ideal value of 180°. In that sense, these complexes can be considered to be strained. Dissociation of one of the arms of the nitrogen ligand, relieving the strain, can be expected to be a low-energy process, which indeed is observed in the experimental and theoretical studies. The strain in the ligand backbone in the terdentate coordinated situations obviously increases in the order **6** < **2** < **4**, reflecting the tendency of the ligand to coordinate in a bidentate fashion. However, ligands **6** and **2** can both create space with the same ease by rotating the dangling pyridyl group, whereas creation of space is much more difficult in the case of ligand **4**. Thus, we believe that the higher insertion rate for **2e** and **4e** relative to **6e** reflects the higher strain in **2e** and **4e**. Furthermore, the higher insertion rate for **2e** relative to **4e** is most probably caused by more facile creation of a free coordination site.

Complexes **2f**−**6f** showed further reactivity toward CO and nbd, but the complexity of the ^{1}H-NMR spectra made assignment difficult. Furthermore, further insertions are expected to proceed alike, and our results have demonstrated that not only complexes containing flexible terdentate nitrogen ligands, but also complexes containing rigid terdentate nitrogen ligands are useful in studying the intimate steps of the catalytic cycle of polyketone formation.

Conclusion

We have shown that ionic methyl- and acetylpalladium complexes containing flexible and rigid terdentate nitrogen ligands undergo sequential insertion of carbon monoxide and strained alkenes. Although nitrogen dissociation was expected to be difficult for complexes containing rigid terdentate nitrogen ligands, ab initio MO calculations show that the mechanism of both insertion reactions unexpectedly proceeds by substitution of one of the distal nitrogen atoms of the terdentate nitrogen ligand, followed by a rate-determining migratory insertion reaction. These theoretical results, which indicate that even rigid terdentate nitrogen ligands may coordinate in a bidentate fashion, are fully supported by the experimentally observed bidentate coordination mode of both flexible and rigid terdentate nitrogen ligands in alkylpalladium complexes, obtained after norbornadiene insertion and the kinetic study of this insertion reaction. In our attempt to prevent nitrogen dissociation by employing rigid terdentate nitrogen ligands, the opposite effect has been observed, as the increasing rigidity of this particular set of terdentate nitrogen ligands leads to increasing strain, *facilitating* nitrogen dissociation.

This work was supported by the *Netherlands Foundation for Chemical Research (SON)* with financial aid from the *Netherlands Organization for Scientific Research (NWO)*. P. H. M. B. thanks Dr. *J.H. van Lenthe* (Utrecht University) for generous amounts of computer time. Q. X. and R. P. T. thank the *Robert A. Welch Foundation* and the *National Science Foundation* (Grant CHE-9224686) for the financial support. We thank Dr. *R. E. Rülke* for helpful discussions and for the GC-MS measurements, and *J. W. H. Peeters* for the mass-spectrometry measurements.

Experimental Section

General: All manipulations were carried out in purified dry nitrogen by using standard Schlenk techniques. Solvents were dried and stored under nitrogen. Carbon monoxide 99.5% was purchased from HoekLoos and was used without further purification. The compounds 1,2,3,4,5,6,7,8-octahydroacridine-4,5-dione[83], 2-(2′-pyridyl)-1,10-phenanthroline (**2**)[44], 1,2-dihydrodipyrido[4,3-*b*;5,6-*b*]-acridine (**3**)[45], dipyrido[4,3-*b*;5,6-*b*]acridine (**4**)[45], 4′-methylthio-2,2′:6′,2′′-terpyridine (**5**)[46], Pd(Me)Cl(COD)[72] (COD = 1,5-cyclooctadiene), [Pd(Me)(**6**)]Cl (**6a**)[32], [Pd{C(O)Me}(**6**)]Cl (**6d**)[32], and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAr′$_4$)[84] were prepared according to the literature. All other starting chemicals were used as commercially obtained. Silver trifluoromethanesulfonate was stored under nitrogen in the dark. − ^{1}H- and ^{13}C-NMR spectra (300.13 and 75.48 MHz, respectively) were recorded with a Bruker AMX 300 spectrometer at 20°C, unless noted otherwise. Chemical shifts are in ppm relative to TMS as external standard (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quadruplet, qq = quadruplet of quadruplet, sept = septuplet, m = multiplet, br. = broad). ^{15}N chemical shifts, which are in ppm relative to nitromethane as external standard, were extracted from gradient-selected (^{1}H,^{15}N)-HMQC experiments[85][86][87] with a Bruker DRX 300 spectrometer. For adopted numbering schemes see Figure 1. − IR spectra were obtained with a Bio-Rad FTS-7 spectrophotometer and mass spectra were obtained with a JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-MP7000 data system. GC-MS spectra were obtained with a Hewlett-Packard 5890 series II gas chromatograph with a Gerstel CIS III temperature-controllable injector, an HP 5971A mass-selective detector with electron-impact ionization at 70 eV, and an HP Ultra-2 column (25 m, 0.20 mm inner diameter, 0.33 μm film thickness).

4,5-Bis(isopropylimino)-1,2,3,4,5,6,7,8-octahydroacridine (**1**): A solution of 1,2,3,4,5,6,7,8-octahydroacridine-4,5-dione (1.04 g, 4.84

mmol) in 20 ml of isopropylamine, to which formic acid (2 drops) and $MgSO_4$ (2 g) were added, was stirred at 20°C. After 5 h, the solution was filtered and the isopropylamine was evaporated in vacuo, which resulted in a red oil. Purification by chromatography on neutral alumina with hexane/diethyl ether (4:1) as eluent, resulted in **1** as a yellow oil (704 mg, 49%). – ^{1}H NMR ($CDCl_3$): δ = 7.16 (s, 7-H), 4.85 (d, *J* = 4.8 Hz, 5-H), 4.80 (br., NH), 3.48 (sept, *J* = 6.3 Hz, C*H*Me$_2$), 2.76 (t, *J* = 7.6 Hz, 3-H), 2.35 (m, 4 H, 4-H), 1.24 (d, *J* = 6.3 Hz, CH*Me*$_2$). – ^{13}C NMR ($CDCl_3$): δ = 146.1 (C-1), 139.0 (C-2), 133.8 (C-7), 130.5 (C-6), 94.7 (C-5), 43.5 (*C*HMe$_2$), 27.5, 21.5 (C-3 and C-4), 22.6 (CH*Me*$_2$). – IR (KBr): ν = 3390 cm^{-1} (NH). – MS (EI): calcd. for $C_{19}H_{27}N_3$ 297.2205; found 297.2202.

Chloro(methyl)palladium Complexes **1a–5a**: 4,5-Bis(isopropylimino)-1,2,3,4,5,6,7,8-octahydroacridine (**1**) (714 mg, 2.38 mmol) was added to a solution of Pd(Me)Cl(COD) (431 mg, 1.63 mmol) in 20 ml of toluene. The yellow precipitate, which was formed instantaneously, was separated from the toluene and was washed with diethyl ether (2 × 20 ml). This resulted in **1a** as a yellow solid (577 mg, 78%).

By following the procedure for **1a**, complexes **2a–5a** were synthesized in yields varying from 83 to 95%.

*[Pd(Me)(**1**)]Cl* (**1a**): ^{1}H NMR ($CDCl_3$): δ = 8.03 (s, 7-H), 4.28 (sept, *J* = 6.5 Hz, C*H*Me$_2$), 3.14 (t, *J* = 5.9 Hz, 3-H), 3.09 (t, *J* = 6.4 Hz, 5-H), 2.14 (m, 4 H, 4-H), 1.33 (d, *J* = 6.5 Hz, CH*Me*$_2$), 0.86 (s, Pd–Me). – ^{13}C NMR ($CDCl_3$): δ = 175.6 (C-6), 146.3 (C-1), 142.9 (C-2), 138.9 (C-7), 55.1 (*C*HMe$_2$), 29.9 (C-5), 26.9 (C-3), 22.2 (C-4), 21.5 (CH*Me*$_2$), –6.0 (Pd–Me). – MS (FAB): calcd. for $[C_{20}H_{30}N_3Pd]^+$ 418; found 418. – $C_{20}H_{30}ClN_3Pd \cdot H_2O$: calcd. C 50.85, H 6.83, N 8.90; found C 50.67, H 6.44, N 8.57.

*[Pd(Me)(**2**)]Cl* (**2a**): ^{1}H NMR (CD_3OD): δ = 8.69 (m, 3 H, 1-H, 8-H, and 9-H), 8.50 (d, *J* = 4.7 Hz, 15-H), 8.43 (m, 2 H, 3-H and 12-H), 8.29 (m, 1 H, 13-H), 8.08 (d, *J* = 9.0 Hz, 16-H or 17-H), 8.04 (d, *J* = 9.0 Hz, 16-H or 17-H), 7.92 (dd, *J* = 8.2, 5.2 Hz, 2-H), 7.74 (m, 1 H, 14-H), 0.85 (s, Pd–Me). – ^{13}C NMR (CD_3OD): δ = 157.6, 152.7, 152.1, 149.8, 149.2, 141.8, 140.8, 140.1, 139.3, 131.6, 129.8, 129.5, 129.4, 127.5, 127.2, 125.9, 122.0 (C-1–C-17), 5.3 (Pd–Me). – MS (FAB): calcd. for $[C_{18}H_{14}N_3Pd]^+$ 378.0222; found 378.0242. – $C_{18}H_{14}ClN_3Pd \cdot 1.5\ H_2O$: calcd. C 49.00, H 3.89, N 9.52; found C 49.23, H 4.00 , N 9.60.

*[Pd(Me)(**3**)]Cl* (**3a**): ^{1}H NMR (CD_3OD): δ = 8.38 (d, *J* = 8.1 Hz, 3-H), 8.26 (d, *J* = 5.1 Hz, 1-H), 8.18 (s, 8-H), 7.93 (m, 2 H, 13-H and 15-H), 7.70 (m, 2 H, 16-H and 17-H), 7.63 (dd, *J* = 8.1, 5.1 Hz, 2-H), 7.49 (dd, *J* = 7.8, 5.4 Hz, 14-H), 3.23 (m, 4 H, 18-H and 19-H), 0.47 (s, Pd–Me). – ^{13}C NMR (CD_3OD, –20°C): δ = 153.6, 152.5, 150.7, 148.8, 146.5, 141.2, 139.7, 139.1, 138.5, 136.0, 135.5, 130.7, 130.0, 129.4, 129.0, 126.9, (C-1–C-17), 26.0, 24.4, (C-18 and C-19), 3.3 (Pd–Me). – MS (FAB): calcd. for $[C_{20}H_{16}N_3Pd]^+$ 404.0379; found 404.0391. – $C_{20}H_{16}ClN_3Pd \cdot 2\ H_2O$: calcd. C 50.44, H 4.24, N 8.82; found C 50.37, H 4.51, N 8.69.

*[Pd(Me)(**4**)]Cl* (**4a**): ^{1}H NMR (CD_3OD): δ = 8.85 (s, 8-H), 8.54 (d, *J* = 7.9 Hz, 3-H), 8.42 (d, *J* = 4.7 Hz, 1-H), 7.85 (m, 6 H, 2-H, 16-H, and 17-H), 0.79 (s, Pd–Me). – ^{13}C NMR (CD_3OD): δ = 152.5 (C-1), 148.0, 139.2 (C-5 and C-6), 139.8 (C-3), 135.3 (C-8), 131.1, 128.0 (C-4 and C-7), 128.7, 128.2, 127.2 (C-2, C-16 and C-17), 3.7 (Pd–Me). – MS (FAB): calcd. for $[C_{20}H_{14}N_3Pd]^+$ 402.0222; found 402.0200. – $C_{20}H_{14}ClN_3Pd \cdot 2.5\ H_2O$: calcd. C 49.71, H 3.97, N 8.70; found C 50.36, H 4.13, N 8.70.

*[Pd(Me)(**5**)]Cl* (**5a**): ^{1}H NMR (CD_3OD): δ = 8.11 (d, *J* = 6.0 Hz, 1-H), 8.03 (pst, 2-H), 7.96 (d, *J* = 5.0 Hz, 4-H), 7.59 (s, 7-H), 7.48 (pst, 3-H), 2.58 (s, SMe), 0.20 (s, Pd–Me). – ^{13}C NMR (CD_3OD): δ = 159.6 (C-8), 156.1, 150.2 (C-5 and C-6), 151.8 (C-1), 141.6 (C-3), 129.0 (C-2), 125.4 (C-4), 118.9 (C-7), 14.5 (SMe), 6.6 (Pd–Me). – MS (FAB): calcd. for $[C_{17}H_{16}N_3PdS]^+$, 400; found 400. – $C_{17}H_{16}ClN_3PdS \cdot 1.5\ H_2O$: calcd. C 44.07, H 4.14, N 9.07; found C 43.83, H 4.02, N 8.90.

*[Pd(Me)(**1**)]SO$_3$CF$_3$* (**1b**): To a solution of [Pd(Me)(**1**)]Cl (**1a**) (56.9 mg, 0.12 mmol) in a mixture of 20 ml of dichloromethane and 0.5 ml of acetonitrile was added $AgSO_3CF_3$ (34.6 mg, 0.13 mmol), and the mixture was stirred in the dark at 20°C. After 10 min, the mixture was evaporated to dryness and 20 ml of dichloromethane were added. After filtering the solution through Celite and extracting the residue with dichloromethane (5 ml), the combined filtrates were evaporated to dryness. Washing the residue with diethyl ether (2 × 20 ml) and drying in vacuo, yielded **1b** as a yellow solid (62.5 mg, 89%). – ^{1}H NMR ($CDCl_3$): δ = 7.84 (s, 7-H), 4.28 (sept, *J* = 6.6 Hz, C*H*Me$_2$), 3.01 (m, 8 H, 3-H and 5-H), 2.12 (m, 4 H, 4-H), 1.34 (d, *J* = 6.6 Hz, CH*Me*$_2$), 0.88 (s, Pd–Me). – ^{13}C NMR ($CDCl_3$): δ = 175.5 (C-6), 146.3 (C-1), 142.8 (C-2), 138.7 (C-7), 55.3 (*C*HMe$_2$), 29.7 (C-5), 26.6 (C-3), 22.1 (C-4), 21.4 (CH*Me*$_2$), –5.9 (Pd–Me). – MS (FAB): calcd. for $[C_{20}H_{30}N_3Pd]^+$ 418; found 418. – $C_{21}H_{30}F_3N_3O_3PdS$: calcd. C 44.41, H 5.33, N 7.40; found C 44.49, H 5.21, N 7.24.

Methylpalladium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate Complexes **1c–6c**: To a solution of [Pd(Me)(**1**)]Cl (**1a**) (69.6 mg, 0.15 mmol) in 20 ml of dichloromethane, $NaBAr'_4$ (123.3 mg, 0.14 mmol) was added. After stirring for 15 min at 20°C the solution was concentrated to dryness. After addition of 20 ml of diethyl ether, the solution was filtered and concentrated to dryness. The resulting yellow solid was washed with hexane (2 × 20 ml) and dried in vacuo, yielding complex **1c** (148.7 mg, 83%).

By following the procedure for **1c**, complexes **2c–6c** were obtained from the corresponding chloro(methyl)palladium complexes **2a–6a** in yields varying from 78 to 95%.

*[Pd(Me)(**1**)]BAr′$_4$* (**1c**): ^{1}H NMR ($CDCl_3$): δ = 7.70 (s, Ar′ H$_{ortho}$), 7.52 (s, Ar′ H$_{para}$), 7.48 (s, 7-H), 4.23 (sept, *J* = 6.6 Hz, C*H*Me$_2$), 2.87 (t, *J* = 6.5 Hz, 5-H), 2.76 (t, *J* = 6.0 Hz, 3-H), 1.99 (m, 4 H, 4-H), 1.31 (d, *J* = 6.6 Hz, CH*Me*$_2$), 0.97 (s, Pd–Me). – ^{13}C NMR ($CDCl_3$): δ = 174.4 (C-6), 161.5 (q, *J* = 50 Hz, Ar′ C$_{ipso}$), 146.3 (C-1), 142.2 (C-2), 137.9 (C-7), 134.6 (Ar′ C$_{ortho}$), 128.7 (qq, *J* = 31, 3 Hz, Ar′ C$_{meta}$), 124.3 (q, *J* = 273 Hz, Ar′ CF$_3$), 117.3 (Ar′ C$_{para}$), 55.4 (*C*HMe$_2$), 29.5, 26.5 (C-3 and C-5), 21.8 (C-4), 21.3 (CH*Me*$_2$), –4.8 (Pd–Me). – MS (FAB): calcd. for $[C_{20}H_{30}N_3Pd]^+$ 418.1474; found 418.1435. – $C_{52}H_{42}BF_{24}N_3Pd$: calcd. C 48.71, H 3.30, N 3.28; found C 48.35, H 3.33, N 3.13.

*[Pd(Me)(**2**)]BAr′$_4$* (**2c**): ^{1}H NMR ($CDCl_3$): δ = 8.81 (dd, *J* = 5.0, 0.9 Hz, 1-H), 8.65 (d, *J* = 5.1 Hz, 15-H), 8.49 (dd, *J* = 8.3, 0.9 Hz, 3-H), 8.41 (d, *J* = 8.6 Hz, 12-H), 8.05 (m, 3 H, 8-H, 9-H, and 13-H), 7.92 (d, *J* = 8.9 Hz, 16-H or 17-H), 7.86 (d, *J* = 8.9 Hz, 16-H or 17-H), 7.86 (dd, *J* = 8.3, 5.0 Hz, 2-H), 7.74 (s, Ar′ H$_{ortho}$), 7.64 (m, 1 H, 14-H), 7.48 (s, Ar′ H$_{para}$), 1.11 (s, Pd–Me). – ^{13}C NMR ($CDCl_3$): δ = 161.5 (q, *J* = 50 Hz, Ar′ C$_{ipso}$), 134.5 (Ar′ C$_{ortho}$), 128.7 (qq, *J* = 31, 3 Hz, Ar′ C$_{meta}$), 124.2 (q, *J* = 273 Hz, Ar′ CF$_3$), 117.3 (Ar′ C$_{para}$), 157.6, 152.3, 151.3, 150.0, 149.5, 141.7, 140.4, 139.0, 138.2, 131.2, 129.3, 129.0, 128.1, 126.4, 123.9, 120.4 (C-1–C-17), 5.6 (Pd–Me). – MS (FAB): calcd. for $[C_{18}H_{14}N_3Pd]^+$ 378; found 378. – $C_{50}H_{26}BF_{24}N_3Pd$: calcd. C 48.36, H 2.11, N 3.38; found C 48.51, H 2.16, N 3.37.

*[Pd(Me)(**3**)]BAr′$_4$* (**3c**): ^{1}H NMR ($CDCl_3$): δ = 8.76 (dd, *J* = 5.0, 1.0 Hz, 1-H), 8.44 (dd, *J* = 8.3, 1.2 Hz, 3-H), 8.39 (d, *J* = 5.2 Hz, 15-H), 8.17 (s, 8-H), 7.84 (d, *J* = 8.9 Hz, 16-H or 17-H), 7.79

(d, J = 8.9 Hz, 16-H or 17-H), 7.71 (s, Ar′ H_{ortho}), 7.52 (dd, J = 8.0, 5.2 Hz, 14-H), 7.47 (s, Ar′ H_{para}), 3.30 (m, 4 H, 18-H and 19-H), 1.09 (s, Pd−Me), signals of 2-H, 3-H, and 13-H are overlapping with signals of protons from $BAr'_4{}^-$. − ^{13}C NMR ($CDCl_3$): δ = 161.5 (q, J = 51 Hz, Ar′ C_{ipso}), 134.5 (Ar′ C_{ortho}), 128.7 (qq, J = 31, 3 Hz, Ar′ C_{meta}), 124.2 (q, J = 273 Hz, Ar′ CF_3), 117.3 (Ar′ C_{para}), 154.4, 151.7, 150.2, 149.8, 147.0, 140.5, 140.3, 139.7, 138.8, 137.2, 134.7, 134.6, 130.6, 129.9, 128.4, 126.3, 126.0 (C-1−C-17), 26.0, 24.5 (C-18 and C-19), 3.4 (Pd−Me). − MS (FAB): calcd. for $[C_{20}H_{16}N_3Pd]^+$ 404; found, 404. − $C_{52}H_{28}BF_{24}N_3Pd$: calcd. C 49.26, H 2.23, N 3.31; found C 49.27, H 2.62, N 3.31.

*[Pd(Me)(**4**)]BAr′$_4$* (**4c**): ^1H NMR ($CDCl_3$): δ = 8.90 (s, 8-H), 8.86 (dd, J = 4.9, 0.9 Hz, 1-H), 8.52 (dd, J = 8.4, 0.9 Hz, 3-H), 8.01 (d, J = 9.2 Hz, 16-H or 17-H), 7.90 (d, J = 9.2 Hz, 16-H or 17-H), 7.93 (dd, J = 8.4, 4.9 Hz, 2-H), 7.72 (s, Ar′ H_{ortho}), 7.46 (s, Ar′ H_{para}), 1.26 (s, Pd−Me). − ^{13}C NMR ($CDCl_3$): δ = 161.5 (q, J = 50 Hz, Ar′ C_{ipso}), 151.9 (C-1), 150.0, 141.3 (C-5 and C-6), 138.9 (C-3), 134.5 (Ar′ C_{ortho}), 131.3, 128.7 (C-4 and C-7), 128.7 (qq, J = 31, 3 Hz, Ar′ C_{meta}), 128.2, 127.0, 126.9 (C-2, C-16, and C-17), 124.2 (q, J = 273 Hz, Ar′ CF_3), 117.2 (Ar′ C_{para}), 3.4 (Pd−Me), signal of C-8 is overlapping with signal of Ar′ C_{ortho}. − MS (FAB): calcd. for $[C_{20}H_{14}N_3Pd]^+$ 402; found 402. − $C_{52}H_{26}BF_{24}N_3Pd$: calcd. C 49.34, H 2.07, N 3.32; found C 49.73; H 2.06, N 3.18.

*[Pd(Me)(**5**)]BAr′$_4$* (**5c**): ^1H NMR ($CDCl_3$): δ = 8.58 (d, J = 5.4 Hz, 1-H), 8.00 (m, 4 H, 3-H and 4-H), 7.72 (m, 10 H, Ar′ H_{ortho} and 7-H), 7.59 (m, 2 H, 2-H), 7.51 (s, Ar′ H_{para}), 2.60 (s, SMe), 0.94 (s, Pd−Me). − ^{13}C NMR ($CDCl_3$): δ = 161.5 (q, J = 50 Hz, Ar′ C_{ipso}), 158.8 (C-8), 157.6, 149.9 (C-5 and C-6), 151.4 (C-1), 140.1 (C-3), 134.6 (Ar′ C_{ortho}), 128.7 (qq, J = 32, 3 Hz, Ar′ C_{meta}), 127.8 (C-2), 124.3 (q, J = 273 Hz, Ar′ CF_3), 123.3 (C-4), 117.2 (Ar′ C_{para}), 117.1 (C-7), 14.0 (SMe), 7.0 (Pd−Me). − MS (FAB): calcd. for $[C_{17}H_{16}N_3SPd]^+$ 400; found 400. − $C_{49}H_{28}BF_{24}N_3PdS$: calcd. C 46.56, H 2.23, N 3.32; found C 46.65, H 2.28, N 3.30.

*[Pd(Me)(**6**)]BAr′$_4$* (**6c**): ^1H NMR ($CDCl_3$): δ = 8.60 (d, J = 5.1 Hz, 1-H), 8.08 (m, 2 H, 3-H), 7.97 (d, J = 8.1 Hz, 4-H), 7.91 (m, 1 H, 8-H), 7.85 (m, 2 H, 7-H), 7.73 (s, Ar′ H_{ortho}), 7.64 (m, 2 H, 2-H), 7.50 (s, Ar′ H_{para}), 0.99 (s, Pd−Me). − ^{13}C NMR ($CDCl_3$): δ = 161.5 (q, J = 50 Hz, Ar′ C_{ipso}), 157.6, 150.9 (C-5 and C-6), 151.4 (C-1), 140.7 (C-8), 140.3 (C-3), 134.5 (Ar′ C_{ortho}), 128.8 (qq, J = 32, 3 Hz, Ar′ C_{meta}), 127.9 (C-2), 124.2 (q, J = 273 Hz, Ar′ CF_3), 123.6 (C-4), 122.1 (C-7), 117.2 (Ar′ C_{para}), 8.1 (Pd−Me). − MS (FAB): calcd. for $[C_{16}H_{14}N_3Pd]^+$, 354; found 354. − $C_{48}H_{26}BF_{24}N_3Pd$: C 47.34, H 2.15, N 3.45; found C 46.82, H 2.28, N 3.42.

Acetylchloropalladium Complexes **1d−5d**: Carbon monoxide was bubbled through a glass capillary into a solution of ca. 5 mg of the methylpalladium complexes **1a−5a** in 0.5 ml of solvent (**1a**, $CDCl_3$, **2a−5a**, CD_3OD). After 0.5 min, the products were identified by ^1H-NMR spectroscopy. Complexes **1d−5d** could not be isolated due to rapid decomposition.

*[Pd{C(O)Me}(**1**)]Cl* (**1d**): ^1H NMR ($CDCl_3$, −35°C): δ = 7.95 (s, 7-H), 4.15 (sept, J = 6.2 Hz, C*H*Me_2), 3.03 (m, 8 H, 3-H and 5-H), 2.67 [s, C(O)Me], 2.11 (m, 4 H, 4-H), 1.16 (d, J = 6.2 Hz, CH*Me*$_2$).

*[Pd{C(O)Me}(**2**)]Cl* (**2d**): ^1H NMR (CD_3OD): δ = 8.83 (1 H, m), 8.66 (2 H, m), 8.47 (3 H, m), 8.20 (1 H, m), 8.03 (2 H, m), 7.95 (1 H, m), 7.70 (1 H, m), 2.72 [s, C(O)Me].

*[Pd{C(O)Me}(**3**)]Cl* (**3d**): ^1H NMR (CD_3OD): δ = 9.13 (d, J = 5.4 Hz, 1-H), 8.89 (s, 8-H), 8.84 (dd, J = 8.1, 1.5 Hz, 3-H), 8.38 (d, J = 8.9 Hz, 16-H or 17-H), 8.34 (d, J = 8.9 Hz, 16-H or 17-H), 7.98 (m, 2 H, 13-H and 15-H), 7.69 (dd, J = 8.1, 5.4 Hz, 2-H), 7.33 (dd, J = 7.9, 5.4 Hz, 14-H), 1.62 [s, C(O)Me], signals of 18-H and 19-H are overlapping with signals of the solvent.

*[Pd{C(O)Me}(**4**)]Cl* (**4d**): ^1H NMR (CD_3OD): δ = 8.60 (s, 8-H), 8.58 (d, J = 4.7 Hz, 1-H), 8.36 (d, J = 8.1 Hz, 3-H), 7.73 (m, 6 H, 2-H, 16-H, and 17-H), 2.75 [s, C(O)Me].

*[Pd{C(O)Me}(**5**)]Cl* (**5d**): ^1H NMR (CD_3OD): δ = 8.50 (d, J = 7.8 Hz, 4-H), 8.42 (d, J = 5.4 Hz, 1-H), 8.26 (m, 2 H, 3-H), 8.15 (s, 7-H), 7.73 (m, 2 H, 2-H), 2.77 [s, C(O)Me], 2.64 (s, SMe).

Acetylpalladium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate Complexes **1e−6e**: A solution of [Pd(Me)(**1**)]BAr′$_4$ (**1c**) (20.3 mg, 0.016 mmol) in 20 ml of dichloromethane was stirred at 20°C in CO. After 10 min, the solution was filtered through Celite and the residue was extracted with dichoromethane (5 ml). The combined filtrates were concentrated to dryness and the product was washed with hexane (2 × 20 ml), giving **1e** as a yellow solid (18.3 mg, 86%).

By following the procedure for **1e**, complexes **2e−6e** were obtained from **2c−6c** in yields of 85−97%. Analytical data and mass spectra for **1e−6e** could not be obtained due to decarbonylation in the solid state.

*[Pd{C(O)Me}(**1**)]BAr′$_4$* (**1e**): ^1H NMR ($CDCl_3$): δ = 7.70 (s, Ar′ H_{ortho}), 7.52 (s, Ar′ H_{para}), 7.47 (s, 7-H), 4.13 (sept, J = 6.6 Hz, C*H*Me_2), 2.86 (t, J = 6.6 Hz, 5-H), 2.75 (t, J = 6.0 Hz, 3-H), 2.63 [s, C(O)Me], 1.98 (m, 4 H, 4-H), 1.17 (d, J = 6.6 Hz, CH*Me*$_2$). − ^{13}C NMR ($CDCl_3$): δ = 171.8 (C-6), 161.4 (q, J = 50 Hz, Ar′ C_{ipso}), 145.6 (C-1), 141.9 (C-2), 139.2 (C-7), 134.5 (Ar′ C_{ortho}), 128.7 (qq, J = 31, 3 Hz, Ar′ C_{meta}), 124.3 (q, J = 273 Hz, Ar′ CF_3), 117.3 (Ar′ C_{para}), 54.8 (*C*HMe_2), 34.5 [C(O)*Me*], 29.2, 26.6 (C-3 and C-5), 22.0 (CH*Me*$_2$), 21.5 (C-4), signal of *C*(O)Me was not observed. − IR (KBr): ν = 1689 cm^{-1} (CO).

*[Pd{C(O)Me}(**2**)]BAr′$_4$* (**2e**): ^1H NMR ($CDCl_3$): δ = 8.83 (d, J = 5.0 Hz, 1-H), 8.63 (d, J = 5.2 Hz, 15-H), 8.51 (d, J = 8.2 Hz, 3-H), 8.38 (d, J = 8.6 Hz, 12-H), 8.06 (m, 3 H, 8-H, 9-H, and 13-H), 7.92 (d, J = 9.0 Hz, 16-H or 17-H), 7.85 (d, J = 9.0 Hz, 16-H or 17-H), 7.89 (dd, J = 8.2, 5.0 Hz, 2-H), 7.72 (s, Ar′ H_{ortho}), 7.70 (m, 1 H, 14-H), 7.47 (s, Ar′ H_{para}), 2.74 [s, C(O)Me]. − ^{13}C NMR ($CDCl_3$): δ = 161.5 (q, J = 50 Hz, Ar′ C_{ipso}), 134.5 (Ar′ C_{ortho}), 128.7 (qq, J = 31, 3 Hz, Ar′ C_{meta}), 124.2 (q, J = 272 Hz, Ar′ CF_3), 117.3 (Ar′ C_{para}), 154.8, 152.9, 152.3, 149.9, 147.4, 141.5, 140.8, 139.6, 139.4, 131.0, 129.0, 128.9, 128.3, 126.5, 123.8, 120.3 (C-1−C-17), 29.2 [C(O)*Me*], signal of *C*(O)Me was not observed. − IR (KBr): ν = 1695 cm^{-1} (CO).

*[Pd{C(O)Me}(**3**)]BAr′$_4$* (**3e**): ^1H NMR ($CDCl_3$): δ = 8.84 (d, J = 5.1 Hz, 1-H), 8.46 (m, 2 H, 3-H and 15-H), 8.16 (s, 8-H), 7.85 (m, 2 H, 16-H/17-H and 13-H), 7.78 (d, J = 9.0 Hz, 16-H or 17-H), 7.70 (s, Ar′ H_{ortho}), 7.56 (dd, J = 7.8, 5.4 Hz, 14-H), 7.46 (s, Ar′ H_{para}), 3.26 (m, 4 H, 18-H and 19-H), 2.71 [s, C(O)Me], signal of 2-H is overlapping with signals from $BAr'_4{}^-$. − ^{13}C NMR ($CDCl_3$): δ = 161.5 (q, J = 50 Hz, Ar′ C_{ipso}), 134.5 (Ar′ C_{ortho}), 128.7 (qq, J = 32, 3 Hz, Ar′ C_{meta}), 124.2 (q, J = 272 Hz, Ar′ CF_3), 117.3 (Ar′ C_{para}), 152.2, 151.6, 150.7, 149.5, 147.0, 140.2, 139.4, 138.8, 137.1, 136.1, 134.4, 130.5, 130.3, 128.4, 126.3, 126.0 (C-1−C-17), 27.3 [C(O)*Me*], 26.0, 24.5 (C-18 and C-19), signal of *C*(O)Me was not observed. − IR (KBr): ν = 1698 cm^{-1} (CO).

*[Pd{C(O)Me}(**4**)]BAr′$_4$* (**4e**): ^1H NMR ($CDCl_3$): δ = 8.98 (d, J = 5.1 Hz, 1-H), 8.87 (s, 8-H), 8.50 (d, J = 8.1 Hz, 3-H), 7.99 (d, J = 9.1 Hz, 16-H or 17-H), 7.90 (d, J = 9.1 Hz, 16-H or 17-H), 7.95 (dd, J = 8.1, 5.1 Hz, 2-H), 7.71 (s, Ar′ H_{ortho}), 7.46 (s, Ar′ H_{para}), 2.81 [s, Pd−C(O)Me]. − ^{13}C NMR ($CDCl_3$): δ = 161.5 (q, J = 50 Hz, Ar′ C_{ipso}), 152.1 (C-1), 147.1, 141.4 (C-5 and C-6),

139.4 (C-3), 136.0 (C-8), 134.5 (Ar′ C_{ortho}), 131.0, 128.3 (C-4 and C-7), 128.7 (qq, J = 32, 3 Hz, Ar′ C_{meta}), 128.1, 127.0, 126.8 (C-2, C-16, and C-17), 124.2 (q, J = 272 Hz, Ar′ CF_3), 117.3 (Ar′ C_{para}), 26.4 [C(O)*Me*], signal of *C*(O)Me was not observed. − IR (KBr): ν = 1703 cm^{-1} (CO).

*[Pd{C(O)Me}(**5**)]BAr′*$_4$ (**5e**): ^{1}H NMR ($CDCl_3$): δ = 8.47 (d, J = 4.8 Hz, 1-H), 8.02 (m, 6 H, 3-H, 4-H, and 7-H) 7.72 (s, Ar′ H_{ortho}), 7.61 (m, 2 H, 2-H), 7.50 (s, Ar′ H_{para}), 2.64 [s, C(O)Me], 2.59 (s, SMe). − ^{13}C NMR ($CDCl_3$): δ = 231.8 [*C*(O)Me], 161.5 (q, J = 50 Hz, Ar′ C_{ipso}), 160.1 (C-8), 155.2, 149.9 (C-5 and C-6), 152.5 (C-1), 140.5 (C-3), 134.5 (Ar′ C_{ortho}), 128.7 (qq, J = 32, 3 Hz, Ar′ C_{meta}), 128.0 (C-2), 124.3 (q, J = 273 Hz, Ar′ CF_3), 123.3 (C-4), 117.2 (Ar′ C_{para}), 30.7 [C(O)*Me*], 13.9 (SMe), signal of C-7 is overlapping with signal of Ar′ C_{para}. − IR (KBr): ν = 1685 cm^{-1} (CO).

*[Pd{C(O)Me}(**6**)]BAr′*$_4$ (**6e**): ^{1}H NMR ($CDCl_3$): δ = 8.47 (d, J = 4.3 Hz, 1-H), 8.05 (m, 2 H, 3-H), 7.96 (d, J = 6.9 Hz, 4-H), 7.91 (m, 1 H, 8-H), 7.83 (m, 2 H, 7-H), 7.72 (s, Ar′ H_{ortho}), 7.64 (m, 2 H, 2-H), 7.49 (s, Ar′ H_{para}), 2.66 [s, C(O)Me]. − ^{13}C NMR ($CDCl_3$): δ = 161.5 (q, J = 50 Hz, Ar′ C_{ipso}), 156.7, 150.9 (C-5 and C-6), 152.5 (C-1), 141.8 (C-8), 140.8 (C-3), 134.5 (Ar′ C_{ortho}), 128.7 (qq, J = 32, 3 Hz, Ar′ C_{meta}), 128.1 (C-2), 124.2 (q, J = 273 Hz, Ar′ CF_3), 123.5 (C-4), 122.0 (C-7), 117.3 (Ar′ C_{para}), 30.8 [C(O)*Me*], signal of *C*(O)Me was not observed. − IR (KBr): ν = 1689 cm^{-1} (CO).

Alkylpalladium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate Complexes **2f**−**6f**: Norbornadiene (30 µl, 0.28 mmol) was added to a solution of [Pd{C(O)Me}(**2**)]BAr'_4 (**2e**) (98.0 mg, 0.077 mmol) in 20 ml of dichloromethane. The solution was stirred at 20°C and after 30 min concentrated to dryness. The product was washed with hexane (2 × 20 ml) and dried in vacuo, yielding **2f** as a yellow oil (91.3 mg, 86%).

By following the procedure for **2f**, complexes **3f**−**6f** were synthesized from complexes **3e**−**6e** in yields of 88−91%. Since the complexes **2f**−**6f** were isolated as oils, correct analytical data could not be obtained.

*[Pd{C$_7$H$_8$C(O)Me}(**2**)]BAr′*$_4$ (**2f**): ^{1}H NMR ($CDCl_3$): δ = 8.78 (m, 2 H, 1-H and 15-H), 8.61 (d, J = 8.4 Hz, 8-H), 8.52 (dd, J = 8.1, 1.5 Hz, 3-H), 8.30 (d, J = 8.4 Hz, 9-H), 8.02 (d, J = 9.0 Hz, 16-H or 17-H), 7.92 (d, J = 9.0 Hz, 16-H or 17-H), 7.84 (m, 3 H, 2-H, 12-H, and 13-H), 7.73 (s, Ar′ H_{ortho}), 7.50 (s, Ar′ H_{para}), 7.45 (dd, J = 4.5, 1.2 Hz, 14-H), 6.22 (dd, J = 5.5, 3.0 Hz, =CH), 6.15 (dd, J = 5.5, 3.0 Hz, =CH), 3.03 (br., CHC=), 2.97 (br., CHC=), 2.52 (dd, J = 6.0, 2.1 Hz, PdCH), 2.42 [d, J = 6.0 Hz, C*H*C(O)Me], 1.96 [s, C(O)Me], 1.71 (d, J = 9.3 Hz, CH_2), 1.42 (d, J = 9.3 Hz, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 235.3 [*C*(O)Me], 161.5 (q, J = 50 Hz, Ar′ C_{ipso}), 134.6 (Ar′ C_{ortho}), 128.7 (qq, J = 32, 3 Hz, Ar′ C_{meta}), 124.3 (q, J = 272 Hz, Ar′ CF_3), 117.2 (Ar′ C_{para}), 159.5, 154.9, 149.7, 149.5, 147.4, 143.6, 139.3, 138.8, 136.3, 135.3, 133.9, 130.6, 129.1, 127.7, 127.1, 126.5, 125.2, 124.5, 124.3 (C-1−C-17 and 2× =CH), 62.2 [*C*HC(O)Me], 48.2, 47.9, 47.8 (PdCH and 2 × *C*HC=), 45.2 (CH_2), 26.2 [C(O)*Me*]. − ^{15}N NMR ($CDCl_3$, −60°C): δ = −68.0, −158.4 (N1 and N3), signal of N2 was not observed due to the absence of a hydrogen atom with a sufficiently large N-H coupling constant. − IR (KBr): ν = 1612 cm^{-1} (CO). − MS (FAB): calcd. for $[C_{26}H_{22}N_3OPd]^+$ 498.0798; found 498.0779.

*[Pd{C$_7$H$_8$C(O)Me}(**3**)]BAr′*$_4$ (**3f**): ^{1}H NMR ($CDCl_3$): δ = 8.79 (d, J = 4.8 Hz, 1-H), 8.59 (d, J = 4.8 Hz, 15-H), 8.47 (d, J = 7.8 Hz, 3-H), 8.33 s (8-H), 7.89 (d, J = 9.0 Hz, 16-H or 17-H), 7.85 (d, J = 9.0 Hz, 16-H or 17-H), 7.82 (dd, J = 7.8, 4.8 Hz, 2-H), 7.73 (m, 9 H, Ar′ H_{ortho} and 13-H), 7.51 (s, Ar′ H_{para}), 7.37 (dd, J = 7.8, 4.8 Hz, 14-H), 6.26 (dd, J = 5.1, 3.0 Hz, =CH), 6.20 (dd, J = 5.1, 3.0 Hz, =CH), 3.26 (m, 2 H, 18-H or 19-H), 3.15 (m, 2 H, 18-H or 19-H), 3.08 (m, 2 H, 2 × CHC=), 2.52 (dd, J = 6.0, 2.1 Hz, PdCH), 2.46 [d, J = 6.0 Hz, C*H*C(O)Me], 2.05 [s, C(O)Me], 1.98 (d, J = 9.0 Hz, CH_2), 1.58 (d, J = 9.0 Hz, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 233.0 [*C*(O)Me], 161.5 (q, J = 50 Hz, Ar′ C_{ipso}), 134.6 (Ar′ C_{ortho}), 128.7 (qq, J = 32, 3 Hz, Ar′ C_{meta}), 124.3 (q, J = 272 Hz, Ar′ CF_3), 117.2 (Ar′ C_{para}), 153.4, 149.3, 149.1, 148.2, 147.4, 143.4, 138.7, 137.7, 136.4, 136.3, 136.0, 135.3, 134.0, 129.9, 129.5, 127.1, 126.9, 125.2, 124.7 (C-1−C-17 and 2 × =CH), 62.2 [*C*HC(O)Me], 48.2, 47.9, 46.7 (PdCH and 2 × *C*HC=), 45.3 (CH_2), 27.5, 26.8 (C-18 and C-19), 26.4 [C(O)*Me*]. − IR (KBr): ν = 1624 cm^{-1} (CO). − MS (FAB): calcd. for $[C_{28}H_{24}N_3OPd]^+$ 524.0954; found 524.0921.

*[Pd{C$_7$H$_8$C(O)Me}(**4**)]BAr′*$_4$ (**4f**): ^{1}H NMR ($CDCl_3$): δ = 9.03 (s, 8-H), 8.92 (dd, J = 4.8, 1.2 Hz, 1-H), 8.43 (dd, J = 8.0, 1.2 Hz, 3-H), 8.05 (d, J = 9.0 Hz, 16-H or 17-H), 7.92 (d, J = 9.0 Hz, 16-H or 17-H), 7.84 (dd, J = 8.0, 4.8 Hz, 2-H), 7.74 (s, Ar′ H_{ortho}), 7.50 (s, Ar′ H_{para}), 6.30 (dd, J = 5.4, 3.0 Hz, =CH), 6.26 (dd, J = 5.4, 3.0 Hz, =CH), 3.23 (br., CHC=), 3.17 (br., CHC=), 2.58 (dd, J = 6.0, 2.1 Hz, PdCH), 2.52 [d, J = 6.0 Hz, C*H*C(O)Me], 2.22 (d, J = 9.0 Hz, CH_2), 1.72 (d, J = 9.0 Hz, CH_2), 2.15 [s, C(O)Me]. − ^{13}C NMR ($CDCl_3$): δ = 231.2 [*C*(O)Me], 161.5 (q, J = 50 Hz, Ar′ C_{ipso}), 148.8 (C-1), 146.2, 144.8 (C-5 and C-6), 137.5, 135.2, 134.3 (C-8 and 2 × =CH), 137.4 (C-3), 134.6 (Ar′ C_{ortho}), 130.6, 128.9 (C-4 and C-7), 128.7 (qq, J = 32, 3 Hz, Ar′ C_{meta}), 127.7, 126.7, 125.3 (C-2, C-16, and C-17), 124.3 (q, J = 272 Hz, Ar′ CF_3), 117.2 (Ar′ C_{para}), 62.1 [*C*HC(O)Me], 48.3, 47.9, 46.4 (PdCH and 2 × *C*HC=), 45.4 (CH_2), 26.5 [C(O)*Me*]. − ^{15}N NMR ($CDCl_3$, −60°C): δ = −130.1 (coordinated N1), signals of N2 and noncoordinated N1 were not observed due to the absence of a hydrogen atom with a sufficiently large N-H coupling constant. − IR (KBr): ν = 1624 cm^{-1} (CO). − MS (FAB): calcd. for $[C_{28}H_{22}N_3OPd]^+$ 522.0797; found 522.0781.

*[Pd{C$_7$H$_8$C(O)Me}(**5**)]BAr′*$_4$ (**5f**): ^{1}H NMR ($CDCl_3$): δ = 8.57 (d, J = 4.5 Hz, 1-H), 8.00 (d, J = 7.5 Hz, 4-H), 7.89 (m, 2 H, 3-H), 7.82 (s, 7-H), 7.71 (s, Ar′ H_{ortho}), 7.52 (s, Ar′ H_{para}), 7.48 (m, 2 H, 2-H), 6.14 (dd, J = 5.5, 3.0 Hz, =CH), 6.10 (dd, J = 5.5, 3.0 Hz, =CH), 2.95 (br., CHC=), 2.82 (br., CHC=), 2.65 (s, SMe), 2.32 [d, J = 6.1 Hz, C*H*C(O)Me], 2.28 (dd, J = 6.1, 2.2 Hz, PdCH), 1.87 [s, C(O)Me], 1.57 (d, J = 9.6 Hz, CH_2), 1.42 (d, J = 9.6 Hz, CH_2). − ^{13}C NMR ($CDCl_3$): δ = 235.0 [*C*(O)Me], 161.5 (q, J = 50 Hz, Ar′ C_{ipso}), 157.6 (C-8), 155.9, 150.5 (C-5 and C-6), 149.5 (C-1), 139.8 (C-3), 134.6 (Ar′ C_{ortho}), 135.2 (=CH), 133.8 (=CH), 128.7 (qq, J = 32, 3 Hz, Ar′ C_{meta}), 125.6 (C-2), 124.3 (q, J = 272 Hz, Ar′ CF_3), 123.6 (C-4), 117.2 (Ar′ C_{para}), 62.1 [*C*HC(O)Me], 48.1, 48.0, 47.5 (PdCH and 2× *C*HC=), 45.2 (CH_2), 26.1 [C(O)*Me*], 13.9 (SMe), signal of C-7 is overlapping with signal of Ar′ C_{para}. − IR (KBr): ν = 1610 cm^{-1} (CO). − MS (FAB): calcd. for $[C_{25}H_{25}N_3OPdS]^+$ 520.0675; found 520.0647.

*[Pd{C$_7$H$_8$C(O)Me}(**6**)]BAr′*$_4$ (**6f**): ^{1}H NMR ($CDCl_3$): δ = 8.58 (d, J = 5.1 Hz, 1-H), 8.14 (m, 1 H, 8-H), 8.05 (m, 2 H, 7-H), 7.97 (d, J = 7.8 Hz, 4-H), 7.90 (m, 2 H, 3-H), 7.72 (s, Ar′ H_{ortho}), 7.50 (s, Ar′ H_{para}), 6.15 (dd, J = 5.4, 3.0 Hz, =CH), 6.11 (dd, J = 5.4, 3.0 Hz, =CH), 2.96 (br., CHC=), 2.85 (br., CHC=), 2.33 [m, 2 H, C*H*C(O)Me and PdCH], 1.88 [s, C(O)Me], 1.60 (d, J = 9.3 Hz, CH_2), 1.44 (d, J = 9.3 Hz, CH_2), signal of 2-H is overlapping with signal of Ar′ C_{para}. − ^{13}C NMR ($CDCl_3$): δ = 234.4 [*C*(O)Me], 161.5 (q, J = 50 Hz, Ar′ C_{ipso}), 155.9 (C-5 or C-6), 149.6 (C-1), 140.2, 138.2 (C-3 and C-8), 135.3 (=CH), 133.9 (=CH), 134.5 (Ar′ C_{ortho}), 128.7 (qq, J = 32, 3 Hz, Ar′ C_{meta}), 128.7, 126.1, 123.6 (C-2, C-4, and C-7), 124.2 (q, J = 272 Hz, Ar′ CF_3), 117.2 (Ar′ C_{para}),

61.9 [*C*HC(O)Me], 48.1, 48.0, 47.5 (PdCH and 2× *C*HC=), 45.2 (CH_2), 26.2 [C(O)*Me*], signal of C-5 or C-6 is overlapping with signal of Ar′ C_{para}. − ^{15}N NMR ($CDCl_3$, −60°C): δ = −155.0 (coordinated N1), signals of N2 and noncoordinated N1 were not observed due to the absence of a hydrogen atom with a sufficiently large N-H coupling constant. − IR (KBr): ν = 1610 cm^{-1} (CO). − MS (FAB): calcd. for $[C_{24}H_{22}N_3OPd]^+$ 474.0798; found 474.0801.

Kinetics: The rates of the reactions of norbornadiene with complexes **1e**−**6e**, resulting in complexes **1f**−**6f**, were followed spectrophotometrically by repetitive scanning of the spectrum at suitable time intervals at a fixed wavelength, at which the difference between absorbance of educt and product was largest. The reactions were started by addition of norbornadiene to a $1.9\cdot10^{-4}$ M solution of the acetylpalladium complex in a quartz cell, which was placed in the thermostated cell compartment of a Perkin-Elmer Lambda 5 spectrophotometer, with a temperature accuracy of ± 0.5°C. The use of at least a 10-fold excess of norbornadiene over acetylpalladium complex ensured pseudo-first-order kinetics in all runs. All reactions, except for the reaction of **3e** with nbd, were clean and quantitative, and in all cases isosbestic points were obtained. Furthermore, the reactions obeyed a first-order rate law for at least four half-lives of the reaction. The rate constants k_{obsd} were calculated from the slopes of plots of $\ln\{(A_t - A_\infty)/(A_0 - A_\infty)\}$ vs time (A_0 = absorbance after mixing of the reagents, A_∞ = absorbance at completion of the reaction). The activation parameters $\Delta S^{\neq}$ and $\Delta H^{\neq}$ were obtained from an Eyring plot.

X-ray Structure Determinations of **1b** *and* **4c**[88]: Crystals suitable for X-ray structure determination were mounted on a Lindemann-glass capillary and transferred to an Enraf-Nonius CAD4-Turbo diffractometer on rotating anode. Accurate unit-cell parameters and an orientation matrix were determined by least-squares fitting of the setting angles of a set of well-centered reflections (SET4).[89] Reduced-cell calculations did not indicate higher lattice symmetry.[90] Crystal data and some details on data collection are given in Table 5. Reflection data were collected at 150 K in ω-scan mode, using graphite-monochromated Mo-K_α radiation (λ = 0.71073A). Data were corrected for Lp effects and for the linear instability of the reference reflections, but not for absorption. The structure of **1b** was solved by automated direct methods (SHELXS96)[91]; the structure of **4c** was solved by automated Patterson methods (SHELXS86)[92]. Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-96);[93] no observance criterion was applied during refinement. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. In complex **4c** two CF_3 groups of the counterion displayed conformational disorder. A two-site model was introduced to describe this disorder. Severely disordered solvent molecules occupy two of the crystallographic inversion centers of structure **4c**. Since no discrete solvent model could be refined, this electron density was taken into account using the SQUEEZE/BYPASS procedure[94], as implemented in PLATON[95]. The two solvent areas were found to have a volume of 100.5 and 80.5 A^3, containing 38.9 and 24.7 e, respectively. Non-hydrogen atoms were refined with anisotropic thermal parameters, with exception of the minor component of the disordered atoms. The hydrogen atoms were refined with a fixed isotropic displacement parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography[96]. Geometrical calculations and illustrations were performed with PLATON[95].

Ab initio MO Calculations on the Insertion Reactions: The split-valence 3-21G basis was used for C, N, O, and H atoms.[97] The Pd basis was based on the (18s,11p,9d)→[6s,5p,3d] basis of Godbout[98], but the (9d)→[3d] contraction was replaced by a (9d)→[4d] contraction by releasing the most diffuse d primitive of the middle d shell. In order to save computational time, ligand HN=CHCH$_2$N=CHCH=NH (**7**) was used as a model and solvation and counter anions were left out. To simulate the enforced planarity of the rigid ligands used in the experimental study, the structure of **7** was forced to keep a horizontal mirror plane (local C_s symmetry). Apart from this restriction, all structures were fully optimized (in particular, the metal atom and remaining fragments were allowed to move out of the ligand plane). All structures were optimized at the restricted Hartree-Fock (RHF) level; improved single-point energies were then obtained from second-order Møller-Plesset perturbation (MP2) calculations at the RHF optimized geometries. To enable comparison with bidentate systems, a similar set of calculations was performed on ligand HN=CHCH$_2$N=CH$_2$ (**8**), which was again forced to have local C_s symmetry. All calculations were carried out using the GAMESS[99] and Gaussian[100] packages.

Table 5. Crystallographic data for **1b** and **4c**

Complex	**1b**	**4c**
Formula	$[C_{20}H_{30}N_3Pd]^+$ $[CF_3SO_3]^-$	$[C_{20}H_{14}N_3Pd]^+$ $[C_{32}H_{12}BF_{24}]^-$[a]
Molecular weight	567.97	1265.99[a]
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a [A]	13.521(6)	12.3298(14)
b [A]	8.791(6)	15.1874(19)
c [A]	21.507(7)	15.443(3)
α [°]	−	66.060(12)
β [°]	115.13(3)	71.132(11)
γ [°]	−	84.576(9)
V [A^3]	2314(2)	2498.8(7)
$D_{calcd.}$ [$g\cdot cm^{-3}$]	1.630(1)	1.6826(5)[a]
Z	4	2
F(000)	1160	1252[a]
μ [Mo-K_α] [$^{-1}$]	9.4	5.0
Crystal color	yellow	yellow
Crystal size [mm]	0.08×0.23×0.53	0.4×0.4×0.5
θ_{min}, θ_{max} [°]	1.05, 27.50	1.47, 27.50
Total, unique data	14444, 5316	13732, 11429
Final R[b]	0.0634 [3395 $F_o > 4\sigma(F_o)$]	0.0552 [9467 $F_o > 4\sigma(F_o)$]
Final $wR2$[c]	0.1628	0.1493
Goodness of fit	1.018	1.027
Min. and max. residual density [e A^{-3}]	−1.42, 1.23	−1.63, 1.11

[a] Without disordered solvent contribution. − [b] $R = \Sigma||F_o - F_c| / \Sigma F_o$. − [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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