Insertion Reactions Involving Palladium Complexes with Nitrogen Ligands. 2. Carbon monoxide and Alkene Insertion Reactions with Novel Palladium Compounds Containing Terdentate Ligands

Richard E. Rülke, Vincent E. Kaasjager, Dave Kliphuis, Cornelis J. Elsevier, Piet W. N. M. van Leeuwen, and Kees Vrieze*

Anorganisch Chemisch Laboratorium, J. H. van't Hoff Research Institute, Universiteit van Amsterdam, Nieuwe Achtergracht 166, NL 1018 WV Amsterdam, The Netherlands

Kees Goubitz

Laboratorium voor Kristallografie, Amsterdam Institute for Molecular Studies, Universiteit van Amsterdam, Nieuwe Achtergracht 166, NL 1018 WV Amsterdam, The Netherlands

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Neutral and ionic methylpalladium compounds containing trinitrogen ligands (N-N-N)-Pd(Me)(Y) (N-N-N = trinitrogen ligand; Y = Cl^-, $CF_3SO_3^-$, 4-Me-$C_6H_4SO_3^-$) have been synthesized and characterized by spectroscopic methods. The coordination mode of the trinitrogen ligand depends not only on the rigidity of the ligand but also on the solvent and on the anion Y. With the weakly coordinating ligands $CF_3SO_3^-$ and BF_4^- the trinitrogen ligands readily adopt a terdentate coordination mode, resulting in complexes of the type [(σ^3-N-N-N)Pd(Me)]Y. In methylchloropalladium compounds, the flexible trinitrogen ligands adopt a bidentate coordination mode, resulting in the complexes (σ^2-N-N-N)Pd(Me)(Cl), whereas the terdentate coordination mode has been found for rigid ligands, resulting in the ionic complexes [(σ^3-N-N-N)Pd(Me]Cl. Polar solvents, such as acetonitrile, stabilize the formation of ionic complexes. The methylpalladium compounds readily insert carbon monoxide, resulting in the facile formation of the acetylpalladium compounds (σ^2-N-N-N)-Pd(C(O)Me)(Cl) and [(σ^3-N-N-N)Pd(C(O)Me)]Y (Y = Cl^-, OTf^-), in which the coordination mode of the ligands remains unchanged. CO insertion half-lives of the methylpalladium compounds show that substituents adjacent to one nitrogen donor atom accelerate the insertion for both the neutral and the ionic complexes. Interestingly, the CO insertion half-life is not correlated to the rigidity of the trinitrogen ligand, since the compound [(terpy)-Pd(Me)]Cl, which contains the rigid ligand terpy, undergoes a faster carbon monoxide insertion than analogous complexes with the flexible ligands C_5H_4N-2-C(H)=N$(CH_2)_2C_5H_4N$. Alkene insertion has been tested by reacting the acetylpalladium compounds with norbornadiene (NBD). The NBD-inserted compounds contain the $C_7H_8C(O)CH_3$ moiety coordinating in an unprecedented monodentate σ-C fashion. Peculiarly, [(terpy)Pd(C(O)Me)]Cl not only undergoes NBD insertion but does so at a very high rate. On the basis of these findings a tentative mechanism is suggested.

Introduction

Intimate steps of homogeneously catalyzed reactions, in particular those mediated by organopalladium or -platinum compounds, have been investigated mainly by using monodentate and bidentate phosphorus and nitrogen ligands.[1−7] In our investigation of the intimate steps of the copolymerization of CO and alkenes, homogeneously catalyzed by palladium complexes,[8−10] we have employed bidentate ligands and we have found that the rate of CO and alkene insertion into the Pd−C

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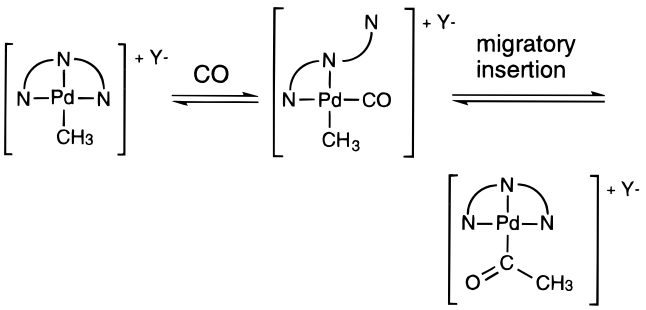
Scheme 1. Stabilization of a Free Coordination Site by Introducing a Third Donor Atom



bond of methylpalladium and acylpalladium complexes (L-L)Pd(R)(Y) (L-L = bidentate ligand; R = CH_3, C(O)-CH_3; Y = Cl, CF_3SO_3, BF_4, PF_6) decreases in the order N-N > P-P ≫ P-N.[9] Also, it was found that insertion is facilitated in the case of phosphorus ligands by flexible diphosphine ligands with a large bite angle, while in the case of nitrogen ligands rigid diimine ligands with a small bite angle appear to enhance the insertion rate.[8] Finally, CO and alkene insertions proceed much faster for complexes containing weakly coordinating ligands such as triflate,[8] due to the readily available coordination position for the incoming substrate.[11,12]

Since ionic palladium compounds having such a readily available coordination position may be sensitive to several side reactions (e.g. β-hydride abstraction, metathesis with halogenated solvents, and reductive-elimination reactions, resulting in Pd blackening), we thought of employing hemilabile trinitrogen ligands (Scheme 1).

Some theoretical[13] and kinetic[14] studies have been carried out on (di)phosphine-containing compounds to unravel the mechanism of CO and alkene insertion reactions. These studies appear to support the insertion mechanism proposed by Drent *et al.*,[11] which is based on the continuous creation of an open coordination position *cis* to the migrating group R, while the diphosphine ligand remains bonded to the palladium in a bidentate fashion. In two elegant studies, van Leeuwen *et al.* very recently published spectroscopic evidence for this mechanism by employing palladium and platinum

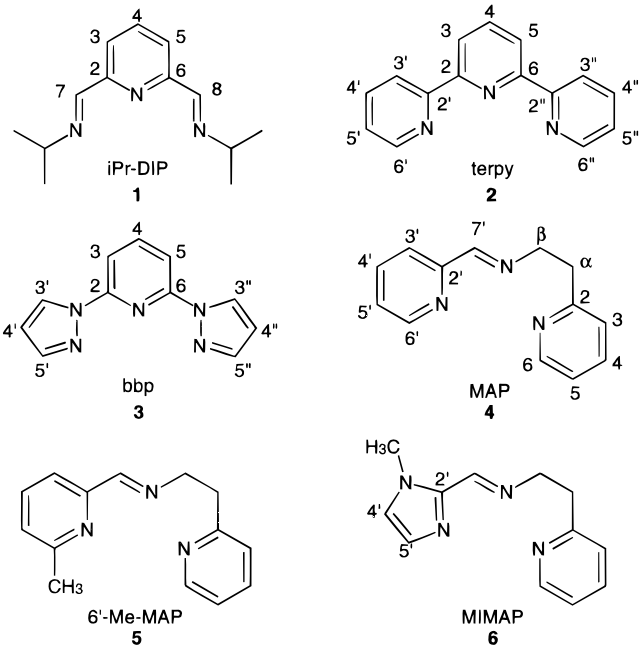


Figure 1. Structures and adopted numbering schemes of the ligands **1**−**6**. In the case of the complexes **1a**−**c**, H^7 indicates the coordinating imino nitrogen and H^8 the noncoordinating imino nitrogen.

complexes with nonsymmetric diphosphine and phosphine−phosphinite ligands.[14f,g] However, in the case of bidentate nitrogen ligands there are some indications that these nitrogen ligands may also be bonded in a monodentate fashion during some stages of the insertion reaction with involvement of transient three-coordinate T-shaped species.[15,16] At the same time, theoretical studies indicate that insertions may also proceed via five-coordinate species when using terdentate nitrogen ligands.[5c,17] We are interested in obtaining insight into the possible mechanisms by focusing on the steric and electronic properties of nitrogen ligands in general. In this study we consider the influence and electronic properties of trinitrogen ligands on the insertion of CO and alkenes into the Pd−C bonds of methyl- and acetylpalladium compounds.

We have used the ligands **1**−**6**, which have varying flexibilities and different electron-donating properties (Figure 1). The ligands **1**−**6** can be considered as functional derivatives of bidentate ligands such as bpy and R-PyCa (R-PyCa = pyridyl-2-(R)-carbaldimine; R = alkyl, aryl),[18] which have recently been used in CO and alkene insertion reactions involving methyl- and acylpalladium compounds,[5,19] including trinitrogen ligands with a diaminopyridyl donor set.[5] Novel methyl- and acetylpalladium compounds containing **1**−**6** have been synthesized, and the insertion of CO and of alkenes, respectively, has been studied by spectroscopic methods. Preliminary results involving **1** and **2**[20] and also the complex coordination chemistry of the neutral

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Table 1. Numbering of the Organopalladium Compounds Containing Ligands 1−6

L		Y	R: CH_3	R: $C(O)CH_3$	R: $C_7H_8C(O)CH_3$
1	i-Pr-DIP	Cl	**1a**	**1b**	**1c**
1	iPr-DIP	OTf	**11a**	**11b**	
2	terpy	Cl	**2a**	**2b**	**2c**
3	bbp	OTos	**13a**		
4	MAP	Cl	**4a**	**4b**	**4c**
4	MAP	OTf	**14a**	**14b**	**14c**
5	MeMAP	Cl	**5a**	**5b**	**5c**
5	MeMAP	OTf	**15a**	**15b**	**15c**
6	MIMAP	Cl	**6a**	**6b**	**6c**
6	MIMAP	OTf	**16a**		

methylchloropalladium complexes with nonsymmetric ligands **4** and **5**[21] have been reported, and in this article we publish the results of our investigations involving **1**−**6** in full detail.

Results

Synthesis. The ligands 2,6-bis((isopropylimino)-methyl)pyridine (iPr-DIP, **1**), 2-(2-((2′-pyridylmethylene)amino)ethyl)pyridine (MAP, **4**), 2-(2-(((6′-methyl-2′-pyridyl)methylene)amino)ethyl)pyridine (MeMAP, **5**) and 2-(2-(((1′-methyl-2′-imidazolyl)methylene)amino)-ethyl)pyridine (MIMAP, **6**) have been prepared by literature methods,[20−22] while 2,6-bis(*N*-pyrazolyl)pyridine (bbp, **3**) has been prepared according to the method of Goldsby.[23]

The numbering of the trinitrogen ligands **1**−**6** in the various neutral and ionic methyl-, acetyl-, and (6-acetyl-[2.2.1]bicyclohept-1-en-5-yl)palladium complexes (which will be denoted as Pd−$C_7H_8C(O)CH_3$ in the course of this article) are presented in Table 1.

The methylchloropalladium compounds **1a**, **2a**, and **4a**−**6a** have been prepared by substitution of the diene in (COD)Pd(Me)(Cl)[21,24] (COD = 1,5-cyclooctadiene) by the ligands **1**, **2** (in CH_3CN), **4**, **5**, and **6** (in CH_2Cl_2 or $CHCl_3$) at room temperature, respectively. The same procedure performed with **3** in several solvents did not lead to a well-defined palladium complex.

The methylpalladium triflate compounds **11a** and **14a**−**16a** were prepared by reaction of the chloro compounds **1a** and **4a**−**6a** with silver triflate in acetonitrile.[21] Compound **13a** was prepared by substitution of the chloride of (COD)Pd(CH_3)(Cl) in dichloromethane by the weakly coordinating tosylate prior to the addition of the ligand and subsequent substitution of COD by **3**.

The acetylpalladium compounds **1b**−**16b** have been prepared by treatment of the methylpalladium compounds **1a**−**16a** in solution under 1.5 bar of carbon monoxide at room temperature.[8] In order to determine the relative CO insertion rates, CO insertion was performed with a gas buret (see Experimental Section).

Alkene insertion was tested by the addition of 1.1 equiv of the alkene (ethene, styrene, methyl acrylate, norbornene, norbornadiene, and dicyclopentadiene) to an *in situ* formed solution of the acetylpalladium complexes **1b**−**16b** in tha NMR tube and was followed by ^{1}H NMR and IR spectroscopy.

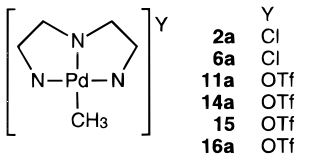
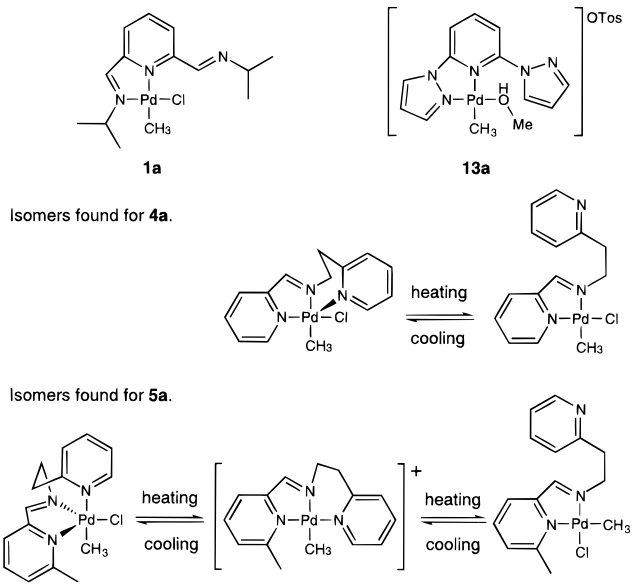


Figure 2. Structures of the ionic methylpalladium compounds **2a**, **6a**, **11a**, and **14a**−**16a**.

Scheme 2. Structure of Compounds 1a and 13a and of the Coordination Isomers Observed with ^{1}H NMR for 4a and 5a between 193 and 363 K in Chloroform and Dichloromethane[21]



It should be noted that, unfortunately, elemental analysis of the compounds was only possible for **1a** and **2a**. In the case of the methylpalladium compounds **4a**−**6a** this was not possible because these compounds are oils which contain small amounts of solvents. The acetylpalladium compounds **1b**−**16b** and the Pd−$C_7H_8C(O)CH_3$ compounds **1c**−**15c** were stable for only a few hours and therefore did not allow out-of-house elemental analysis.

Methylpalladium Compounds. Upon addition of the trinitrogen ligand to the Pd(CH_3)(Cl) moiety, the neutral complexes (NNN)Pd(CH_3)(Cl) (**1a**, **4a**, and **5a**; see Scheme 2)—with the ligand coordination in a bidentate fashion—and ionic complexes [(NNN)Pd(CH_3)]Cl (**2a**, **6a**, **11a**−**16a**; see Figure 2)—with a terdentate ligand—have been obtained. Upon treatment with silver trifluoromethanesulfonate, the neutral complexes were converted into ionic ones, except for **13a**, which has bbp coordinated in a bidentate fashion. The presence of terdentate coordination apparently depends on the rigidity of the trinitrogen ligand (**2a**), on the coordination properties of the anionic ligand Y (**11a**−**16a**), and on the coordination properties of the trinitrogen ligand (**6a**) and offers no surprises, although in the last case the terdentate coordination of MIMAP in **6a** was quite unexpected.

In the case of **1a** and **13a** the σ^2-coordinated ligands show dynamic behavior on the ^{1}H NMR time scale, indicating a rapid exchange of the free and the coordi-

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Table 2. Conductometric Data for 6a and 14a−16a

compd	solvent	conductivity, μS M^{-1} (T,K)
6a	$CHCl_3$	29 (233); 35 (293); 43 (315)
6a	CH_3CN	22 700 (233); 48 500 (295); 5800 (319)
16a	$CHCl_3$	52 (233); 98 (293); 106 (315)
16a	CH_3CN	29 400 (232); 62 100 (298); 70 700 (314)
14a[a]	CH_3CN	51 400 (240); 91 100 (295); 111 200 (317)
15a[a]	CH_3CN	44 550 (233); 60 600 (267); 87 150 (293)

[a] For comparison.

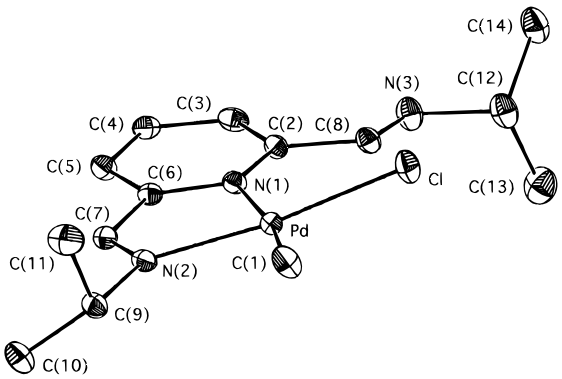

Figure 3. ORTEP plot (drawn at the 50% probability level) and adopted numbering scheme of (σ^2-iPr-DIP)Pd(CH_3)(Cl) (**1a**).

nated side arms on palladium, as expected for symmetric trinitrogen ligands. A fluxional behavior was also observed for **4a** and **5a** involving the flexible ethylpyridyl group.[21]

Whereas **1a** and **4a**−**6a** readily dissolve in CH_2Cl_2, $CHCl_3$, and CH_3CN, **13a** is only soluble in methanol and DMSO and **2a** only in methanol, ethanol, and water. The structure of **13a** (Scheme 2) is observed in methanol, while in DMSO **13a** disproportionates into **3** and a stable methylpalladium tosylate complex solvated by DMSO.

The coordination mode of the ligand in **6a** was determined by investigation of the ^{1}H NMR spectrum (especially the resonances of the CH_2CH_2 moiety) in combination with conductometry (Table 2). Whereas **4a** and **5a** have the trinitrogen ligands coordinating predominantly in a bidentate fashion (see scheme 2),[21] in **6a** the (quite similar) ligand coordinates both in nonpolar chloroform and in polar acetonitrile in a static terdentate fashion between 233 and 315 K, resulting in the ionic methylpalladium compound [(σ^3-MIMAP)-Pd(CH_3)]Cl (Figure 2). Reaction of **6a** with silver triflate leads to the formation of the isostructural complex [(σ^3-MIMAP)Pd(CH_3)]OTf (**16a**). Accordingly, ionic **11a**, **14a**, and **15a** were obtained when the coordinating chloride ligands in **1a**, **4a**, and **5a**, respectively, were placed in acetonitrile by the weakly coordinating ligand triflate (Figure 2). Unfortunately, **11a** decomposes within a few hours in solution and in 1 day as the solid without recovery of **1**. Treatment of **2a** with silver triflate also gave the triflate analogue **12a**. However, the salmon-colored compound is insoluble in any type of solvent tested. In contrast to **11a**, the structural analogues **14a**−**16a** are stable both in solution and as a solid.

Molecular Structure of (σ^2-iPr-DIP)Pd(CH_3)(Cl) (1a). The solid-state structure of **1a** with the adopted numbering scheme is shown in Figure 3. Tables 3 and 4 contain the bond distances and the bond angles involving the non-hydrogen atoms of **1a**, respectively. The crystal and refinement data for **1a** are listed in Table 8. The molecular structure of **1a** shows **1** coordinating in a bidentate fashion. The noncoordinating imino group of **1a** is coplanar with the coordinating part of the ligand.

Table 3. Bond Distances (Å) for the Non-Hydrogen Atoms of 1a (with Esd's in Parentheses)

Pd−C(1)	2.01(1)	N(1)−C(6)	1.340(9)
Pd−Cl	2.324(3)	N(2)−C(7)	1.27(1)
Pd−N(1)	2.270(7)	N(2)−C(9)	1.48(1)
Pd−N(2)	2.065(6)	N(3)−C(8)	1.26(1)
N1−C(2)	1.34(1)	C(6)−C(7)	1.46(1)
C(2)−C(3)	1.41(1)	N(3)−C(12)	1.47(1)
C(2)−C(8)	1.47(1)	C(9)−C(10)	1.52(1)
C(3)−C(4)	1.37(1)	C(9)−C(11)	1.51(1)
C(4)−C(5)	1.38(1)	C(12)−C(13)	1.54(1)
C(5)−C(6)	1.38(1)	C(12)−C(14)	1.51(2)

Table 4. Bond Angles (deg) for the Non-Hydrogen Atoms of 1a (with Esd's in Parentheses)

C(1)−Pd−Cl	85.1(3)	C(3)−C(4)−C(5)	119.0(9)
Cl−Pd−N(1)	102.2(2)	C(4)−C(5)−C(6)	118.4(7)
N(1)−Pd−N(2)	78.2(3)	N(1)−C(6)−C(5)	124.0(7)
N(2)−Pd−C(1)	94.2(3)	N(1)−C(6)−C(7)	117.5(8)
Pd−N(1)−C(2)	134.8(5)	C(5)−C(6)−C(7)	118.5(7)
Pd−N(1)−C(6)	107.6(5)	C(8)−N(3)−C(12)	118.9(9)
C(2)−N(1)−C(6)	117.4(7)	N(2)−C(7)−C(6)	121.1(7)
Pd−N(2)−C(7)	114.9(5)	N(3)−C(8)−C(2)	120.2(9)
Pd−N(2)−C(9)	127.2(6)	N(2)−C(9)−C(10)	115.3(8)
C(7)−N(2)−C(9)	117.9(7)	N(2)−C(9)−C(11)	108.5(7)
N(1)−C(2)−C(3)	121.8(7)	C(10)−C(9)−C(11)	111.2(8)
N(1)−C(2)−C(8)	118.7(8)	N(3)−C(12)−C(13)	109.0(7)
C(3)−C(2)−C(8)	119.3(7)	N(3)−C(12)−C(14)	109(1)
C(2)−C(3)−C(4)	119.1(8)	C(13)−C(12)−C(14)	113.0(9)

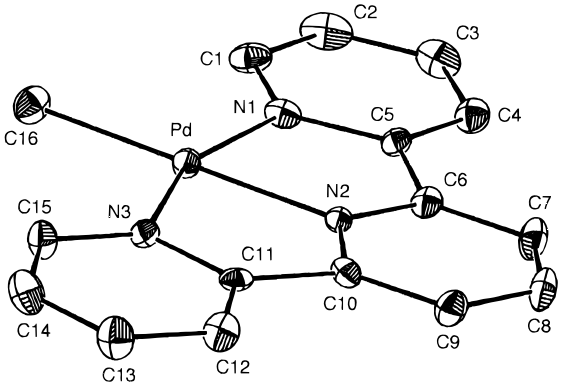

Figure 4. ORTEP plot (drawn at the 50% probability level) and adopted numbering scheme of the cationic [(σ^3-terpy)Pd(CH_3)]$^+$ moiety of **2a**.

The configuration of **1a**, with the two strongest σ-donors, in this case the methyl and the imino groups,[25] *cis*, agrees with literature reports of related compounds.[19,26] The bond distances and bond angles are within the range found for analogous R-PyCa complexes.[19]

Molecular Structure of [(σ^3-terpy)Pd(CH_3)]$^+$[(Cl)-(H_2O)$_2$]$^-$ (2a). The molecular structure of **2a**, with the terpy ligand coordinating in a terdentate fashion, is shown in Figure 4. The bond distances and the bond angles of the non-hydrogen atoms of **2a** are listed in Tables 5 and 6, respectively. The crystal and refinement data for **2a** are listed in Table 8.

(25) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(26) (a) Albano, V. G.; Braga, D.; de Felice, V.; Panunzi, A.; Vitagliano, A. *Organometallics* **1987**, *5*, 517. (b) de Felice, V.; Ganis, P.; Vitagliano, A.; Valle, G. *Inorg. Chim. Acta* **1988**, *144*, 57.

Table 5. Bond Distances (Å) for the Non-Hydrogen Atoms of 2a (with Esd's in Parentheses)

Pd−C(16)	2.04(1)	C(1)−C(2)	1.381(18)
Pd−N(1)	2.048(9)	C(3)−C(4)	1.358(18)
Pd−N(2)	2.007(7)	C(4)−C(5)	1.382(15)
Pd−N(3)	2.057(8)	C(5)−C(6)	1.489(15)
C(1)−N(1)	1.359(14)	C(5)−N(1)	1.387(13)
C(2)−C(3)	1.370(18)	C(6)−C(7)	1.380(16)
C(10)−N(2)	1.335(13)	C(10)−C(11)	1.486(14)
C(11)−C(12)	1.391(16)	C(11)−N(3)	1.375(13)
C(6)−N(2)	1.330(13)	C(12)−C(13)	1.375(16)
C(7)−C(8)	1.399(18)	C(13)−C(14)	1.356(18)
C(8)−C(9)	1.361(16)	C(14)−C(15)	1.371(17)
C(9)−C(10)	1.384(15)	C(15)−N(3)	1.341(13)

Table 6. Bond Angles (deg) for the Non-Hydrogen Atoms of 2a (with Esd's in Parentheses)

C(16)−Pd−N(1)	100.6(4)	C(9)−C(10)−N(2)	119.5(9)
C(16)−Pd−N(3)	99.8(4)	C(11)−C(10)−N(2)	112.7(8)
N(1)−Pd−N(2)	79.8(3)	C(10)−C(11)−C(12)	123.8(9)
N(2)−Pd−N(3)	79.8(3)	C(10)−C(11)−N(3)	116.2(9)
C(2)−C(1)−N(1)	122(1)	C(12)−C(11)−N(3)	119.9(9)
C(1)−C(2)−C(3)	120(1)	C(11)−C(12)−C(13)	120(1)
C(2)−C(3)−C(4)	119(1)	C(12)−C(13)−C(14)	119(1)
C(3)−C(4)−C(5)	121(1)	C(13)−C(14)−C(15)	120(1)
C(4)−C(5)−C(6)	124.6(9)	C(14)−C(15)−N(3)	122(1)
C(4)−C(5)−N(1)	120.6(10)	Pd−N(1)−C(1)	128.8(7)
C(6)−C(5)−N(1)	114.8(8)	Pd−N(1)−C(5)	113.7(7)
C(5)−C(6)−C(7)	126.9(10)	C(1)−N(1)−C(5)	117.5(9)
C(5)−C(6)−N(2)	113.5(9)	Pd−N(2)−C(6)	118.1(7)
C(7)−C(6)−N(2)	119.6( )	Pd−N(2)−C(10)	118.3(6)
C(6)−C(7)−C(8)	117(1)	C(6)−N(2)−C(10)	123.5(8)
C(7)−C(8)−C(9)	122(1)	Pd−N(3)−C(11)	113.0(6)
C(8)−C(9)−C(10)	118(1)	Pd−N(3)−C(15)	128.4(7)
C(9)−C(10)−C(11)	127.7(10)	C(11)−N(3)−C(15)	118.6(9)

All bond distances and bond angles are within the range normally observed for comparable structural subunits such as the $[(terpy)Pd(Cl)]^+$ cation.[27] The narrow angle N(1)−Pd−N(3) of 159.7(3)° in combination with the short Pd−N(2) distance of 2.007(7) Å is normal for terpy complexes[27] and has also been reported for manganese[28a] and rhodium[28b,c] complexes with comparable symmetric trinitrogen ligands.

CO Insertion Reactions. Treatment of the methylpalladium compounds **1a**−**16a** in solution with CO for 5−30 min resulted in the quantitative formation of the corresponding acetylpalladium compounds **1b**−**16b**, except compound **13a**, which did not react at all with CO. Since the structural features and the reactivities of **6a**, **b** and **16a**, **b** proved to be similar, only the behavior of **6a** will be discussed in the course of this article. The products **1b**−**15b** are stable in solution for a few hours, except **11b**, which is stable only for a few minutes. The formation of the acetyl group is revealed by the dissappearing Pd−CH_3 resonance at *ca.* 1.0 ppm and by the growing Pd−C(O)CH_3 resonance at *ca.* 2.3 ppm in the ^{1}H NMR spectrum and by the growing C═O stretching vibration at *ca.* 1600 cm^{-1} in the IR spectrum.

With a few exceptions the configuration of the ligands around the palladium atom of the acetylpalladium compounds **1b**−**16b** proved to be identical with that of the parent compounds **1a**−**16a**. The dynamic behavior observed for **1a** is not present for **1b**. According to the

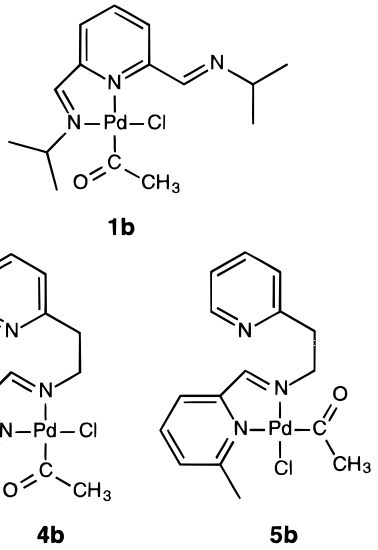

Figure 5. Structures of the neutral acetylpalladium complexes **1b**, **4b**, and **5b**.

Table 7. CO Insertion Half-lives (minutes:seconds) and Infrared Carbonyl Stretching Frequencies (cm^{-1}) Determined for Compounds 1a−15a[a]

compd	solvent	CO insertion half-life	IR
1a	CH_2Cl_2	6:00 (±0:30)	1712
5a	CH_2Cl_2	8:15 (±0:30)	1708
$[(bpy)Pd(CH_3)]OTf$[19]	CH_3CN	8:30 (±0:30)	1690
2a	C_2H_5OH	10:00 (±0:30)	1682
15a	CH_3CN	12:30 (±0:30)	1698
6a	CH_2Cl_2	22:30 (±0:30)	1696
11a	CH_3CN	25:00 (±0:30)	1700
$(bpy)Pd(CH_3)(Cl)$[19]	CH_2Cl_2	28:30 (±0:30)	1690
4a	CH_2Cl_2	32:15 (±0:30)	1694
14a	CH_3CN	39:30 (±0:30)	1690

[a] Conditions: [Pd] = 40 mM, P(CO) = 2 bar, T = 293 K.

^{1}H NMR spectra of **1b** the ligand is still nonsymmetric, indicating that the bidentate coordination mode of **1** is retained (Figure 5). Whereas the methylpalladium complexes **4a** and **5a** display fluxionality on the NMR time scale due to isomerization (Scheme 2), the acetylchloropalladium analogues **4b** and **5b** have sharp resonances between 223 and 323 K in $CDCl_3$ and no signs of other isomeric structures have been observed, while **4b** and **5b** occur in the same (bidentate) configuration as **4a** and **5a**, *trans* for **4b** and *cis* for **5b** (Figure 5). As expected, the ligands in **2b**, **6b**, **11b**, **14b**, and **15b** coordinate in a static terdentate fashion, analogous to the parent complexes **2a**, **6a**, **11a**,**14a**, and **15a**, respectively.

The CO insertion half-lives are presented in Table 7. For comparison, the CO insertino half-lives determined for $(bpy)Pd(CH_3)(Cl)$ and $[(bpy)Pd(CH_3)]OTf$,[19] two complexes used in model studies of CO/alkene copolymerization reactions in the literature,[5,6] have been included.

Alkene Insertion Reactions. Ethene, methyl acrylate, and styrene do not insert into the Pd−C bond of the acetylpalladium compounds **1b**−**15b**. However, alkene insertion does take place for norbornene (NB), dicyclopentadiene (DCPD), and norbornadiene (NBD). Because of the complex NMR spectra, the products obtained from the insertion of NB and DCPD into the Pd−C bonds of the acetylpalladium compounds were difficult to characterize. For this reason, only the results of NBD insertion will be discussed here.

(27) Intille, G. M.; Pfluger, C. E.; Baker, W. A. *J. Cryst. Mol. Struct.* **1973**, *3*, 47.

(28) (a) Stor, G. J.; van der Vis, M.; Stufkens, D. J.; Oskam, A.; Fraanje, J.; Goubitz, K. *J. Organomet. Chem.* **1994**, *482*, 15. (b) Nishyama, H.; Kondo, M.; Nahamura, T.; Itoh, K. *Organometallics* **1991**, *9*, 500. (c) Haarman, H. F.; Vrieze, K. To be submitted for publication.

Norbornadiene insertion proceeds very quickly for all acetylpalladium compounds tested, but the products **1c**−**15c** could only be characterized by spectroscopic methods, and none could be isolated because of degradation reactions. Only for compounds **1c**, **2c**, **4c**, and **6c** does the insertion of NBD lead to the formation of one, well-defined insertion product. In contrast to the CO insertion rates (*vide supra*) the NBD insertion rates as determined with ^{1}H NMR differ only little between the compounds **1b**−**15b**, neutral or ionic, and insertion is completed within 30 min, which is only slightly slower than found for the neutral complexes (Ar-BIAN)Pd(C(O)Me)(Cl) (Ar-BIAN = bis(arylimino)acenaphthene)[8] but faster than for the analogous neutral bpy complex is (N-N)Pd(C(O)Me)(Cl) (N-N = bpy, 4,7-diphenyl-1,10-phenanthroline).[15] The ionic compounds [(N-N)Pd(C(O)Me)(S)]Y (N-N = bidentate nitrogen ligand; S = solvent; Y = weakly coordinating ligand), however, undergo NBD insertion at a much higher rate.[5,8]

The organic product which was formed after the degradation reaction of **1c**−**15c** was isolated and analyzed with ^{1}H NMR and GC−MS (see Experimental Section). Expectedly, the product proved to be 2-acetyl-[2.2.1]bicyclohepta-2,5-diene.

Insertion of NBD into the Pd−C bond of the above-mentioned acetylpalladium complexes was easily monitored by ^{1}H NMR spectroscopy since (i) the olefinic resonance of free NBD vanishes upon insertion, while simultaneously a new set of resonances belonging to the remaining olefinic hydrogens grows (ii) the C_7H_8 moiety of the inserted NBD becomes nonsymmetric, and (iii) the acetyl resonance is replaced by a new acetyl resonance, which is found at a higher chemical shift (see Experimental Section). The expected *syn-exo* addition of NBD can be easily distinguished by the 6−9 Hz coupling constants of the former double-bond hydrogens (10−15 Hz for *syn-endo* addition and 1−2 Hz for *anti* addition).[7] In the literature, only examples of *syn* addition of the Pd−C bond on the *exo* face of the NBD double bond have been reported.[5,7−9]

In addition NBD insertion may lead to two different products, a Pd−$C_7H_8C(O)CH_3$, σ-C-bonded compound and a Pd−$C_7H_8C(O)CH_3$ compound as a C−O chelate (Scheme 3). Until now, only bidentate coordination as a C−O chelate has been observed,[5−9] while monodentate σ-C coordination has only been observed for the acylpalladium compounds Pd−$C(O)C_7H_8C(O)CH_3$, obtained after carbonylation of the Pd−$C_7H_8C(O)CH_3$ compounds.[5,6,8] The formation of a C−O chelate is easily derived from (i) the CO stretching vibration in the IR spectrum at *ca*. 1600 cm^{-1}, (ii) the chemical shifts of the remaining olefinic hydrogens in the ^{1}H NMR spectrum, which are *ca*. 0.5 ppm apart, and (iii) the CO resonance at *ca*. 240 ppm in the ^{13}C NMR spectrum. In contrast, the monodentate $C_7H_8C(O)CH_3$, σ-C coordination mode is evident from (i) the CO vibration in the IR spectrum at *ca*. 1700 cm^{-1}, (ii) the chemical shifts of the remaining olefinic hydrogens in the ^{1}H NMR spectrum, which are very close together or have even coincided to a multiplet, and (iii) the CO resonance at 210−230 ppm in the ^{13}C NMR spectrum.

Surprisingly, the spectral data of **1c**, **2c**, **4c**, and **6c** clearly indicate a monodentate σ-C coordination mode of the $C_7H_8C(O)CH_3$ moiety; the olefinic hydrogens are very close together in the ^{1}H NMR spectrum (*e.g.* 5.95 and 6.02 ppm for **4c**), and in the IR spectrum CO stretching frequencies of 1700−1712 cm^{-1} are visible.

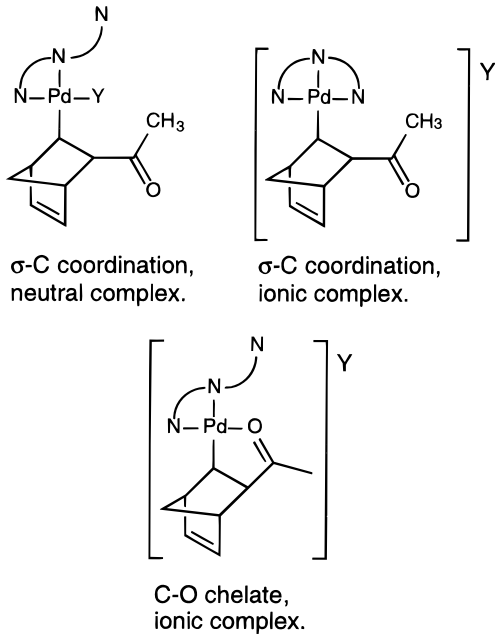

Figure 6. Possible isomers of Pd−$C_7H_8C(O)Ch_3$ compounds containing trinitrogen ligands.

Insertion of NBD also proceeds for **5b**, **14b**, and **15b**, as judged from the vanishing NBD resonances in the ^{1}H NMR and the simultaneously growing resonances at *ca*. 6 ppm, which are the new olefinic hydrogens in the $C_7H_8C(O)CH_3$ moiety. However, these new signals represent more than one NBD-insertion product, possibly comprising several isomers which could not be characterized in detail (Figure 6).

Discussion

Stability. Whereas the methylpalladium compounds **1a**−**16a** are fairly stable (between 1 day and years), except for **11a**, the corresponding acetylpalladium and Pd−$C_7H_8C(O)CH_3$ compounds only have a limited stability (a few hours). Such an instability is not uncommon for the acetylpalladium complexes. They easily deinsert CO and are also prone to hydrolysis. Only in the case of neutral acetylpalladium complexes with diphosphine ligands, bpy, or tmeda have acetylpalladium compounds been reported that are stable for months.[5,7,9]

The elimination product 2-acetyl[2.2.1]bicyclohepta-2,5−diene is rapidly formed from the complexes **1c**−**15c**, while complexes containing bidentate nitrogen or phosphorus ligands usually give very stable NBD-insertion products.[5−9] The known NBD-inserted complexes with diphosphine ligands, bpy, or tmeda are fairly stable, due to the C−O chelate which prevents degradation reactions.[5,7−9] Most probably, the degradation process of **1c**−**15c** proceeds similarly to the base-assisted process published by Chiusoli *et al*., causing both the β-elimination and the *exo*−*endo* isomerization of Pd−$C_7H_8C(O)CH_3$ complexes (see Scheme 3).[29]

Coordination Chemistry. The observed strong tendency of **6** to coordinate in a terdentate fashion is

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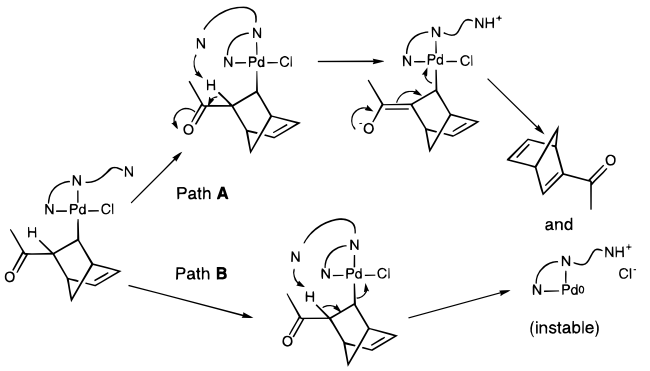
Scheme 3. Mechanism Rationalizing the Degradation of Pd($C_7H_8C(O)CH_3$) Compounds, Intramolecularly Assisted by the Noncoordinating Nitrogen Donor Atom



rather unexpected, since the closely related ligands **4** and **5** coordinate in a bidentate fashion in the case of methylchloropalladium compounds. It is clear that for flexible trinitrogen ligands terdentate coordination involves a very subtle, not yet fully understood balance of donating and accepting properties of *trans*-positioned atoms, most probably in combination with steric interactions.

The poor coordinating properties of 2,6-bis(*N*-pyrazolyl)pyridine (**3**) for methylpalladium compounds is interesting, since **3** resembles the strongly coordinating ligands **1** and **2**. This behavior must be caused by the poor coordinating properties of the pyrazolyl groups.[30] Although **3** coordinates in methanol as a bidentate ligand in **3a**, the ligand was completely substituted by using DMSO as solvent. The fact that **3** failed to react with (COD)Pd(CH_3)(Cl) and (COD)$PdCl_2$ may also be attributed to its poor coordinating properties.

Carbon Monoxide Insertion Reactions. The trends of the CO insertion half-lives (Table 7) are similar to results recently obtained for methylpalladium complexes with bidentate nitrogen ligands.[19] First, relatively little difference is observed between the half-lives of the neutral and the ionic compounds. However, this might be due to the difference in solvents, since the neutral complexes have been measured in CH_2Cl_2 and the ionic ones in CH_3CN. The fact that acetonitrile may act as a ligand itself may rationalize the unexpectedly long insertion half-lives of the ionic methylpalladium complexes.

Second, the methyl substituent in **5** clearly accelerates CO insertion, since compounds **5a** and **15a** have much shorter CO insertion half-lives than **4a** and **14a**. This striking accelerating ortho effect has also been observed recently for methylpalladium complexes containing bidentate nitrogen ligands.[19] The fast CO insertion observed for **1a** can now be understood, since in **1a** the ligand may be regarded as a bidentate nitrogen ligand having a bulky substituent (i.e. the −C(H)═N-iPr group) at the 6-position. Although the implications of having bulky substituents close to one N-donor atom are not completely understood as yet, and elaborate kinetic studies are required to unravel their effects the best fitting mechanism seems to be the one that involves dissociation of the nitrogen donor atom facilitated by a bulky substituent as the key step in the CO insertion reaction.[31−34]

We now turn our attention to the CO insertion half-life of **2a**, which is unexpectedly short in light of the rigidity of **2**. Even NBD, which is much bulkier than CO, inserts rapidly into the Pd−C bond of **2b**. Unfortunately, the insertion of CO had to be measured—for reasons of solubility—in ethanol, which may make comparison less useful. Replacement of one outer pyridyl group by a CO molecule in itself does not yet explain the fast migration. However, terpy—now coordinating as a bidentate ligand—could be regarded as bpy with a bulky substituent close to one nitrogen donor atom, which rationalizes a very fast CO insertion rate for **2a**.

Alkene Insertion Reactions. The fact that the acetylpalladium compounds **1b**−**15b** failed to react with unstrained alkenes such as ethene, styrene, and methyl acrylate is not very surprising, since they lack a readily available coordination position; insertion of unstrained alkenes has until now only been observed for ionic complexes with a free coordination position, [(L-L)Pd(S)($C(O)CH_3$)]Y (L-L = bidentate ligand; S = solvent; Y^- = weakly coordinating ligand).[5−9] If one considers the reactivity of the ionic compounds **6b**−**15b** toward alkene insertion, it is clear that, although they are ionic compounds, **6b**−**15b** react rather as neutral compounds, due to the fact that these ionic compounds do not have a readily available coordination position.

The observation that the $C_7H_8C(O)CH_3$ moiety in **1c**, **2c**, **4c**, and **6c** coordinates in a monodentate σ-C fashion is very surprising, since these are the first examples of this coordination mode for this moiety on palladium. However, there are strong indications of monodentate coordination of the $C_7H_8C(O)CH_3$ moiety for the *neutral* palladium compounds (N-N)Pd($C_7H_8C(O)CH_3$)(Cl) (N-N = 2,2-bipyridine, 4,7-diphenyl-1,10-phenanthroline, and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline),[15] while Brookhart has recently observed similar transient complexes with *ionic* (bpy)palladium compounds.[6]

The large influence of substituents close to one N-donor atom observed for the CO insertion into palladium−methyl bonds (*vide supra*) was not observed for the insertion of NBD into palladium−acetyl bonds. Most probably this is caused by the fact that only 1 equiv of the alkene was used, while a large excess of CO was used in the carbonylation reaction (pseudo-first-order kinetics). Still, the very facile formation of **2c** via the insertion of NBD into the Pd−C bond of **2b** is astounding when one considers the steric bulk of NBD and the rigidity of terpy. Possibly, both CO insertion and alkene insertion proceed via the same mechanism, although it might well be that CO and alkene insertion reactions proceed partly via different intermediates. For instance, it is known that five-coordinate palladium complexes with alkenes have a trigonal-pyramidal (TBP) geometry, while those with CO have a geometry between TBP and square pyramidal.[35]

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(33) Fanizzi, F. P.; Intille, F. P.; Maresca, L.; Natile, F.; Lanfranchi, M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1991**, 1007.

(34) Albano, V. G.; Castellari, C.; Cucciolito, M. E.; Panunzi, A.; Vitagliano, A. *Organometallics* **1990**, *9*, 1269.

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Conclusions

Although an increased stability of alkylpalladium compounds and acyl species was expected upon the introduction of a third nitrogen-donor atom in the spectator ligand, the opposite effect has been observed. Apparently, the third donor atom does not sufficiently stabilize palladium compounds by occupation of an open coordination site on the metal. Instead, the third donor atom may serve as a shuttle for hydrolysis or as an intramolecular base, accelerating the β-hydride elimination reaction.

An interesting and unprecedented σ-C monodentate coordination mode of the $C_7H_8C(O)CH_3$ moiety has been observed for the (6-acetyl[2.2.1]bicyclohept-1-en-5-yl)-chloropalladium complexes. This coordination mode may be attributed to the presence of highly coordinating donor atoms (third nitrogen or chloride ligand).

Experimental Section

Materials and Apparatus. All manipulations were carried out under an atmosphere of purified dry nitrogen by using standard Schlenk techniques. Solvents were dried and stored under nitrogen. All starting chemicals were used as commercially obtained, including terpy (**2**). The starting compounds 1-methylimidazolyl-2-carboxaldehyde,[36] (COD)Pd(CH_3)(Cl),[21,24] and ligands **1**, **3**,[23] and **6**[21,22] and the compounds **4a**, **5a**, **14a**, and **15a**[21] have been prepared according to the methods given in the literature.

^{1}H NMR spectra were recorded on Bruker AC 100 and AMX 300 spectrometers and IR spectra on Perkin-Elmer PE 283 and Bio-Rad FTS-7 spectrophotometers; mass spectra were obtained on a Varian MAT 711 doublet-focusing mass spectrometer fitted with a 10 μm tungsten FD emitter. GC−MS was performed on 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). Elemental analyses were carried out by the Elemental Analysis section of the ITC/TNO, Zeist, The Netherlands.

Ligands. The numbering schemes of the ligands are presented in Figure 1.

1: ^{1}H NMR ($CDCl_3$) δ 1.20 (d, iPr), 3.58 (septet, iPr), 7.89 (d, H^3 and H^5), 7.96 (t, H^4), 8.42 (s, H^7 and H^8).

3: ^{1}H NMR ($CDCl_3$) δ 6.51 (dd, 2H, $H^{4'}$ and $H^{4''}$), 7.77 (d, 2H, $H^{5'}$ and $H^{5''}$), 7.90 (m, 3H, H^3, H^4, and H^5), 8.58 (d, 2H, $H^{3'}$ and $H^{3''}$).

6: ^{1}H NMR ($CDCl_3$) δ 3.15 (t, H^α), 3.90 (s, $H^{6'}$), 3.99 (dt, H^β), 6.89 (d, $H^{5'}$), 7.07 (d, $H^{4'}$), 7.11 (ddd, H^5), 7.16 (d, H^3), 7.56 (dt, H^4), 8.26 (s, $H^{7'}$), 8.54 (d, H^6).

Methylpalladium Compounds. (σ^2-iPr-DIP)Pd(CH_3)(Cl) (1a). A solution of 265 mg (1 mmol) of (COD)Pd(Me)(Cl) and 250 μL (1 mmol) of **1** in acetonitrile was stirred for 5 min at 20 °C. Dark red crystals of **1a** formed immediately after cooling the solution to −10 °C. After these crystals were decanted, they were washed with diethyl ether to give 282 mg (0.75 mmol; 75%) of dark red crystals. ^{1}H NMR ($CDCl_3$): hydrocarbyl ligand, δ 1.17 (s, Me); nitrogen ligand, δ 1.24 (d, 1Pr), 1.39 (d, iPr), 3.82 (sept, iPr), 4.18 (sept, iPr), 7.75 (d, H^5), 8.01 (t, H^4), 8.26 (d, H^3), 8.45 (s, H^7), 9.62 (s, H^8). Anal. Calcd for $C_{14}H_{22}ClN_3Pd$: C, 44.93; H, 5.93; N, 11.23. Found: C, 44.65; H, 5.94; N, 11.12. Mp: 161 °C dec. MS: correct isotope pattern at *m/z* 358 $[M - Cl]^{\bullet+}$ and at *m/z* 373 $[M]^{\bullet+}$ for ^{106}Pd and ^{35}Cl.

2a. The synthesis was carried out similar by that of **1a**, except that **2a** precipitated instantaneously at room temperature. Yield: 96% of pale yellow **2a**. ^{1}H NMR (CD_3OD): hydrocarbyl ligand, δ 0.81 (s, Me); nitrogen ligand, δ 7.74 (dd, $H^{5'}$ and $H^{5''}$), 8.30 (m, other H's), 8.54 (d, $H^{6'}$ and $H^{6''}$). Anal. Calcd for $C_{16}H_{18}ClN_3O_2Pd$: C, 45.11; H, 4.26; N, 9.86. Found: C, 44.91; H, 4.29; N, 9.88. MS: correct isotope pattern for $[M - Cl - 2H_2O]^{\bullet+}$ with *m/z* 354 and for ^{106}Pd.

6a. The synthesis was carried out similarly to that of **1a**, except that the reaction was performed in chloroform at room temperature. Yield: 83% of dark yellow **6a**. ^{1}H NMR ($CDCl_3$): hydrocarbyl ligand, δ 0.90 (s, Me); nitrogen ligand, δ 3.25 (bt, H^α), 4.05 (bt, H^β), 4.25 (s, $H^{6'}$), 7.07 (d, $H^{5'}$), 7.25 (d, $H^{4'}$), 7.34 (ddd, H^5), 7.54 (d, H^3), 7.71 (dt, H^4), 8.47 (d, H^6), 10.23 (s, $H^{7'}$).

11a. To a solution of 45.2 mg (0.12 mmol) of **1a** in 2 mL of acetonitrile was added 31.1 mg (0.12 mmol) of silver trifluoromethanesulfonate. A white precipitate (AgCl) was formed instantaneously. The precipitate was filtered off, and the solvent was removed under reduced pressure from the solution. The pale yellow solid was washed with 3 × 2 mL of diethyl ether and dried *in vacuo*. Yield: 53.2 mg (90%) of pale yellow **11a**. ^{1}H NMR ($CDCl_3$): hydrocarbyl ligand, δ 0.81 (s, Me); nitrogen ligand, δ 1.37 (d, iPr), 4.03 (septet, iPr), 8.08 (d, 2H, H^3 and H^5), 8.26 (t, H^4), 8.46 (s, 2H, H^7 and H^8).

13a. To a stirred solution of 50 mg (0.189 mmol) of (COD)-Pd(Me)(Cl) in 10 mL of dichloromethane at room temperature was added 63 mg of silver tosylate (0.226 mmol, 1.2 equiv). After 15 min the white precipitate that formed (AgCl) was filtered off and 40 mg of 2,6-bis(*N*-pyrazolyl)pyridine (0.189 mmol, 1.0 equiv) was added and the solution was stirred for 1 h. The solvent was removed from the resulting pale yellow solution *in vacuo* to constant weight. Yields: 63.5 mg (0.127 mmol, 67%) of pale yellow **13a**. ^{1}H NMR (223 K, CD_3OD): hydrocarbyl ligand, δ 0.39 (s, methyl); nitrogen ligands, δ 2.37 (s, OTos), 6.56 (t, $H^{4''}$), 6.87 (t, $H^{4'}$), 7.24 (d, OTos), 7.67 (d, OTos), 7.81 (d, H^5), 7.84 (d, $H^{5''}$), 7.91 (d, $H^{5'}$), 8.39 (d, H^3), 8.51 (t, H^4), 8.52 (d, $H^{3''}$), 9.15 (d, $H^{3'}$).

16a. The synthesis was carried out similarly to that of **11a**. Yield: 70% of pale yellow **16a**. ^{1}H NMR ($CDCl_3$): hydrocarbyl ligand, δ 1.08 (s, Me); nitrogen ligand, δ 3.40 (bt, H^α), 3.96 (bt, H^β), 4.03 (s, $H^{6'}$), 7.33 (d, $H^{5'}$), 7.47 (d, $H^{4'}$), 7.55 (ddd, H^5), 7.69 (d, H^3), 8.12 (dt, H^4), 8.64 (d, H^6), 8.67 (s, $H^{7'}$).

CO Insertion Reactions. Preparative Carbonylation. In a typical procedure, a Schlenk vessel containing a solution of ca. 20 mg of the methylpalladium compounds **1a**−**15a** in 2 mL of solvent (**1a** and **4a**−**6a**, CH_2Cl_2, $CHCl_3$; **11a**−**15a**, CH_3CN; **2a**, CH_3OH, C_2H_5OH) was carefully evacuated and then brought under CO three times and the mixture stirred. After the insertion reaction was completed, typically between 5 and 30 min, the solution was filtered. The solvent was removed under reduced pressure, yielding the corresponding acetylpalladium(II) compounds **1b**−**15b**.

1b. ^{1}H NMR (223 K, $CDCl_3$): hydrocarbyl ligand, δ 2.67 (s, C(O)Me); nitrogen ligand, δ 1.21 (d, iPr), 1.34 (d, iPr), 3.81 (septet, iPr), 3.95 (septet, iPr), 7.75 (d, H^5), 7.99 (t, H^4), 8.26 (d, H^3), 8.41 (s, H^7), 9.50 (s, H^8). IR: ν(CO) 1712 cm^{-1}.

2b. ^{1}H NMR (CD_3OD): hydrocarbyl ligand, δ 2.65 (s, C(O)-Me); nitrogen ligand, δ 7.74 (dt, $H^{5'}$ and $H^{5''}$), 8.23 (dt, $H^{4'}$ and $H^{4''}$), 8.35 (m, other H's), 8.47 (dd, $H^{6'}$ and $H^{6''}$). IR: ν(CO) 1682 cm^{-1}.

4b. ^{1}H NMR (CD_2Cl_2): hydrocarbyl ligand, δ 2.59 (s, C(O)-Me); nitrogen ligand, δ 3.18 (t, H^α), 4.16 (t, H^β), 7.12 (dd, H^5), 7.24 (d, H^3), 7.58 (m, 3H, $H^{3'}$, H^4, and $H^{5'}$), 7.96 (t, $H^{4'}$), 8.18 (s, $H^{7'}$), 8.50 (d, H^6), 8.64 (d, $H^{6'}$). IR: ν(CO) 1694 cm^{-1}.

5b. ^{1}H NMR ($CDCl_3$): hydrocarbyl ligand, δ 2.64 (s, C(O)-Me); nitrogen ligand, δ 2.79 (s, 6′-Me), 3.15 (t, H^α), 4.04 (t, H^β), 7.08 (dd, H^5), 7.17 (d, H^3), 7.29 (d, $H^{3'}$), 7.38 (d, $H^{5'}$), 7.53 (t, H^4), 7.72 (t, $H^{4'}$), 8.16 (s, $H^{7'}$), 8.46 (d, H^6). IR: ν(CO) 1708 cm^{-1}.

6b. ^{1}H NMR (193 K, CD_2Cl_2): hydrocarbyl ligand, δ 2.44 (s, C(O)Me); nitrogen ligand, δ 3.08 (t, H^α), 3.34 (d, H^α), 3.60 (t, H^β), 4.05 (d, H^β), 4.21 (s, $H^{6'}$), 6.80 (d, $H^{5'}$), 7.35 (m, $H^{4'}$ and

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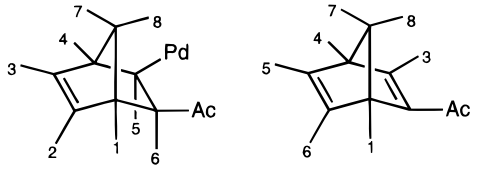

Figure 7. Numbering scheme of the $C_7H_8C(O)CH_3$ moiety in **1c**, **2c**, **4c**, and **6c** (left) and of 2-acetyl[2.2.1]bicyclohepta-2,5-diene (right).

H^5), 7.49 (d, H^3), 7.89 (dt, H^4), 8.46 (d, H^6), 9.70 (s, $H^{7'}$). IR: ν(CO) 1696 cm^{-1}.

11b. ^1H NMR (223 K, $CDCl_3$): hydrocarbyl ligand, δ 2.63 (s, C(O)Me); nitrogen ligand, δ 1.29 (d, iPr), 3.94 (septet, iPr), 8.04 (m, 3H, H^3, H^4, and H^5), 8.89 (s, 2H, H^7 and H^8). IR: ν-(CO) weak, broad resonance around 1700 cm^{-1}.

14b. ^1H NMR (CD_3CN): hydrocarbyl ligand, δ 2.62 (s, C(O)-Me); nitrogen ligand δ 3.47 (t, H^α), 3.96 (bs, H^β), 7.59 (ddd, H^5), 7.76 (d, H^3), 7.87 ($H^{5'}$), 8.08 (dt, H^4), 8.16 ($H^{3'}$), 8.34 ($H^{4'}$), 8.47 (d, H^6), 8.52 (d, $H^{6'}$), 8.70 (s, $H^{7'}$). IR: ν(CO) 1690 cm^{-1}.

15b. ^1H NMR (223 K, $CDCl_3$): hydrocarbyl ligand, δ 2.64 (s, C(O)Me); nitrogen ligand, δ 2.95 (s, 6′-Me), 3.18 (t, H^α), 4.07 (t, H^β), 7.13 (dd, H^5), 7.23 (d, $H^{5'}$), 7.32 (d, $H^{3'}$), 7.37 (d, H^3), 7.59 (dt, H^4), 7.75 (t, $H^{4'}$), 8.09 (s, $H^{7'}$), 8.52 (d, H^6). IR: ν(CO) 1698 cm^{-1}.

CO Insertion Half-Life Measurements. The CO insertion half-lives were determined at 293 K with a homemade gas buret. In a typical experiment, a 12 mL vessel was filled under nitrogen with 5 mL of a 0.4 mM solution of the methylpalladium complex (see Table 7 for the solvent) and stirred. The vessel was carefully evacuated three times and connected to the CO-filled gas buret. The measurement was started by opening the valve between the CO and the vigorously stirred solution of the methylpalladium compound. After equilibrium was reached, the time for every 0.25 mL of CO take up was recorded until the CO uptake had stopped (i.e. at least 3 half-lives) and the half-life calculated. Blank experiments in several solvents showed that the CO diffusion time was *ca*. 20 s.

Norbornadiene Insertion Reactions. (σ^2-iPr-DIP)Pd-($C_7H_8C(O)CH_3$)(Cl) (1c). CO was bubbled for 3 min through a solution of 7 mg (0.019 mmol) of **1a** in 0.6 mL of deuteriochloroform in a Schlenk vessel. Subsequently, a small stream of nitrogen was bubbled through the solution for a few seconds to remove dissolved CO. The solution of the *in situ* formed **1b** was filtered and transferred into a NMR tube, and 2.2 μL (1.9 mg; 0.021 mmol; 1.1 equiv) of NBD was added. The formation of **1c** was then followed by ^1H NMR. After the reaction was completed, infrared spectroscopy was carried out on the same solution. In some cases, the solvent was removed *in vacuo* and the solid washed with 0.5 mL of diethyl ether. Due to the small amount of product, no yield of **1c** was determined. Compounds **2c** (CD_3OD, C_2D_5OD), **4c**, **5c**, and **6c** (CD_2Cl_2, $CDCl_3$), and **14c** and **15c** (CD_3CN) have been synthesized according to the same procedure. The numbering scheme of the 6-acetyl[2.2.1]bicyclohept-1-en-5-yl moiety is presented in Figure 7.

1c. ^1H NMR (253 K, CD_2Cl_2): hydrocarbyl ligand, δ 2.51 (s, C(O)Me), 2.86 (s, H^4), 3.16 (s, H^1), 6.12 (dd, H^3), 6.18 (dd, H^2), H^5, H^6, H^7, and H^8 of the $C_7H_8C(O)CH_3$ moiety are concealed by the isopropyl signals; nitrogen ligand, δ 1.19 (d, iPr), 1.21 (d, iPr), 3.63 (sept, iPr), 3.95 (sept, iPr), 7.92 (d, H^5), 8.12 (t, H^4), 8.32 (d, H^3), 8.74 (s, H^7), 9.73 (s, H^8). IR: ν(CO) 1700 cm^{-1}.

2c. ^1H NMR (223 K, $CDCl_3$): hydrocarbyl ligand, δ 1.44 (d, H^7), 1.68 (d, H^8), 1.98 (s, C(O)Me), 2.35 (dd, H^5), 2.52 (d, H^6), 2.92 (s, H^4), 3.08 (s, H^1), 6.18 (dd, H^3), 6.26 (dd, H^2); nitrogen ligand, δ 7.71 (t, $H^{5'}$ and $H^{5''}$), 8.18 (t, $H^{4'}$ and $H^{4''}$), 8.35 (m, other H's), 8.66 (d, $H^{6'}$ and $H^{6''}$). IR: ν(CO) weak, broad resonance around 1700 cm^{-1}.

4c. ^1H NMR (223 K, $CDCl_3$): hydrocarbyl ligand, δ 1.26 (d, H^7), 1.66 (d, H^8), 2.37 (m, C(O)Me, H^5 and H^6), 2.78 (s, H^4), 2.94 (s, H^1), 5.95 (m, H^3), 6.02 (m, H^2); nitrogen ligand, δ 3.14 (t, H^α), 4.10 (t, H^β), 6.93 (t, H^5), 7.11 (d, H^3), 7.40 (t, $H^{5'}$), 7.61 (t, H^4), 7.96 (t, $H^{4'}$), 8.16 (d, $H^{3'}$), 8.29 (d, $H^{6'}$), 8.37 (d, H^6), 8.87 (s, $H^{7'}$); H^{13} concealed. IR: ν(CO) 1712 cm^{-1}.

6c. ^1H NMR (223 K, $CDCl_3$): hydrocarbyl ligand, δ 1.35 (d, H^7), 1.47 (d, H^8), 1.62 (d, H^5), 1.90 (d, H^6), 2.54 (s, C(O)-Me), 3.06 (s, H^4), 3.17 (s, H^1), 6.27 (m, H^3), 6.32 (m, H^2); nitrogen ligand, δ 3.47 (bt, H^α), 3.95 (s, $H^{6'}$), 4.17 (bt, H^β), 7.17 (d, $H^{5'}$), 7.30 (d, $H^{4'}$), 7.38 (ddd, H^5), 7.71 (d, H^3), 7.88 (dt, H^4), 8.49 (s, $H^{7'}$), 8.59 (d, H^6). IR: ν(CO) 1705 cm^{-1}.

Degradation Product from 1c, 2c, 4c, and 6c. The degradation products from **1c**−**15c** were obtained by evaporation of the solvent and extraction with hexane. The numbering scheme is presented in Figure 7. ^1H NMR ($CDCl_3$): δ 0.97 (d, H^7), 2.10 (s, C(O)Me), 3.75 (bs, H^4), 3.99 (bs, H^1), 6.73 (dd, H^5), 6.88 (dd, H^6), 7.72 (d, H^3); H^8 concealed. GC-MS: *m*/*z* 134 (18, $M^{\bullet+}$), 133 (6, $[M - H]^{\bullet+}$), 119 (6, $[M - CH_3]^{\bullet+}$), 91 (35, $[M - C(O)Me]^{\bullet+}$), 66 (34, $[C_5H_6]^{\bullet+}$; retro Diels−Alder products), 65 (23), 51 (8), 43 (100, $[C(O)Me]^{\bullet+}$). These spectral data are correct for 2-acetyl[2.2.1]bicyclohepta-2,5-diene. No other organic compounds were isolated.

Table 8. Crystal and refinement data for 1a and 2a

	1a	2a
formula	$C_{14}H_{22}ClN_3Pd$	$C_{16}H_{14}ClN_3Pd{\cdot}2H_2O$
fw	374.204	426.19
a, Å	8.723(5)	16.174(5)
b, Å	9.422(5)	12.997(4)
c, Å	11.292(7)	8.086(3)
α, deg	113.86(7)	90
β, deg	90.23(6)	100.56(3)
γ, deg	108.50(7)	90
V, Å^3	795.5(7)	1671
cryst size, mm	0.04 × 0.35 × 0.50	0.03 × 0.20 × 0.45
T, K	293	293
λ, Å	0.710 69	0.710 69
space group	$P\bar{1}$	$P2_1/a$
Z	2	4
d_{exptl}, g cm^{-3}	1.56	1.69
μ, cm^{-1}	13.1	12.68
R	0.053	0.048
R_w	0.084	0.054

X-ray Data Collection and Structure Refinement. (2-(σ(*N*)-(Isopropylimino)methyl)-6-((isopropylimino)methyl)-σ(*N*′)-pyridyl)chloromethylpalladium(II) (1a). Crystals of **1a** suitable for X-ray diffraction have been obtained by cooling a concentrated solution of **1a** in acetonitrile in an ice−salt bath for 10 min, yielding bright red crystals. Crystal data for **1a** are presented in Table 8. A crystal of **1a** with dimensions 0.35 × 0.04 × 0.50 mm was measured on an Enraf-Nonius CAD 4 diffractometer by employing graphite-monochromated Mo Kα radiation. A total of 4602 reflections were collected in the range $2.2° < 2\theta < 60°$ ($-12 \le h \le 12$, $-13 \le k \le 13$, $0 \le l \le 15$), of which 3215 reflections with $I > 2.5\sigma(I)$ were used in the structure determination.

The structure was solved by means of a Patterson minimum function based on Pd and Cl positions. The remaining non-hydrogen atoms were found in a subsequent difference Fourier synthesis. The hydrogen atoms of C(1) were found, and the positions of the other hydrogen atoms were calculated. The non-hydrogen atoms were refined anisotropically; the hydrogen atoms were not refined. Refinement proceeded through anisotropic block-diagonal least-squares calculations employing a weighting scheme; $w = (4.74 + F_o + 0.026F_o^2)^{-1}$. An empirical absorption correction (DIFABS)[37] was used, and an extinction correction was applied.[38] The anomalous dispersion of Pd and Cl was taken into account. Convergence to $R = 0.055$ and $R_w = 0.088$ was obtained. Calculations were carried out with

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XRAY76.[39] Scattering factors[40] and dispersion corrections[41] were taken from the literature.

(σ-2,2′:6′,2″-Terpyridyl-*N*,*N*′,*N*″)methylpalladium(II) Chloride Dihydrate (2a). Crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent of **2a** in methanol at −20 °C, which resulted in a small crop of yellow needles. Crystal data for **2a** are presented in Table 8. A crystal of compound **2a**, with dimensions 0.03 × 0.20 × 0.45 mm, was measured in the same way as for complex **1a**. A total of 2927 reflections were collected in the range $2.2° < 2\theta < 50°$ ($-19 \le h \le 19$, $0 \le k \le 15$, $0 \le l \le 19$) of which 1712 reflections with $I > 2.5\sigma(I)$ were used in the structure determination. The structure was solved in a way similar to that for **1a**, except that the hydrogen atoms were refined isotropically. The weighting scheme $w = (4.14 + F_o + 0.052F_o^2)^{-1}$ was used. Convergence was reached at $R = 0.048$ and $R_w = 0.054$.

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Supporting Information Available: Tables of fractional atomic coordinates for **1a** and **2a** (2 pages). Ordering information is given on any current masthead page.

OM9504361

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