Alkene and Carbon Monoxide Insertion Reactions of Nitrogen-Coordinated Monoorganopalladium(II) Complexes: The Stepwise Construction of Alternating Copolymers of CO and Alkenes on a Palladium(II) Center

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Abstract: The stepwise synthesis of a palladium(II) bound alternating oligomer of CO and strained alkenes is described together with the factors that allow full control of each successive step. The sequence starts with acetylpalladium(II) complexes PdX(COMe)(N-N) (**2**, **4**), (X = Cl(**a**), Br(**b**), or I(**c**); N−N = *N,N,N′,N′*-tetramethylethylenediamine (tmeda) or 2,2′-bipyridyl (bpy)). The bpy-coordinated acetyl complexes (**4a−c**) show an unexpected isomerization reaction of the groups around the metal center for which thermodynamic parameters have been determined. A mechanism for the isomerization is proposed. The ionic complexes [Pd(COMe)(MeCN)(N-N)]OTf (**5**, **6**; OTf = trifluoromethanesulfonate), obtained *in situ* from reaction of **2a−c** and **4a−c** with AgOTf, react with a number of alkenes. Nonstrained alkenes do insert, but decomposition (probably involving β-elimination) is fast. Alkenes containing potential donor groups do not insert at all. Only in the case of strained alkenes like norbornene and its derivatives were the insertion products isolated and fully characterized by ^{13}C NMR, IR, and X-ray analysis. Crystals of the dicyclopentadiene insertion product [Pd($C_{10}H_{12}$COMe)(bpy)]OTf (**8c**) are monoclinic, space group $P2_1/n$, a = 8.3086(4) Å, b = 15.3894(6) Å, c = 18.1479(9) Å, β = 99.98(1)°, V = 2285.36(19) Å^3, Z = 4, R = 0.042 (wR = 0.034). Here, the alkene insertion has occurred in cis,exo fashion on the norbornene-type alkene moiety, indicating this reaction to be both stereo- and chemoselective. The molecular structure shows that the acyl group is coordinated to the metal. Products resulting from a second CO insertion into the Pd−C bond of **8a**, *i.e.* PdX(COC_7H_{10}COMe)(bpy) (X = Cl (**12a**) or I (**12b**)), were formed in the presence of a large excess of a sodium halide salt. Reaction of **12a,b** with AgOTf and norbornene gave the alkyl complex [Pd($C_7H_{10}COC_7H_{10}$COMe)(bpy)]OTf (**13a**). Norbornadiene was inserted similarly. Attempted recrystallization of the insertion product of 5-norbornene-*endo*-2,3-dicarboxylic anhydride (**13c**) gave the alkyl complex **8a**. This is the first example of a reversible alkene insertion reaction on an isolated palladium complex. Addition of CO and excess NaI (20 equiv) to **13a** gave the neutral acyl complex PdI($COC_7H_{10}COC_7H_{10}$COMe)(bpy) (**14**), the first isolated and fully characterized CO/alkene oligomer still connected to the palladium(II) catalytic site. Crystals are triclinic, space group $P\bar{1}$ with a = 10.128(2) Å, b = 11.655(2) Å, c = 13.633(2) Å, α = 109.89(1)°, β = 100.58(1)°, γ = 92.92(2)°, V = 1476.3(4) Å^3, Z = 2 and R = 0.044 (wR = 0.057). Norbornadiene also reacts with 2 equiv. of **5** or **6** to give the homoligated dinuclear complexes [(N-N)Pd{(C_7H_8)($COMe)_2$-2,5}Pd(N-N)]$(OTf)_2$ with N-N = tmeda (**9**) or bpy (**10**). Crystals of **9** are orthorhombic, space group $P2_12_12_1$, a = 11.176(3) Å, b = 11.362(1) Å, c = 30.394(3) Å, V = 3859(1) Å^3, Z = 4, $wR2$ = 0.124, R = 0.049. In this complex a double alkene insertion reaction has taken place involving both alkene functionalities of a dialkene: **9** is symmetrically substituted with the Pd atoms at opposite (trans) positions.

Introduction

The insertion of unsaturated molecules into metal−carbon bonds is a key step in metal-mediated synthesis and catalysis.[1] Currently, much interest is devoted to alkoxycarbonylation of alkenes[2] and alkynes[3] and, in particular, to the copolymerization of alkenes with carbon monoxide[4,5] using palladium-based catalysts. The most favored mechanism of these copolymerization reactions contains two propagation steps: (1) CO

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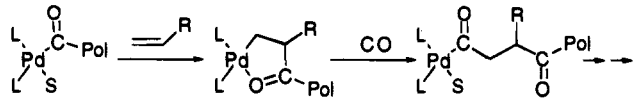
Scheme 1

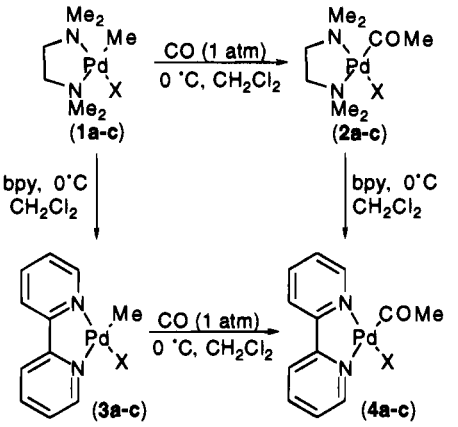


Pol = polymer chain, S = solvent or anion

migratory insertion into a Pd−alkyl bond and (2) alkene insertion into a Pd−acyl bond (Scheme 1).[4,5] Another mechanism, proposed by Consiglio *et al.*,[5f] invokes palladium−carbene intermediates to account for the high stereoregularity of the copolymerization and the formation of a spiroketal structure instead of the linear polymer. This mechanism has gained little support so far. The second step in Scheme 1, *i.e.*, the carbonylation of metal−alkyl complexes, has been the subject of many model studies,[6−9] and two insertion mechanisms have been proposed. The most favored is a dissociative mechanism, in which one of the ligands is displaced by CO after which insertion from a four-coordinate intermediate occurs. Recent *ab initio* calculations on ionic complexes containing nitrogen donor ligands suggest that Pd−N bond dissociation might be assisted by coordination of CO to palladium in an apical position thus lowering the activation energy of this step.[9d] This leads to a four-coordinate intermediate in which migratory CO insertion takes place. The second mechanism is associative, *i.e.*, CO adds as a fifth ligand to the metal followed by insertion.

In contrast, studies of the first step in Scheme 1, *i.e.*, the insertion of alkenes into the palladium−acyl bond, are relatively scarce.[7d,8a,b,h−m,9c,10] Generally, it is found that ionic complexes react more readily than neutral complexes with alkenes. This suggests that the presence of an easily accessible coordination site at the cationic metal center of the former is responsible. Sen *et al.* have shown that for both neutral and ionic monodentate phosphorus complexes insertion occurs from a four-coordinate intermediate.[4d,7d] The most stable insertion products are obtained with strained alkenes, like norbornene and derivatives. Other alkenes also insert, but the insertion products rapidly decompose via β-elimination.[8b]

Scheme 2



X = Cl (**a**), Br (**b**) or I (**c**)

Although the CO/alkene copolymerization is well-known,[4,5] little is known about the sequential insertion of alkenes and CO at a metal center.[8j−m] Brookhart *et al.* were able to observe the intermediate acyl complexes in the alternating insertion of 4-*tert*-butylstyrene and CO by ^{13}C NMR when $[B(C_6H_3\{CF_3\}_2\text{-}3,5)_4]^-$ is used as the anion.[8j] Recently, Elsevier *et al.* reported the sequential insertion of CO and norbornadiene starting from PdClMe(BIAN) (BIAN = bis(arylimino)acenaphthenes) to form the metal-bound oligomer $PdCl(COC_7H_8COC_7H_8COMe)$(BIAN) and isolated the acyl and alkyl intermediates.[8k,m] Their method seems to be restricted to norbornadiene, as other strained alkenes like norbornene and dicyclopentadiene give only incomplete insertion into the Pd−C(acyl) bond.

In the present paper we describe the synthesis of acetylpalladium(II) complexes and report a study of an isomerization process occurring in these complexes. We have extended the range of alkenes which can be inserted into both neutral and ionic acyl complexes containing bidentate nitrogen donor ligands, and we report in more detail on the stepwise and stereoregular construction of CO/alkene co-oligomers on a palladium(II) center as well as the structural details of the first isolated and fully characterized CO/alkene oligomer still connected to the Pd^{II} catalytic site. Preliminary reports of this work have appeared.[8h,l]

Results

Synthesis and Properties of Acetyl Complexes. Based on the method found by de Graaf et al.,[8g] the complexes PdX(COMe)(bpy), with X = Cl (**4a**),[11] Br (**4b**), or I (**4c**), were obtained *via* two routes from PdXMe(tmeda) (**1a−c**) as presented in Scheme 2. The overall yield is *ca.* 85%, independent of the halide and the route followed. Both the tmeda (**2a−c**) and bpy (**4a−c**) acetyl complexes are surprisingly stable, and they can be kept at room temperature in air for

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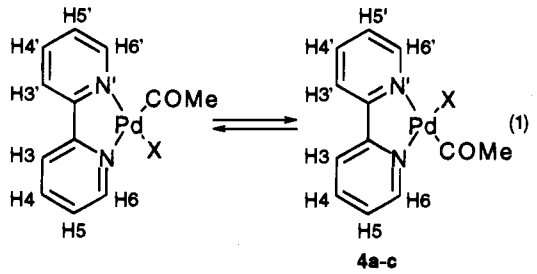
Table 1. Activation and Thermodynamical Parameters of the Isomerization of **4a–c**

complex	solvent	ln *A*	E_{act}, kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1}	$\Delta G^{\ddagger}_{298}$, kcal mol^{-1}
4a	$CDCl_3$	23 ± 1	14 ± 1	13 ± 1	−14 ± 2	18 ± 1
	CD_3COCD_3	15 ± 1	10 ± 1	9 ± 1	−29 ± 1	18 ± 1
4b	$CDCl_3$	29 ± 1	18 ± 1	17 ± 1	−1 ± 2	17 ± 1
	CD_3COCD_3	17 ± 2	10 ± 1	10 ± 1	−24 ± 4	17 ± 2
4c	$CDCl_3$	30 ± 3	17 ± 2	17 ± 2	1 ± 7	17 ± 4

several months without decomposition. In solution ($CDCl_3$ or CD_3COCD_3) the complexes are less stable, but these solutions remain unchanged for a few days when stored at −20 °C. The complexes PdXMe(bpy) (**3a–c**) were identical to those obtained by Byers and Canty *via* another route.[12]

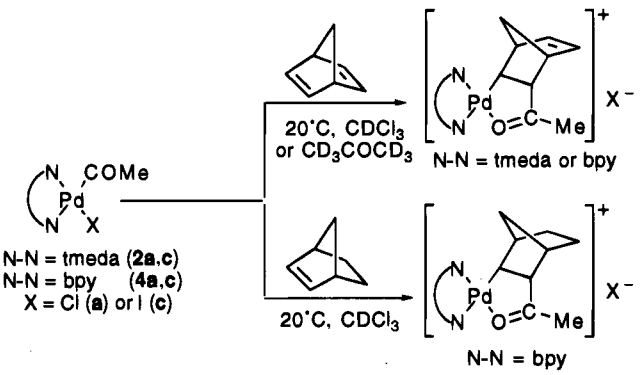
The bpy-H6 and -H6′ NMR resonances of **4a–c** are very sensitive to the ligand which is in the cis position at the metal center, *i.e.*, either the halide anion or the metal group, and can therefore be readily assigned like those of **3a–c**. We observed that, when the H6 proton next to the halide is irradiated, the resonance of H6′ also disappears and *vice versa*. This can be explained by fast spin transfer between these two nuclei caused by exchange of coordination positions on the NMR time scale, *i.e.*, an isomerization of the acetyl complexes, see eq 1:



Similar observations were reported by van Asselt *et al.*[13] No such effects were found in the methyl complexes **3a–c**. Spin saturation transfer measurements using the Forsén–Hoffman method[14] allowed the determination of the thermodynamic parameters of the isomerization of **4a–c** (Table 1). Unfortunately, PdI(COMe)(bpy) (**4c**) is only slightly soluble in $CDCl_3$, leading to large errors for this solvent, while in acetone the low solubility of **4c** did not allow ^{1}H NMR experiments at all. The other two complexes (**4a,b**) were soluble in both solvents. The neutral acetyl complexes **2** and **4** can be readily and quantitatively converted to their ionic analogs [Pd(COMe)(MeCN)(N-N)]OTf, with N-N = tmeda (**5**) or bpy (**6**), by reacting them with silver trifluoromethanesulfonate (AgOTf, Scheme 4). These complexes are, however, unstable and do not allow characterization.

Alkene Insertion into Pd–COMe Bonds. The neutral complexes PdX(COMe)(N-N) (**2a,c** and **4a,c**) were reacted with norbornene and norbornadiene at room temperature, and the reactions (Scheme 3) were monitored by NMR in either CD_3COCD_3 or $CDCl_3$. The insertion of norbornadiene into the Pd–C(acyl) bond of **4c** was very fast (<5 min) in both solvents but was much slower in CD_3COCD_3 (30 min) than in $CDCl_3$ (10 min) for **4a**. Similar observations were obtained in $CDCl_3$ for **2a** (80% in 45 min) and **2c** (100% in 8 min). Norbornene was found to react very differently from norbornadiene. The tmeda complexes **2a,c** did not react with norbornene in either of the two solvents. The bpy complexes **4a,c** were only reactive

Scheme 3



toward norbornene in $CDCl_3$ giving 16% conversion in 90 min (**4a**) and 50% conversion in 60 min (**4b**), respectively. No insertion of norbornene was observed in acetone. Unfortunately, the neutral alkene insertion products are all unstable and decomposed significantly during the NMR experiments.

The ionic complexes [Pd(COMe)(MeCN)(N-N)]OTf (**5**, **6**) are much more reactive toward alkenes (Scheme 4). Complex **5** (N-N = tmeda), prepared in situ, was reacted with norbornene, norbornadiene, dicyclopentadiene, and α-methylstyrene. The latter alkene did not insert, but the other insertion products (**7a–c**) were isolated in good yield and were characterized by NMR and IR (Table 2). The norbornadiene insertion product (**7b**) could not be obtained pure as samples always contained some of the homoligated dinuclear complex [(tmeda)Pd{$(MeCO)_2$-C_7H_8}Pd(tmeda)]$(OTf)_2$ (**9**), which was prepared independently (*vide infra*). The scope of the alkene-insertion reaction was investigated for [Pd(COMe)(MeCN)(bpy)]OTf (**6**). Four categories of alkenes were used: (i) the strained alkenes norbornene, norbornadiene, dicyclopentadiene, 5-norbornene-*endo*-2,3-dicarboxylic anhydride, and 7-oxa-5-norbornene-*exo*-2,3-dicarboxylic anhydride; (ii) the nonstrained alkenes styrene, cyclopentene, cyclohexene, cycloheptene, ethylene; (iii) the nonstrained alkenes containing a potential donor atom 2-vinylpyridine and 2,3-dihydrofuran; and (iv) the nonstrained alkenes containing electron withdrawing substituents, methyl methacrylate, benzylideneacetone, methyl vinyl ketone, and maleic anhydride. Only the strained alkenes of type (i) insert to give stable products (**8a–e**, Scheme 4) which are readily isolable in good yield. These products were characterized by NMR and IR (Table 2). **8c** was identified by X-ray analysis (*vide infra*). The type (ii) and (iv) alkenes styrene, cyclopentene, cyclohexene, cycloheptene, ethylene, methyl methacrylate, and methyl vinyl ketone did insert, as shown by the characteristic ν(C–O) of the insertion products (Table 2), but these products could not be isolated pure and were very unstable in solution even at lower temperature (−20 °C). The other alkenes, *i.e.*, 2-vinylpyridine, benzylideneacetone, 2,3-dihydrofuran, and maleic anhydride, did not give insertion products observable by ^{1}H NMR or IR spectroscopy.

The carbonyl stretching frequencies ν(C–O) for **7a–c** and **8a–e** have in all cases rather low values of *ca.* 1590–1600 cm^{-1} (Table 2) which are attributed to coordination of the oxygen atom of the ketone to the metal. Similarly, the ^{13}C NMR resonances are significantly shifted to lower field (*ca.* 240 ppm, Table 2) with respect to those of normal organic ketones. This is also caused by ketone coordination because palladium induces low-field shifts of the resonances of nuclei close to the metal.

The ^{1}H NMR spectra of the dicyclopentadiene insertion products **7c** and **8c** indicate that only the strained norbornene-type double bond is involved in the insertion. This was further substantiated by the X-ray structure of **8c** (*vide infra*). The unreacted double bond of **7c** and **8c** appears as two sets of ^{1}H

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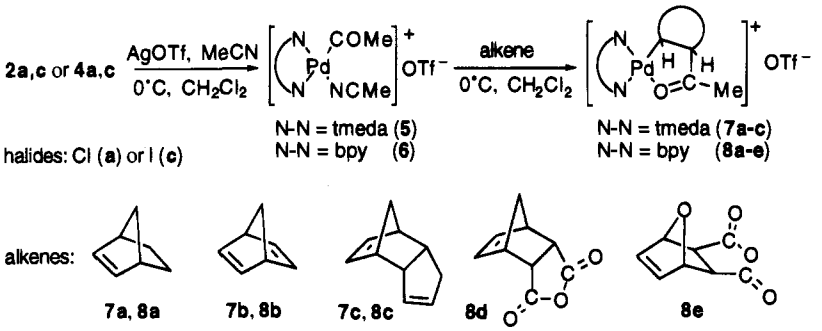
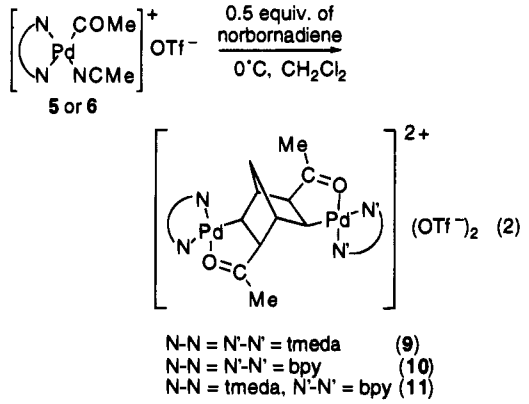
Scheme 4



NMR resonances in a 1:1.1 (**7c**) and a 1:1.7 (**8c**) ratio because in each case two regioisomers form in unequal amounts upon insertion.

Double Insertion. When norbornadiene is reacted with 2 equiv of the ionic acetyl complexes [Pd(COMe)(MeCN)(N-N)]-OTf (**5** or **6**), prepared in situ, the homoligated dinuclear complexes [(N-N)Pd-{C_7H_8(COMe)$_2$-2,5}Pd(N-N)](OTf)$_2$ are obtained in moderate yields (eq 2), *i.e.*, 49% (**9**, N-N = tmeda, always present as impurity in **7b**) and 47% (**10**, N-N = bpy).



Complex **10** was slightly soluble only in acetonitrile. The IR and NMR spectra (Table 2) of **9**, before and after purification, indicate that the complex has C_2 symmetry, *i.e.*, addition of the second palladium center occurs *trans* to the first. This is corroborated by the molecular structure of this complex (*vide infra*). The heteroligated dinuclear complex [(bpy)Pd{C_7H_8-(COMe)$_2$-2,5}Pd(tmeda)](OTf)$_2$ (**11**) was best obtained by reacting [Pd(C_7H_8COMe)(bpy)]OTf (**8b**) with 1 equiv of, *in situ* prepared, [Pd(COMe)(MeCN)(tmeda)]OTf (**5**). This complex is, however, very unstable both in solution and in the solid state, allowing only characterization by IR (Table 2).

Molecular Structures of the Cations [Pd($C_{10}H_{12}$COMe)-(bpy)]$^+$ (8c) and [(tmeda)Pd{C_7H_8(COMe)$_2$-2,5}Pd(tmeda)]$^{2+}$ (9). ORTEP representations of the cations of **8c**[8h] and **9** are presented in Figures 1 and 2, respectively, with selected bond distances and angles in Table 3. The molecular structure of the cation of **8c** (Figure 1) shows the carbonyl group to be coordinated to the metal (Pd−O = 2.026(3) Å) resulting in the formation of a five-membered PdCCCO chelate ring. The palladium center in **8c** has a square planar geometry involving the C,O-chelate bonded ligand and the 2,2′-bipyridyl ligand. The Pd−C11 distance of the C,O-chelate bonded ligand (2.023-(4) Å) is comparable to those found for other palladium-bound sp^3-carbons *trans* to a sp^2-nitrogen atom (2.036(6) Å).[8h,l,9a,b,15] The C21−O1 bond distance (1.249(6) Å) is normal for a noncoordinated carbonyl group. The molecular structure clearly shows that the dicyclopentadiene moiety has selectively reacted, on the exo face, with the 5,6-double bond rather than with the 2,3-double bond. This exo-mode of insertion is consistent with

Table 2. Selected ^{13}C NMR and IR Data of the Alkene Insertion Products

complex	ν(C−O), cm^{-1}	δ, ppm
7a	1599	238.70
7b	1607	239.28
7c	1605	239.16/240.77
8a	1601	240.83
8b	1603	239.00
8c	1603	243.45/244.68
8d	1604	242.75
8e	1612	239.54
9	1595	238.62
10	1601	*a*
11	1606	*b*

[a] Not determined due to low solubility. [b] Not determined due to fast decomposition.

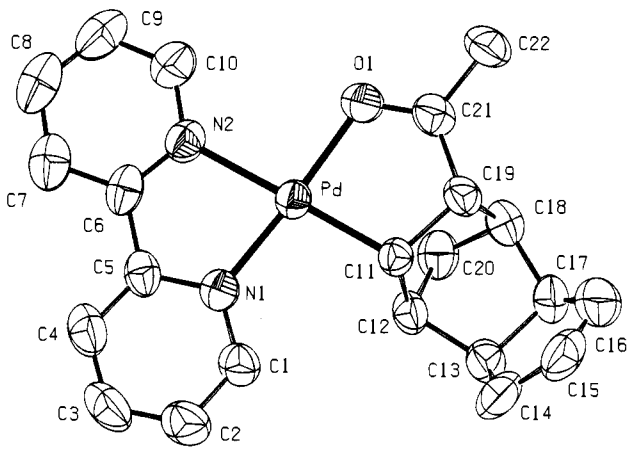


Figure 1. ORTEP plot (50% probability level) of the structure of the cation of [Pd($C_{10}H_{12}$COMe)(bpy)]OTf (**8c**).

the results of Sen *et al.*, who showed that insertion of norbornene in *trans*-[Pd(COMe)(MeCN)(PPh_3)$_2$]BF_4 also takes place on the exo face of the norbornene moiety.[7d] The fact that the observed bond distances for C14−C15 (1.425(9) Å) and C15−C16 (1.391(9) Å) differ only slightly, with values in between a single and a double bond, suggests that these bond distances are the average of the distances of the two isomers (*vide supra*) present in the crystal. The molecular structure of the cation of **9** (Figure 2) clearly shows the C_2 symmetric addition of the two Pd−COMe moieties on the two double bonds of norbornadiene. The structural features of this cation are similar to those of **8c**, except that the Pd−N bonds are significantly longer. The Pd−O bond distances of **9** (2.016(5) and 2.033(5) Å) and **8c** (2.026(3) Å) are approximately the same, which is consistent with the comparable *trans*-influence of a tertiary amino and a pyridyl-imino group.

Sequential Insertion of CO and Alkenes. After the insertion of an alkene into the Pd−C bond of the acetyl complexes a new Pd−alkyl bond is obtained. This should, in

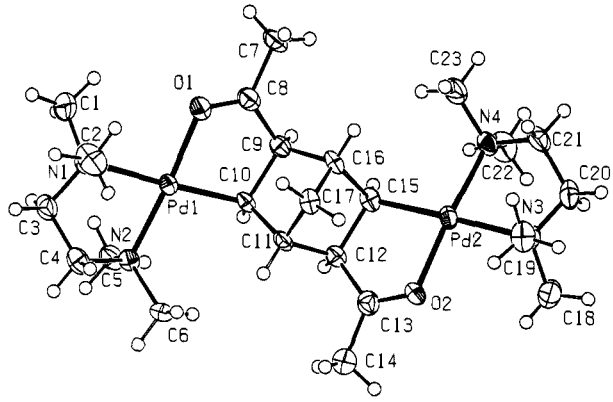
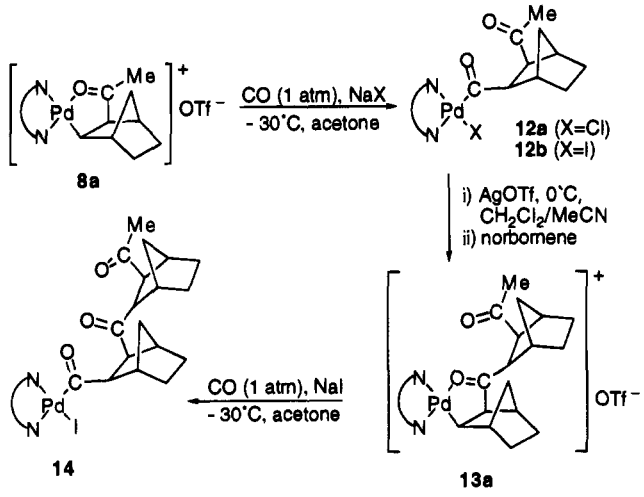


Figure 2. ORTEP plot (50% probability level) of the structure of the cation of [(tmeda)Pd{$C_7H_8(COMe)_2$-2,5}Pd(tmeda)](OTf)$_2$ (**9**).

Scheme 5



principle, allow the insertion of another molecule of CO into the Pd−C(alkyl) bond like in the methyl complexes. Initial attempts to insert CO at low or high pressure (at 1 or at 40 atm) into the Pd−C(alkyl) bond of [Pd(C_7H_{10}COMe)(bpy)]OTf (**8a**) did not give an isolable acyl complex. This suggests that either the insertion does not take place or that the reaction is reversible and that, upon attempted isolation, the complex deinserts CO. The latter conclusion agrees with the results of van Leeuwen *et al.*, who studied the bidentate phosphine complexes [Pd(COMe)(MeCN)(dppp)]OTf and PdCl(COMe)-(dppp) (dppp = 1,3-bis(diphenylphosphino)propane).[8b] These complexes require the presence of a CO atmosphere during the reaction with norbornene due to the instability of both the neutral and the ionic acetyl complex toward decarbonylation. The reaction of norbornene with the neutral complex gave the expected alkene insertion product, but also a secondary product that was suggested to result from a subsequent CO insertion yielding a new acyl complex. The same reaction with the ionic acetyl complex showed only the alkene insertion product. These results do suggest that the presence of a strongly coordinating anion is necessary to enable the isolation of an acyl complex. Indeed, by adding a large excess of a sodium halide, *i.e.*, at least 20 equiv excess of either NaCl or NaI, prior to CO addition to [Pd(C_7H_{10}COMe)(bpy)]OTf (**8a**, Scheme 5), we were able to obtain the neutral acyl complexes PdX(COC_7H_{10}COMe)(bpy), with X = Cl (**12a**) or I (**12b**), in excellent yields (83 and 93%, respectively). As an alternative to the synthesis described above, **12b** (X = I) could also be obtained by reacting **12a** (X = Cl) with 4 equiv of sodium iodide in acetone. Isomerization of **12a,b**, similar to **4a−c**, was not observed when either the bpy-H6 or the bpy-H6′ resonance was irradiated. The palladium-bound carbonyl groups have IR absorptions and ^{13}C NMR shifts (Table 4) that are normal for acylpalladium(II) compounds.[6-9,10]

Having found the correct conditions for both insertion of norbornene into acyl complex **4a** (to afford alkyl complex **8a**) and for the further reaction of **8a** with carbon monoxide to give the doubly CO inserted products **12a,b**, the next step is to attempt a second insertion of norbornene. This was successfully accomplished, analogously to the synthesis of **8a**, by reacting either **12a** or **12b** first with silver trifluoromethanesulfonate (AgOTf) and then with norbornene (Scheme 5), thus affording complex **13a** in 98% yield. This complex contains two carbonyl and two cis,exo substituted norbornyl fragments and shows the characteristic low frequency infrared stretching vibration at 1582 cm^{-1} of a carbonyl group coordinating to palladium (*cf.* **8c**, 1598 cm^{-1}). The IR absorption of the other carbonyl group is at 1708 cm^{-1}, a normal value for a free carbonyl group. The ^{13}C NMR resonances of the carbonyl carbon atoms of **13a** have characteristic positions, *i.e.*, 243.4 ppm for the one coordinated *via* its oxygen atom to the metal (*cf.* 240.8 for **8c**) and 208.0 ppm for the other. Both the IR and ^{13}C NMR spectra (Table 4) of complex **13a** clearly show that the structure is comparable to those of the single alkene inserted products **8a−e** (Table 2). Whether the two norbornyl units have adopted *syn* or *anti* positions could not be inferred from the NMR spectra.

Both norbornadiene and 5-norbornene-*endo*-2,3-dicarboxylic anhydride may also be inserted in the second alkene insertion step to give the insertion products **13b** and **13c**, respectively, both of which could not be obtained analytically pure. Nevertheless, satisfactory NMR and IR spectra could be obtained for **13b**. Surprisingly, an attempt to recrystallize **13c** resulted in the formation of **8a**,[16] whereas nonpurified **13c** gave an IR spectrum (Table 4) that unambiguously showed the presence of the insertion product. Even though the ^{1}H NMR spectrum of impure **13c** was very complex and did not allow proper analysis, no resonances corresponding to either **8a** or **12a** were present.

Starting from complex **13a** a further successful insertion of carbon monoxide was accomplished, in the presence of 20 equiv of sodium iodide, yielding the neutral acyl complex **14** (Scheme 5) in 88% yield. Recrystallization from acetone gave crystals suitable for an X-ray structural analysis (*vide infra*). The carbonyl groups are again found at characteristic positions in the IR and ^{13}C NMR spectra (Table 4).

Molecular Structure of the Complex PdI(COC_7H_{10}-COC_7H_{10}COMe)(bpy) (14).[81] The asymmetric unit of the crystal structure contains one molecule of **14** together with one acetone solvent molecule. In the molecular structure of **14** (Figure 3, Table 5), the metal has a slightly distorted square-planar surrounding consisting of a bidentate N-bonded bpy ligand (N1, N2), an iodine atom (I), and a C-bonded acyl group (C11). In addition to the expected angular deviations resulting from the five-membered chelate ring (N1−Pd−N2 = 77.8(2)°), the most noticeable distortion around the metal center is concerned with the position of the iodine atom, which lies 0.339 (1) Å above the coordination plane defined by Pd, N1, N2, and

(15) (a) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *Organometallics* **1990**, *9*, 826. (b) Markies, B. A.; Canty, A. J.; Janssen, M. D.; Spek, A. L.; Boersma, J.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 477. (c) Canty, A. J.; Traill, P. R.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1992**, *433*, 213. (d) Byers, P. K.; Canty, A. J.; Skelton, B. W.; Traill, P. R.; Watson, A. A.; White, A. H. *Organometallics* **1992**, *11*, 3085.

(16) The molecular structure of **8a** has also been determined. This complex shows properties similar to **8c**. Crystals were obtained from the deinsertion of the alkene from **13c** during recrystallization from methanol/diethyl ether, but they can also be conveniently obtained via direct crystallization of **8a** from this solvent combination. See: Spek, A. L.; Markies, B. A.; Kruis, D.; Boersma, J.; van Koten, G. *Acta Crystallogr.*, in press.

Table 3. Selected Bond Distances (Å) and Angles (deg) of [Pd($C_{10}H_{12}$COMe)(bpy)]OTf (**8c**) and of [(tmeda)Pd{C_7H_8(COMe)$_2$-2,5}-Pd(tmeda)](OTf)$_2$ (**9**)

		[Pd($C_{10}H_{12}$COMe)(bpy)]OTf (**8c**)			
Pd−N1	2.013(3)	Pd−C11	2.023(4)	C21−O1	1.249(6)
Pd−N2	2.121(4)	Pd−O1	2.026(3)		
O1−Pd−N1	175.94(13)	O1−Pd−C11	83.64(14)	N1−Pd−C11	99.69(15)
O1−Pd−N2	97.28(14)	N1−Pd−N2	79.50(15)	N2−Pd−C11	177.17(16)
O1−C21−C19	119.4(4)	O1−C21−C22	118.8(5)	C19−C21−C22	121.8(4)
		[(tmeda)Pd{C_7H_8(COMe)$_2$-2,5}-Pd(tmeda)](OTf)$_2$ (**9**)			
Pd1−N1	2.170(6)	Pd1−C10	2.015(6)	C8−O1	1.239(7)
Pd1−N2	2.083(5)	Pd1−O1	2.016(5)	C13−O2	1.236(8)
Pd2−N3	2.166(6)	Pd2−C15	2.037(6)		
Pd2−N4	2.053(5)	Pd2−O2	2.033(5)		
O1−Pd1−N1	92.8(2)	O1−Pd1−C10	84.4(2)	N1−Pd1−C10	177.3(2)
O1−Pd1−N2	176.0(2)	N1−Pd1−N2	84.6(2)	N2−Pd1−C10	98.2(2)
O2−Pd2−N3	93.6(2)	O2−Pd2−C15	84.0(2)	N3−Pd2−C15	177.3(2)
O2−Pd2−N4	173.9(2)	N3−Pd2−N4	84.2(2)	N4−Pd2−C15	98.3(2)
O1−C8−C7	119.7(6)	O1−C8−C9	119.3(5)	C7−C8−C9	121.0(5)
O2−C13−C12	119.7(6)	O2−C13−C14	119.8(6)	C12−C13−C14	120.5(6)

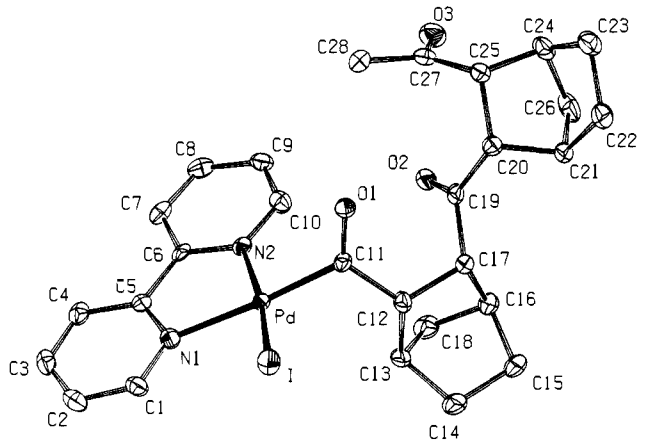


Figure 3. ORTEP plot (50% probability level) of the molecular structure of PdI($COC_7H_{10}COC_7H_{10}$COMe)(bpy) (**14**).

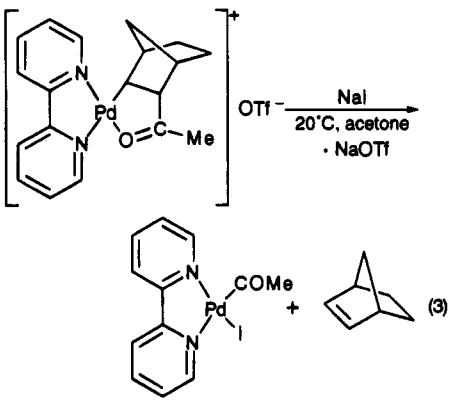
Table 4. Selected ^{13}C NMR and IR Data of the Polyinsertion Products

complex	ν(C−O), cm^{-1}	δ, ppm
12a	1672/1710	210.92/230.63
12b	1663/1706	211.37/229.73
13a	1582/1708	208.00/243.39
13b	1587/1698	208.17/243.53
13c	1601/1698	*a*
14	1669/1715	210.79/213.34/232.73

[a] Not determined due to decomposition.

C11 on the same side as the C11−O1 keto function. The Pd−I (2.5912(7) Å) and the Pd−C11(acyl) bond distances (1.952(5) Å) have normal values for such bonds *trans* to a pyridine nitrogen.[12,15a] The structure of the organic substituent of the acyl group shows that there is no interaction of the three carbonyl groups with the metal or with each other. The carbonyl carbon atom (C11) connected to the palladium center shows angles expected for sp^2 hybridization, and the C12−C11−O1 plane is oriented almost perpendicular to the metal coordination plane (73.6(6)°). Both norbornene moieties are found cis,exo substituted as expected and are syn positioned with respect to each other.

Iodide-Induced Elimination of Norbornene. In an attempt to replace the triflate anion in [Pd(C_7H_{10}COMe)(bpy)]OTf (**8a**) by iodide *via* a methathesis reaction with a large excess (≈20 equiv) of sodium iodide, we observed immediate elimination (<2 min) of norbornene instead of anion exchange (eq 3). Both the complex PdI(COMe)(bpy) and free norbornene were readily identified from the ^{1}H NMR spectrum. The formation of norbornene was confirmed by GC-MS. Sodium chloride does not react accordingly. In a similar way, [Pd(C_7H_8COMe)(bpy)]-OTf (**8b**) was reacted with sodium iodide but neither alkene elimination nor anion exchange was observed. When the higher



oligomer [Pd($C_7H_{10}COC_7H_{10}$COMe)(bpy)]OTf (**13**) was reacted with 3 equiv of sodium iodide, 1 equiv of norbornene was again formed, but the expected organometallic product PdI(COC_7H_{10}-COMe)(bpy) (**12b**) could not be isolated or even identified from the complex ^{1}H NMR spectrum.

Discussion

Properties of the Acetyl Complexes. It is well-known that some organopalladium(II) and -(IV) complexes containing nitrogen ligands are more stable than the corresponding complexes with phosphorus ligands.[8g-m,11,15,17] The neutral acetylpalladium(II) complexes PdX(COMe)(N-N) (**2a−c**, **4a−c**) used in this study are good examples as they are stable toward decarbonylation, whereas their cis-phosphorus coordinated analogs are not.

The isomerization observed in the acetyl complexes **4a−c** is not unprecedented. Bäckvall *et al.* recently found similar isomerizations for bidentate N-donor complexes containing bulky π-allyl groups.[18] They showed that these isomerizations

(17) (a) Canty, A. J. *Acc. Chem. Res.* **1992**, *25*, 83 and references cited therein. (b) Byers, P. K.; Canty, A. J.; Honeyman, R. T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1992**, *433*, 223. (c) Canty, A. J.; Traill, P. R. *J. Organomet. Chem.* **1992**, *435*, C8. (d) Canty, A. J. *Platinum Metals Rev.* **1993**, *37*, 2. (e) Bennett, M. A.; Canty, A. J.; Felixberger, J. K.; Rendina, L. M.; Sunderland, C.; Willis, A. C. *Inorg. Chem.* **1993**, *32*, 1951. (f) Alsters, P. L.; Engel, P. F.; Hogerheide, M. P.; Copijn, M.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 1831. (g) Markies, B. A.; Canty, A. J.; Boersma, J.; van Koten, G. *Organometallics* **1994**, *13*, 2053.

(18) Gogoll, A.; Örnebro, J.; Grennberg, H.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1994**, *116*, 3631.

Table 5. Selected Bond Distances (Å) and Angles (deg) of $PdI(COC_7H_{10}COC_7H_{10}COMe)(bpy)$ (**14**)

Pd−N1	2.161(4)	Pd−C11	1.952(5)	C27−O3	1.217(7)
Pd−N2	2.098(4)	Pd−I	2.5912(7)		
C11−O1	1.211(7)	C19−O2	1.209(7)		
I−Pd−N1	97.67(11)	I−Pd−C11	86.92(15)	N1−Pd−C11	174.95(19)
I−Pd−N2	170.58(14)	N1−Pd−N2	77.81(15)	N2−Pd−C11	97.35(19)
Pd−C11−O1	121.3(4)	Pd−C11−C12	118.3(4)	O1−C11−C12	120.3(5)
O2−C19−C17	121.8(5)	O2−C19−C20	123.1(5)	C17−C19−C20	114.8(4)
O3−C27−C25	121.8(5)	O3−C27−C28	121.1(6)	C25−C27−C28	116.7(5)

Table 6. Details of the Structure Determination and Refinement of **8c**, **9**, and **14**

		Crystal Data	
formula	$C_{22}H_{23}N_2OPd\cdot CF_3O_3S$ (**8c**)	$C_{23}H_{46}N_4O_2Pd_2\cdot 2CF_3O_3S$[a] (**9**)	$C_{28}H_{31}IN_2O_3Pd\cdot C_3H_6O$ (**14**)
molecular weight	586.92	921.62[a]	734.97
crystal system	monoclinic	orthorhombic	triclinic
space group	$P2_1/n$ (no. 14)	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)
a, b, c, Å	8.3086(4), 15.3894(6), 18.1479(9)	11.176(3), 11.362(1), 30.394(3)	10.128(2), 11.655(2), 13.633(2)
α, β, γ, deg	90, 99.98(1), 90	90, 90, 90	109.89(1), 100.58(1), 92.92(2)
V, Å^3	2285.4(2)	3859(1)	1476.3(4)
D_{calc}, g cm^{-3}	1.706	1.586[a]	1.653
Z	4	4	2
$F(000)$	1184	1864[a]	736
μ, cm^{-1}	9.4	11.0[a]	16.9
crystal size, mm	0.12 × 0.23 × 0.60	0.4 × 0.4 × 0.4	0.4 × 0.4 × 0.05
		Data Collection	
temp, K	298	150	150
$\theta_{min}, \theta_{max}$, deg	0.1, 27.5	0.67, 27.5	1.63, 27.5
scan type	$\omega/2\theta$	ω	$\omega/2\theta$
$\Delta\omega$, deg	1.12 + 0.35 tan θ	1.11 + 0.35 tan θ	0.81 + 0.35 tan θ
hor., ver. aperture, mm	3.00, 4.00	3.77, 4.00	3.00, 4.00
X-ray exposure time, h	37	45	26
linear decay, %	10	3	5
reference reflections	$\bar{2}$ 3 3; 1 2 $\bar{4}$; 1 6 2	$\bar{2}\,\bar{2}$ 5, 1 2 $\bar{7}$, $\bar{4}\,\bar{3}\,\bar{2}$	$\bar{2}$ 2 4, $\bar{2}$ 2 $\bar{4}$, $\bar{4}$ 3 2
data set (hkl)	−10:10; 0:19; −23:23	−14:14; 0:14; −39:0	−13:13, −10:15, −17:16
total data	5715	9478	8978
total unique data	4951	8854	6770
observed data	3136 [$I > 2.5\sigma(I)$]	[no obs. crit. applied]	5061 [$I > 2.5\sigma(I)$]
DIFABS corr. range	0.77, 1.21	0.70, 1.20	0.78, 1.21
		Refinement	
no. of refined parameters	312	435	354
final R[b]	0.042 [$I > 2.5\sigma(I)$]	0.049 [8029 $F_o > 4\sigma(F_o)$]	0.044 [$I > 2.5\sigma(I)$]
final $wR2$[c]		0.124	
final R_w[d]	0.034		0.057
goodness of fit	1.48	1.06	2.05
weighting scheme	$1/\sigma^2(F)$	$1/[\sigma^2(F_o^2) + (0.065*P)^2 + 10.78*P]$[e]	$1/[\sigma^2(F) + 0.00111]F^2$
$(\Delta/\sigma)_{av}, (\Delta/\sigma)_{max}$	0.014, 0.39	0.000, 0.002	0.017, 0.090
min. and max. residual density, eÅ^{-3}	−0.42, 0.84	−2.12, 1.55	−1.32, 1.34

[a] Without disordered solvent contribution (see text). [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [d] $R_w = [\sum[w(|F_o| - |F_c|)^2]/\sum[w(F_o^2)]]^{1/2}$. [e] $P = (\max(F_o^2,0) + 2F_c^2)/3$.

occur *via* Pd−N bond breaking followed by isomerization of the resulting three-coordinate intermediate and ligand rotation. The mechanism occurring in our case is yet unknown. However, from Table 1 it can be concluded that the isomerization is faster in acetone, which, together with the negative values of $\Delta S^{\ddagger}$, is consistent with a polar transition state and a nondissociative pathway.

Insertion of Alkenes into Acetylpalladium(II) Complexes. While ionic and neutral phosphorus-coordinated complexes allow insertion of most types of alkenes, N-donor complexes have a strong preference for strained alkenes. Norbornadiene is a special case since it is known to react with both double bonds during CO/alkene copolymerization, and the second double bond may allow the synthesis of dinuclear complexes. Reaction of norbornadiene with 2 equiv of **5** or **6** (eq 2) indeed produced the homoligated dinuclear complexes **9** and **10**, involving most probably **7b** and **8b** as intermediates. Although it could only be shown for the tmeda complex (**9**), we assume that both **9** and **10** occur in the *trans* configuration, *i.e.*, the complexes are C_2 symmetric (cf. the structure in the solid state, Figure 2). Molecular models suggest that the exclusive formation of this configuration is due to steric interactions between the N-donor ligands during insertion.

Nonstrained alkenes containing a potential donor group, *e.g.*, 2-vinylpyridine, do not insert but most probably only coordinate to the metal leading to unstable adducts resulting in rapid palladium metal deposition upon attempted isolation. Nonstrained alkenes that are activated by electron withdrawing substituents, like methyl methacrylate, insert but do not give stable complexes either. Strained norbornene-type alkenes do give stable insertion products, probably by excluding the possibility of β-elimination. The stability of the insertion products will be further enhanced by intramolecular coordination of the carbonyl group. This coordination is particularly efficient for strained alkenes as their rigid geometry forces the acyl group in the direction of the metal. In the case of styrene, only coordination of the acyl group prevents β-hydrogen elimination. Nevertheless, we found evidence for the formation of the insertion product, accompanied by several unidentified side products. This contrasts with the report by Brookhart *et al.* on the clean insertion of 4-*tert*-butylstyrene.[8j] It may be that either the low temperature (*ca.* −80 °C) used by Brookhart *et al.* in

Table 7. Final Coordinates (Å) and Equivalent Isotropic Thermal Parameters (Å^2) of the Non-Hydrogen Atoms for **8c**

atom	x	y	z	U_{eq}[a]
Pd	0.65102(5)	0.38322(2)	0.50879(2)	0.0452(1)
O(1)	0.6496(4)	0.2931(2)	0.59005(16)	0.0604(12)
N(1)	0.6521(5)	0.4793(2)	0.4337(2)	0.0475(14)
N(2)	0.8037(5)	0.4751(3)	0.5743(2)	0.0534(17)
C(1)	0.5665(6)	0.4807(3)	0.3638(3)	0.0557(19)
C(2)	0.5720(7)	0.5484(4)	0.3162(3)	0.073(3)
C(3)	0.6693(8)	0.6194(4)	0.3395(3)	0.078(2)
C(4)	0.7575(7)	0.6188(4)	0.4116(3)	0.070(2)
C(5)	0.7464(6)	0.5499(3)	0.4573(3)	0.0515(17)
C(6)	0.8313(6)	0.5457(3)	0.5359(3)	0.0533(17)
C(7)	0.9354(6)	0.6105(4)	0.5693(3)	0.070(2)
C(8)	1.0072(7)	0.6012(4)	0.6430(4)	0.079(3)
C(9)	0.9770(7)	0.5294(4)	0.6805(3)	0.081(3)
C(10)	0.8752(7)	0.4678(4)	0.6455(3)	0.072(2)
C(11)	0.5146(5)	0.2943(3)	0.4436(2)	0.0424(17)
C(12)	0.6005(6)	0.2589(3)	0.3811(3)	0.0509(17)
C(13)	0.4823(7)	0.1979(3)	0.3287(3)	0.0588(19)
C(14)	0.3077(7)	0.2266(4)	0.3050(3)	0.078(2)
C(15)	0.2080(8)	0.1694(4)	0.3394(3)	0.080(3)
C(16)	0.2971(9)	0.1019(5)	0.3779(3)	0.097(3)
C(17)	0.4735(7)	0.1160(3)	0.3775(3)	0.070(2)
C(18)	0.5848(7)	0.1408(3)	0.4520(3)	0.0613(19)
C(19)	0.4983(6)	0.2124(3)	0.4917(2)	0.0494(17)
C(20)	0.7176(6)	0.1921(3)	0.4239(3)	0.060(2)
C(21)	0.5776(6)	0.2235(3)	0.5702(3)	0.0546(19)
C(22)	0.5718(7)	0.1546(4)	0.6272(3)	0.074(2)
S	0.5723(2)	0.34398(10)	0.16786(8)	0.0684(6)
F(1)	0.4417(5)	0.4407(3)	0.0580(2)	0.1184(19)
F(2)	0.6442(7)	0.4977(3)	0.1312(3)	0.188(3)
F(3)	0.6839(5)	0.4031(4)	0.0533(2)	0.173(3)
O(2)	0.5077(6)	0.2716(3)	0.1221(3)	0.120(2)
O(3)	0.7341(5)	0.3324(3)	0.2058(2)	0.0997(19)
O(4)	0.4596(5)	0.3826(3)	0.20974(19)	0.0814(16)
C(23)	0.5900(9)	0.4240(5)	0.0995(4)	0.094(3)

[a] U_{eq} = 1/3 of the trace of the orthogonalized U.

the alkene insertion reaction slows down the decomposition and/or that the formation of a η^3-benzallyl species provides additional stabilization of the insertion product. In view of our results it seems less likely that the borate anion $[B(C_6H_3\{CF_3\}_2\text{-}3,5)_4]^-$ is involved.

The higher reactivity of the ionic complexes (**5** and **6**) compared to the neutral complexes (**2a**,**c** and **4a**,**c**; Scheme 3) will certainly be related to the better availability of a coordination site. However, Sen *et al.* found that an associative mechanism in which the alkene coordinates in an apical position prior to insertion cannot be fully ruled out even for monodentate phosphine containing complexes.[4d,7d] Our results show that it is not only the nature of the donor atoms of the ligand, *i.e.*, N or P, that influence the insertion reaction but that also the type of donating groups (amine or imine) together with the anion, alkene, and solvent are of importance. For instance, only norbornadiene reacts with all four neutral acetyl complexes, irrespective of the solvent and halide, whereas norbornene only reacts with the neutral bpy complexes (**4a**,**c**) in $CDCl_3$. The nature of the solvent is important since it will compete with the alkene for a coordination site on the metal. This may explain why norbornene does not insert in CD_3COCD_3 while it does so in the more weakly coordinating $CDCl_3$.

Finally, the ligand and the anion are important. Based on the order of *trans*-labilizing influence, *i.e.*, bpy, tmeda < Cl < Br < I < COMe,[19] it is the N-donor of the ligand *trans* to the acetyl group that is expected to dissociate. This would result in an unproductive intermediate because the incoming alkene and the acetyl group are *trans* positioned. The other possibility is that dissociation of the N-donor *trans* to the halide occurs which would result in a *cis*-configuration that allows migratory insertion leading to the insertion product. However, this pathway involves an unfavorable Jahn-Teller isomerization of

Table 8. Final Coordinates (Å) and Equivalent Isotropic Thermal Parameters (Å^2) of the Non-Hydrogen Atoms for **9**

atom	x	y	z	U_{eq}[a]
Pd(1)	0.80013(3)	−0.07745(4)	0.00035(1)	0.0234(1)
Pd(2)	0.89516(4)	0.12867(4)	0.20333(1)	0.0271(1)
O(1)	0.9085(4)	0.0633(4)	−0.00638(13)	0.0340(12)
O(2)	0.7392(4)	0.0368(4)	0.2057(2)	0.0390(14)
N(1)	0.7462(5)	−0.0726(5)	−0.0682(2)	0.0360(16)
N(2)	0.6940(4)	−0.2279(4)	0.0034(2)	0.0243(12)
N(3)	0.8540(5)	0.2303(5)	0.2617(2)	0.0353(16)
N(4)	1.0578(4)	0.2122(5)	0.2069(2)	0.0300(14)
C(1)	0.8525(7)	−0.0634(9)	−0.0987(2)	0.054(3)
C(2)	0.6651(8)	0.0295(7)	−0.0730(3)	0.054(3)
C(3)	0.6814(6)	−0.1843(6)	−0.0766(2)	0.0350(19)
C(4)	0.6158(6)	−0.2165(6)	−0.0360(2)	0.0347(17)
C(5)	0.7750(5)	−0.3320(5)	−0.0017(3)	0.0350(17)
C(6)	0.6195(6)	−0.2439(6)	0.0426(2)	0.0360(19)
C(7)	1.0609(7)	0.1861(7)	0.0226(2)	0.048(3)
C(8)	0.9719(5)	0.0878(6)	0.0258(2)	0.0313(17)
C(9)	0.9567(5)	0.0201(5)	0.0674(2)	0.0263(17)
C(10)	0.8551(5)	−0.0751(5)	0.0635(2)	0.0240(14)
C(11)	0.7652(5)	−0.0331(5)	0.0981(2)	0.0250(16)
C(12)	0.8207(5)	−0.0602(5)	0.1442(2)	0.0257(17)
C(13)	0.7304(6)	−0.0459(6)	0.1795(2)	0.0320(17)
C(14)	0.6278(7)	−0.1295(7)	0.1832(2)	0.045(2)
C(15)	0.9254(5)	0.0324(5)	0.1479(2)	0.0260(17)
C(16)	0.9101(5)	0.1014(5)	0.1050(2)	0.0267(17)
C(17)	0.7762(5)	0.1019(5)	0.0967(2)	0.0263(16)
C(18)	0.8032(9)	0.1585(7)	0.2970(2)	0.051(2)
C(19)	0.7631(7)	0.3214(7)	0.2486(2)	0.044(2)
C(20)	0.9668(7)	0.2839(6)	0.2755(2)	0.0387(19)
C(21)	1.0407(7)	0.3168(6)	0.2353(2)	0.0393(19)
C(22)	1.1462(6)	0.1310(7)	0.2264(2)	0.042(2)
C(23)	1.1095(7)	0.2561(6)	0.1653(2)	0.0397(19)
S(1)	0.8477(2)	0.5643(2)	0.13599(6)	0.0426(5)
F(1)	0.6815(5)	0.4811(5)	0.0839(2)	0.0730(19)
F(2)	0.8548(7)	0.3955(6)	0.0789(2)	0.102(3)
F(3)	0.7314(6)	0.3664(5)	0.1351(2)	0.083(2)
O(3)	0.7520(7)	0.6105(7)	0.1623(3)	0.084(3)
O(4)	0.8869(6)	0.6410(5)	0.1031(2)	0.0613(19)
O(5)	0.9389(6)	0.5102(6)	0.1614(2)	0.059(2)
C(24)	0.7758(10)	0.4463(7)	0.1080(3)	0.060(3)
S(2)	0.3482(2)	−0.0065(2)	0.11446(7)	0.0470(6)
F(4)	0.3345(6)	0.2076(6)	0.0865(3)	0.095(3)
F(5)	0.5106(5)	0.1315(7)	0.0808(3)	0.112(3)
F(6)	0.3769(7)	0.0812(7)	0.0359(2)	0.098(3)
O(6)	0.4166(5)	−0.1063(5)	0.1007(2)	0.0507(19)
O(7)	0.3769(7)	0.0353(7)	0.1567(2)	0.086(3)
O(8)	0.2219(4)	−0.0162(7)	0.1052(3)	0.074(3)
C(25)	0.3949(9)	0.1097(10)	0.0775(4)	0.072(4)

[a] U_{eq} = 1/3 of the trace of the orthogonalized U.

the three-coordinate intermediate. A third possibility involves (partial) Pd−X bond breaking (helped by solvation) to allow alkene coordination cis to the acetyl group. The important role played by the anion is suggested by the fast iodide-induced elimination of norbornene from $[Pd(C_7H_{10}COMe)(bpy)]OTf$ (**8a**) in acetone, and the unreactivity of the norbornadiene insertion product $[Pd(C_7H_8COMe)(bpy)]OTf$ (**8b**) in the same reaction. These results, together with the formation of **8a** from the deinsertion of 5-norbornene-*endo*-2,3-dicarboxylic anhydride during recrystallization of **13c**, strongly suggest that alkene insertion is an equilibrium which can be shifted under the correct conditions.

The molecular structures (Figures 1 and 2) of the ionic alkene insertion products $[Pd(C_{10}H_{12}COMe)(bpy)]OTf$ (**8c**) and $[(tmeda)Pd\{C_7H_8(COMe)_2\text{-}2,5\}Pd(tmeda)](OTf)_2$ (**9**) show several features. Firstly, as is normal observed in palladium chemistry, exclusive *cis*−*exo* addition to the alkene functionality is observed, as the *exo* face is more accessible than the *endo* face. Secondly, the insertion is regioselective as only the norbornene-type double bond of **8c** has reacted. A third feature is the strong coordination between the metal and the carbonyl oxygen. The Pd−O bond distances (2.016(5)−2.026(3) Å (Table 3) are

Table 9. Final Coordinates (Å) and Equivalent Isotropic Thermal Parameters (Å^2) of the Non-Hydrogen Atoms for **14**

atom	x	y	z	U_{eq}[a]
I	0.39269(3)	0.80551(3)	−0.02491(3)	0.0256(1)
Pd	0.17269(4)	0.79948(3)	0.04570(3)	0.0148(1)
O(1)	0.3186(4)	0.8727(3)	0.2552(3)	0.0220(11)
O(2)	0.1735(4)	0.7239(4)	0.3529(3)	0.0238(11)
O(3)	0.1150(4)	0.8881(4)	0.5634(3)	0.0322(14)
N(1)	0.0357(4)	0.8221(4)	−0.0862(3)	0.0191(12)
N(2)	−0.0069(4)	0.8239(4)	0.1022(3)	0.0167(12)
C(1)	0.0612(6)	0.8169(5)	−0.1806(4)	0.0220(17)
C(2)	−0.0262(6)	0.8497(5)	−0.2541(4)	0.0263(17)
C(3)	−0.1444(6)	0.8923(5)	−0.2274(4)	0.0235(17)
C(4)	−0.1745(5)	0.8969(5)	−0.1323(4)	0.0214(16)
C(5)	−0.0836(5)	0.8597(4)	−0.0631(4)	0.0173(12)
C(6)	−0.1072(5)	0.8600(4)	0.0403(4)	0.0163(14)
C(7)	−0.2255(5)	0.8923(5)	0.0760(5)	0.0221(16)
C(8)	−0.2435(5)	0.8864(5)	0.1719(5)	0.0246(16)
C(9)	−0.1420(6)	0.8500(5)	0.2336(4)	0.0225(17)
C(10)	−0.0251(5)	0.8200(5)	0.1958(4)	0.0216(17)
C(11)	0.2852(5)	0.7852(5)	0.1726(4)	0.0172(16)
C(12)	0.3343(5)	0.6613(5)	0.1645(4)	0.0188(16)
C(13)	0.2501(6)	0.5471(5)	0.0778(4)	0.0256(17)
C(14)	0.3406(7)	0.4431(5)	0.0573(5)	0.0316(19)
C(15)	0.3528(6)	0.4096(5)	0.1600(5)	0.0264(17)
C(16)	0.2673(6)	0.4984(5)	0.2252(4)	0.0241(17)
C(17)	0.3489(5)	0.6281(5)	0.2687(4)	0.0191(16)
C(18)	0.1534(6)	0.5072(5)	0.1373(5)	0.0276(17)
C(19)	0.2930(5)	0.7144(5)	0.3610(4)	0.0202(17)
C(20)	0.3957(5)	0.7734(5)	0.4644(4)	0.0199(17)
C(21)	0.4331(6)	0.6726(5)	0.5126(4)	0.0227(17)
C(22)	0.5590(6)	0.7238(6)	0.6020(5)	0.0292(17)
C(23)	0.5045(6)	0.8185(6)	0.6941(5)	0.0292(17)
C(24)	0.3548(6)	0.8116(6)	0.6433(5)	0.0266(17)
C(25)	0.3486(5)	0.8717(5)	0.5583(4)	0.0207(17)
C(26)	0.3202(6)	0.6753(6)	0.5764(5)	0.0310(17)
C(27)	0.2121(6)	0.9144(5)	0.5308(4)	0.0242(17)
C(28)	0.2070(6)	1.0044(6)	0.4732(5)	0.0304(17)
O(4)	0.3062(5)	0.3253(5)	0.6353(5)	0.062(2)
C(29)	0.1031(9)	0.3867(9)	0.5641(8)	0.078(4)
C(30)	0.2151(7)	0.3866(6)	0.6523(6)	0.039(2)
C(31)	0.2111(11)	0.4619(8)	0.7646(7)	0.077(4)

[a] U_{eq} = 1/3 of the trace of the orthogonalized U.

significantly shorter than those in the phosphine coordinated complex [Pd(C$_7$H$_{10}$COMe)(PPh$_3$)$_2$]BF$_4$ (2.114(6) Å),[7d] reflecting again the small *trans* influence of a nitrogen donor compared to phosphorus. Also the (C−O) stretching frequencies and ^{13}C NMR shifts (cf. Table 2) are in accord with strong Pd−O coordination.

Co-oligomerization of CO and Norbornene (Derivatives) on a Metal Center. In the reports published so far, the intermediates during CO/alkene copolymerization are either not isolated or the range of alkenes is limited to norbornadiene. The general route presented here allows the range of alkenes to be extended to other (less) strained alkenes and enables the complete characterization of all intermediates in the step-by-step co-oligomerization. It is now well-understood why a noncoordinating anion is needed in order to produce a good catalyst for the CO/alkene copolymerization. Firstly, ionic acylpalladium(II) complexes are more reactive toward alkenes than their neutral counterparts. Secondly, in order to obtain stable alkene insertion products it is essential that a noncoordinating anion is present (*e.g.*, OTf$^-$) as this allows coordination of the carbonyl group to prevent β-hydrogen elimination. The other propagation step, *i.e.*, the insertion of CO, has also been shown to be much faster for ionic alkyl complexes than for neutral ones.[8c] However, when isolation of the (intermediate) acyl complexes is desired, the presence of a well-coordinating anion (*i.e.*, a halide) to block the decarbonylation pathway is required. This is supported by an earlier study on the carbonylation of allylpalladium(II) complexes reported by Yamamoto *et al.*[20] They found that when complexes of the type [Pd(η^3-allyl)(PMe$_3$)]X (X = halide) were treated with CO (1 atm), the carbonylation products PdX(CO-allyl)(PMe$_3$) could be isolated within a few hours, whereas the corresponding BF$_4^-$ complexes did not undergo CO insertion within 1 day even at 20 atm. Moreover, treatment of the halide complexes with AgBF$_4$ resulted in rapid decarbonylation. They attributed these results to the blocking effect of the halide on the availability of a coordination site.

The second alkene insertion to give **13a−c** can be carried out in the absence of a CO atmosphere without apparent decarbonylation of the ionic acyl intermediate [Pd(COC$_7$H$_{10}$-COMe)(MeCN)(bpy)]OTf on the time scale of the reaction. Nevertheless, attempts to isolate the ionic acyl complex invariably failed and gave the decarbonylation product **8a** instead. This is also observed for the synthesis of **8a−e**, and thus it can be concluded that decarbonylation must be slower than alkene insertion. This is consistent with the reports on CO/alkene copolymerization.[4,5]

As described above, we carried out one more CO insertion into the Pd−C bond of **13a** in the presence of sodium iodide to give PdI(COC$_7$H$_{10}$COC$_7$H$_{10}$COMe)(bpy) (**14**). This neutral complex, which is the result of the stepwise anion-controlled sequential insertion reactions of norbornene, CO, norbornene, and CO starting from the acetyl complexes **4a−c**, is no less than a metal-bound co-oligomer of CO and norbornene. Although we did not pursue further extension of the chain, we expect this can be done at will. Of course, the complex will gradually develop a more organic character, and workup will become more difficult due to its enhanced solubility in hydrocarbons. The molecular structure of **14** (Figure 3) shows a *syn* positioning of the two norbornene moieties. This indicates that the orientation of the second norbornene before and during insertion is governed by the first inserted norbornene. This is consistent with reports on the stereospecific character of the copolymerization of CO with norbornene and other alkenes.[4,5]

Norbornadiene is a special case in these co-oligomerization reactions. As reported by Van Asselt *et al.*, it is the only alkene that allows the synthesis of metal-bound co-oligomers, starting from PdCl(COMe)(BIAN) (**16**), without the need to vary the anion with each successive step.[13] They attributed this to the rigidity of the BIAN ligand which, in their opinion, activates these complexes for this type of reactions. As we observed that the complexes **4a,c**, which contain the less rigid bpy ligand, show the same behavior, it is likely that the nature of the ligand is not the main factor determining the insertion of norbornadiene into the palladium−acyl bond in neutral complexes.

Concluding Remarks

We have shown that the stability of the various products obtained after either alkene or CO insertion is controlled by the type of anion present in the complex. Strongly coordinating anions (*e.g*, halides) stabilize the acyl complexes but destabilize the alkene insertion products, whereas noncoordinating anions (*e.g.*, trifluoromethanesulfonate) have the reverse effect. As a consequence of this, the alkene insertion step is reversible, and the equilibrium involved is controlled by the anion, the nature of the alkene and the solvent. By optimizing the reaction conditions, we are able to perform the copolymerization of strained alkenes, like norbornene and its derivatives, with carbon monoxide on a palladium(II) center with complete control of the intermediate steps. In principle, this route allows the synthesis of highly regioselectively functionalized copolymers. Moreover, since the stereoselectivity of the chain-growth is most probably controlled by the first alkene insertion, it is only necessary to control the stereochemistry of the first alkene

insertion step in order to prepare stereoregular copolymers. The dinuclear palladium−acyl complexes (**9** and **10**) are, in principle, potential bidirectional catalysts, which may allow the synthesis of copolymers with a much higher mean molecular weight. The work presented here complements the earlier reported studies and provides additional insight into factors that may also be important in catalytic CO/alkene copolymerization.

Experimental Section

General Procedures. All operations were conducted in an atmosphere of dry nitrogen using established Schlenk-type techniques. Pentane and diethyl ether were freshly distilled from sodium benzophenone ketyl; methylene chloride was distilled from calcium hydride. All other solvents were used as received. The solvents acetonitrile (p.a.) and acetone (p.a.), and the compounds 2,2′-bipyridyl, norbornene, norbornadiene, dicyclopentadiene, methyl methacrylate, styrene (p.a.), α-methylstyrene, cyclopentene, cyclohexene, cycloheptene, 2-vinylpyridine, methyl vinyl ketone, 2,3-dihydrofuran, maleic anhydride, sodium chloride (p.a.), and anhydrous sodium iodide (99+%) were obtained from Janssen Chimica. Carbon monoxide and ethylene was obtained from AGA gas BV. Silver trifluoromethanesulfonate (AgOTf) and dibenzylideneacetone were obtained from Aldrich. PdXMe(tmeda),[21] PdX(COMe)(tmeda),[8g] 5-norbornene-*endo*-2,3-dicarboxylic anhydride,[22a] and 7-oxa-5-norbornene-*exo*-2,3-dicarboxylic anhydride[22b] were prepared following literature procedures. $CDCl_3$, CD_3OD, and CD_3COCD_3 were obtained from ISOTEC Inc. ^1H (200 or 300 MHz) and ^{13}C (50 or 75 MHz) NMR spectra were recorded on Bruker AC200 or AC300 spectrometers at ambient temperature unless otherwise noted. Chemical shifts (δ) are given in ppm relative to tetramethylsilane. Elemental analyses were performed by the Institute for Applied Chemistry (TNO), Zeist, The Netherlands and by Dornis u. Kolbe, Mülheim a. d. Ruhr, Federal Republic of Germany.

Synthesis of PdXMe(2,2′-bipyridyl) (3a−c) and PdX(COMe)(2,2′-bipyridyl) (4a−c) *via* Ligand Exchange. The following synthesis of **4c** is a typical procedure: To a solution of 0.16 g (0.41 mmol) of PdI(COMe)(tmeda) (**2c**) in 50 mL of methylene chloride was added, at 0 °C, 0.20 g (1.28 mmol) of 2,2′-bipyridyl. After stirring the solution for 16 h the volatiles were evaporated *in vacuo*, and the residue washed with diethyl ether (3× 50 mL) and dried *in vacuo*: yield 0.15 g (85%). The complexes **3a−c** were obtained in similar yields, and the NMR spectra are identical to those reported by Canty and Byers.[12]

PdCl(COMe)(bpy) (4a): yield 89%; mp 163 °C dec; ^1H NMR (200 MHz, $CDCl_3$, δ) 2.64 (s, 3, $COCH_3$), 7.45 (m, 2, bpy), 7.9−8.2 (m, 4, bpy), 8.37 (d, J = 7.6 Hz, 1, bpy), 8.88 (d, J = 7.7 Hz, 1 bpy); ^{13}C NMR (50 MHz, $CDCl_3$, δ) 36.63 ($COCH_3$), 121.93, 122.90, 125.98, 126.62, 139.31, 139.45, 148.95, 150.70, 152.10, 154.49 (bpy), 231.54 (*C*O); IR spectrum (KBr, cm^{-1}) 1664 (CO). Anal. Calcd for $C_{12}H_{11}N_2ClOPd$: C 42.25; H, 3.25; N, 8.21. Found: C, 42.20; H, 3.31; N, 8.29.

PdBr(COMe)(bpy) (4b): yield 74%; mp > 200 °C dec; ^1H NMR (200 MHz, $CDCl_3$, δ) 2.67 (s, 3, $COCH_3$), 7.43 (m, 2, bpy), 7.9−8.4 (m, 5, bpy), 8.94 (d, J = 7.6 Hz, 1, bpy); ^{13}C NMR (50 MHz, $CDCl_3$, δ) 38.88 ($COCH_3$), 122.11, 123.05, 126.09, 126.66, 139.39, 149.74, 150.41, 152.07, 154.39 (bpy), 231.38 (*C*O); IR spectrum (KBr, cm^{-1}) 1665 (CO). Anal. Calcd for $C_{12}H_{11}N_2BrOPd$: C, 37.38; H, 2.88; N, 7.27. Found: 36.51; H, 2.70; N, 7.40.

PdI(COMe)(bpy) (4c): yield 85%; mp 181 °C dec; ^1H NMR (300 MHz, $CDCl_3$, δ) 2.71 (s, 3, $COCH_3$), 7.43 (m, 1, bpy), 7.49 (m, 1, bpy), 7.98 (m, 1, bpy), 8.11 (m, 2, bpy), 8.25 (m, 2, bpy), 9.16 (d, J = 4.7 Hz, 1, bpy); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 42.98 (CH_3), 121.84, 122.69, 126.28, 126.63, 138.96, 139.18, 150.13, 151.72, 152.27, 154.47 (bpy), 205.69 (*C*O). IR spectrum (KBr, cm^{-1}) 1678 (CO). Anal. Calcd for $C_{12}H_{11}N_2IOPd$: C, 33.32; H, 2.57; N, 6.48. Found: C, 33.19; H, 2.56; N, 6.35.

Synthesis of PdX(COMe)(2,2′-bipyridyl) (4a−c) *via* CO Insertion. The following is a typical procedure: Through an ice-cooled solution of 1.13 g (2.8 mmol) of PdIMe(bpy) (**3c**) in 100 mL of methylene chloride, CO was bubbled for 1 min after which the vessel was closed. Stirring was continued for 2.5 h after which the resulting solution was filtered through filter aid, and the volatiles were evaporated in vacuo to give pure **4c**. Yield 1.17 g (97%). The complexes **4a,b** were obtained in similar yields.

NMR Studies of Alkene Insertions into Neutral Acetyl Complexes. A solution of *ca.* 30 mg of the desired acetyl complex in 0.4 mL of $CDCl_3$ or CD_3COCD_3 was prepared and filtered through cotton wool. Subsequently, 1.1 equiv of the appropriate alkene was added, and the reaction followed by ^1H NMR until the reaction was finished or resonances due to decomposition became visible.

General Procedure for the Insertion of Alkenes. The following is a typical procedure: To an ice-cooled solution of 0.20 g of PdI(COMe)(bpy) (**4c**) in 50 mL of methylene chloride were added 2.0 mL of acetonitrile, 56.4 mg (0.60 mmol) of norbornene, and 0.16 g (0.62 mmol) of silver trifluoromethanesulfonate upon which a white solid immediately precipitated. After stirring for 3 h at 0 °C the solution was filtered through filter aid and the volatiles evaporated *in vacuo*. The resulting greenish-white product was washed once with 80 mL of diethyl ether and dried *in vacuo*: yield 0.23 g (91%). The products may be crystallized from acetone/pentane, methylene chloride/diethyl ether, or alcohols (methanol, ethanol).

[Pd(C_7H_{10}COMe)(tmeda)]OTf (7a): yield 93%; mp 89 °C dec; ^1H NMR (300 MHz, $CDCl_3$, δ) 1.30 (m, 4, nbn), 1.61 (m, 2, nbn), 2.07 (m, 2, nbn), 2.27 (s, 3, $COCH_3$), 2.41 (d, J = 3.9 Hz, 1, nbn), 2.57 (s, 3, NMe_2), 2.62 (s, 3, NMe_2), 2.65 (m, 4, nbn or tmeda), 2.66 (s, 3, NMe_2), 2.71 (s, 3, NMe_2), 2.97 (m, 1, nbn or tmeda); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 27.16 ($COCH_3$), 29.36, 29.57, 36.64, 41.62, 42.98, 47.71, 48.08, 48.56, 50.58, 52.68, 56.72, 64.04, 71.01 (alkyl, nbn + tmeda), 238.70 (CO[23]); IR spectrum (KBr, cm^{-1}) 1595 (CO). Anal. Calcd for $C_{16}H_{29}N_2F_3O_4PdS$: C, 37.76; H, 5.75; N, 5.50. Found: C, 37.13; H, 5.21; N, 5.58.

[Pd(C_7H_8COMe)(tmeda)]OTf (7b): yield 93%; mp 109 °C dec; ^1H NMR (300 MHz, CD_3COCD_3, δ) 1.38 (d, J = 9.2 Hz, 1, nbd), 1.62 (d, J = 9.5 Hz, 1, nbd), 1.70 (dd, J = 6.2 and 2.5 Hz, 1, nbd), 2.56 (s, 3, $COCH_3$), 2.6−3.2 (m, 18, tmeda + nbd), 3.38 (s, 1 nbd), 6.32 (m, 2, alkenyl, nbd); ^{13}C NMR (75 MHz, CD_3COCD_3, δ) 27.45 ($COCH_3$), 39.59, 45.31, 47.49, 47.97, 48.33, 49.40, 51.25, 52.61, 57.40, 63.67, 64.80 (alkyl, nbd + tmeda), 129.59, 132.94 (alkenyl, nbd), 239.28 (*C*O); IR spectrum (KBr, cm^{-1}) 1607 (CO).

[Pd($C_{10}H_{12}$COMe)(tmeda)]OTf (7c): yield 91%; mp 117 °C dec; ^1H NMR (300 MHz, $CDCl_3$, δ) 1.58 (t, J = 10.0 Hz, 1, diCp), 1.8−3.3 (m, 28, tmeda + diCp), 5.4−5.8 (mmmm, 4, alkenyl, diCp, isomer ratio 1:1.1); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 26.90, 27.06 ($COCH_3$); 32.43, 32.58, 39.00, 39.32, 39.71, 42.00, 42.57, 44.00, 44.36, 45.76, 46.43, 47.30, 47.62, 48.62, 48.92, 50.00, 50.58, 52.42, 52.70, 52.74, 53.15, 56.65, 64.11, 65.05, 67.61 (alkyl, tmeda + diCp), 130.71, 131.43, 131.74, 133.05 (alkenyl, diCp), 239.61, 240.77 (*C*O); IR spectrum (KBr, cm^{-1}) 1605 (CO). Anal. Calcd for $C_{19}H_{31}N_2F_3O_4PdS$: C, 41.72; H, 5.71; N, 5.12. Found: C, 41.66; H, 5.64; N, 5.18.

[Pd(C_7H_{10}COMe)(bpy)]OTf (8a): yield 91%; mp 115 °C dec; ^1H NMR (300 MHz, $CDCl_3$, δ) 1.36 (d, J = 10.2 Hz, 1, nbn), 1.47 (m, 2, nbn), 1.74 (m, 2, nbn), 1.90 (d, J = 10.2 Hz, 1, nbn), 2.26 (s, br, 1, nbn), 2.48 (s, 3, $COCH_3$), 2.57 (s, br, 1, nbn), 2.69 (d, J = 4.5 Hz, 1, nbn), 2.91 (d, J = 6.3 Hz, 1, nbn), 7.64 (m, 2, bpy), 8.21 (m, 2, bpy), 8.34 (d, 1, bpy), 8.56 (m, 3, bpy); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 27.44 ($COCH_3$), 29.58, 29.67, 36.94, 43.05, 43.33, 53.01, 70.82 (nbn), 123.34, 124.36, 127.38, 127.77, 140.64, 140.87, 148.62, 150.59, 152.11, 156.50 (bpy), 240.83 (CO[23]); IR spectrum (KBr, cm^{-1}) 1598 (CO). Anal. Calcd for $C_{20}H_{21}N_2F_3O_4PdS$: C, 43.77; H, 3.86; N, 5.10. Found: C, 43.49; H, 3.97; N, 5.19.

[Pd(C_7H_8COMe)(bpy)]OTf (8b): yield 83%; mp 153 °C dec; ^1H NMR (300 MHz, $CDCl_3$, δ) 1.47 (d, J = 8.9 Hz, 1, nbd), 1.79 (d, J = 8.9 Hz, 1, nbd), 2.21 (dd, J = 6.0 and 2.2 Hz, 1, nbd), 2.59 (s, 3, $COCH_3$), 2.69 (d, J = 5.9 Hz, 1, nbd), 2.94 (s, 1, nbd), 3.20 (s, 1, nbd), 6.24 (m, 2, alkenyl, nbd), 7.65 (m, 1, bpy), 7.72 (m, 1, bpy), 8.20 (m, 2, bpy), 8.43 (d, J = 5.4 Hz, 1, bpy), 8.54 (m, 2, bpy), 8.60 (d, J = 5.7 Hz, 1, bpy); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 27.58 ($COCH_3$), 45.81, 46.33, 47.71, 48.81, 63.48 (alkyl, nbd), 123.58, 124.65, 127.33, 127.83, 133.47, 136.30, 140.75, 140.99, 148.35, 150.34, 152.26, 156.58

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(bpy + alkenyl, nbd), 239.01 (*C*O); IR spectrum (KBr, cm^{-1}) 1603 (CO). Anal. Calcd for $C_{20}H_{19}N_2F_3O_4PdS$: C, 43.93; H, 3.50; N, 5.12. Found: C, 43.76; H, 3.58; N, 5.15.

[Pd($C_{10}H_{12}$COMe)(bpy)]OTf (8c): yield 85%; mp 141 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.65 (m, 6, alkyl and H_2O), 2.1−3.3 (m, 12, alkyl), 5.6−5.9 (mmm, 2, alkenyl, isomer ratio *ca.* 1:1.7), 7.64 (m, 2, bpy), 8.24 (m, 3, bpy), 8.62 (m, 3, bpy); ^{13}C NMR (75 MHz, CD_2Cl_2, δ) 29.00, 29.16 (CO*C*H_3), 34.38, 34.86, 41.10, 41.64, 44.33, 44.69, 46.28, 47.73, 48.72, 49.14, 49.87, 50.96, 66.91, 69.46 (alkyl, diCp), 124.82, 125.83, 125.88, 129.35, 129.55, 132.87, 133.67, 133.89, 134.92, 142.42, 142.59, 142.61, 150.65, 152.16, 152.32, 154.12, 158.69, 158.73 (bpy + alkenyl, diCp), 243.45, 244.68 (*C*O[23]); IR spectrum (KBr, cm^{-1}) 1601 (CO). Anal. Calcd for $C_{23}H_{23}N_2F_3O_4PdS$: C, 47.07; H, 3.95; N, 4.77. Found: C, 46.31; H, 3.89; N, 4.67.

[Pd($C_9H_8O_3$COMe)(bpy)]OTf (8d): yield 93%; mp 167 °C dec; ^{1}H NMR (300 MHz, CD_3COCD_3, δ) 1.98 (d, J = 10.9 Hz, 1 $C_9H_8O_3$), 2.39 (d, J = 10.9 Hz, 1, $C_9H_8O_3$), 2.66 (s, 3, COCH_3), 2.85 (m, 2, $C_9H_8O_3$), 3.23 (d, J = 6.7 Hz, 1, $C_9H_8O_3$), 3.33 (d, J = 5.4 Hz, 1, $C_9H_8O_3$), 3.71 (m, 1, $C_9H_8O_3$), 3.94 (m, 1, $C_9H_8O_3$), 7.90 (m, 2, bpy), 8.39 (m, 3, bpy), 8.66 (m, 2, bpy), 8.79 (d, J = 5.2 Hz, 1, bpy); ^{13}C NMR (50 MHz, CD_3CN, δ) 28.29 (CO*C*H_3), 41.11, 43.90, 45.83, 45.93, 50.42, 51.30, 66.68 (alkyl, $C_9H_8O_3$), 124.11, 125.08, 128.87, 128.99, 141.93, 142.02, 149.75, 151.34, 153.31, 157.81 (bpy), 173.01, 174.14 (*C*O, $C_9H_8O_3$), 242.52 (*C*OCH_3); IR spectrum (KBr, cm^{-1}) 1604 (CO). Anal. Calcd for $C_{22}H_{19}N_2F_3O_7PdS$: C, 42.70; H, 3.09; N, 4.53. Found: C, 42.61; H, 3.15; N, 4.46.

[Pd($C_8H_6O_4$COMe)(bpy)]OTf (8e): yield 96%; mp 165 °C dec; ^{1}H NMR (300 MHz, CD_3CN, δ) 2.57 (3, s, COCH_3), 2.89 (d, J = 7.0 Hz, 1, $C_8H_6O_4$), 3.47 (d, J = 7.0 Hz, 1, $C_8H_6O_4$), 3.64 (AB, 2, $C_8H_6O_4$), 4.87 (s, 1, $C_8H_6O_4$), 5.24 (s, 1, $C_8H_6O_4$), 7.72 (m, 2, bpy), 8.26 (m, 4, bpy), 8.43 (d, J = 5.3 Hz, 1, bpy), 8.55 (d, J = 5.3 Hz, 1, bpy); ^{13}C NMR (50 MHz, CD_3CN, δ) 28.54 (CO*C*H_3), 43.97, 51.25, 51.54, 68.46, 83.94, 87.26 (alkyl, $C_8H_6O_4$), 124.08, 125.01, 128.82, 129.05, 141.95, 142.10, 149.77, 152.62, 153.57, 157.77 (bpy), 171.57, 172.71 (*C*O, $C_8H_6O_4$), 239.54 (*C*OCH_3); IR spectrum (KBr, cm^{-1}) 1604 (CO). Anal. Calcd for $C_{21}H_{17}N_2F_3O_8PdS$: C, 40.63; H, 2.76; N, 4.51. Found: C, 40.51; H, 2.87; N, 4.58.

Synthesis of [(tmeda)Pd{C_7H_8(COMe)$_2$-2,5}Pd(tmeda)](OTf)$_2$ (9). To an ice-cooled solution of 0.57 g (1.5 mmol) of PdI(COMe)(tmeda) (**2c**) in 25 mL of methylene chloride was added 1 mL of acetonitrile and 0.38 g (1.5 mmol) of silver trifluoromethanesulfonate. To the resulting white suspension, a solution of 0.07 g (0.76 mmol) of norbornadiene in 20 mL of methylene chloride was added dropwise over *ca.* 15 min. After stirring the solution for 3 h at 0 °C and overnight at ambient temperature, the greyish suspension was filtered through filter-aid. The volatiles were then removed *in vacuo* to yield 0.72 g (107%) of a yellow oil. Solid **9** was obtained from methanol/diethyl ether: yield 0.33 g (49%) of light-yellow needles; mp 134 °C dec; ^{1}H NMR (300 MHz, CD_3COCD_3, δ) 1.83 (s, 2, nbd), 2.39 (d, J = 6.6 Hz, 2, nbd), 2.46 (s, 6, COCH_3), 2.65 (d, J = 4.6 Hz, 2, nbd), 2.68 (s, 6, NMe_2), 2.75 (s, 6, NMe_2), 2.80 (m, 4, $-CH_2-$, tmeda); 2.88 (m, 8, tmeda); 2.94 (s, 6 NMe_2), 3.02 (t, J = 5.5 Hz, 2, $-CH_2-$, tmeda), 3.11 (d, J = 6.5 Hz, 2, nbd); ^{13}C NMR (50 MHz, CD_3COCD_3, δ) 27.59 (CO*C*H_3); 35.41, 45.91, 48.10, 48.34, 48.73, 51.73, 52.61, 57.38, 64.69, 71.03 (nbd + tmeda), 238.62 (*C*O); IR (KBr, cm^{-1}) 1606 (CO). Anal. Calcd. for $C_{25}H_{46}N_4F_6O_8Pd_2S_2$: C, 32.58; H, 5.03; N, 6.08. Found: C, 32.54; H, 4.92; N, 6.25.

Synthesis of [(bpy)Pd{C_7H_8(COMe)$_2$-2,5}Pd(bpy)](OTf)$_2$ (10). To an ice-cooled solution of 0.55 g (1.3 mmol) of PdI(COMe)(bpy) (**4c**) in 50 mL of methylene chloride was added 1 mL of acetonitrile and 0.34 g (1.3 mmol) of silver trifluoromethanesulfonate. To the resulting white suspension, a solution of 0.06 g (0.65 mmol) of norbornadiene in 20 mL of methylene chloride was added dropwise over *ca.* 15 min. After stirring the solution for 3 h at 0 °C and overnight at ambient temperature, the greyish suspension was filtered through filter-aid, and the residue washed with 2 × 100 mL of acetonitrile. The volatiles were then removed *in vacuo* to give a light yellow solid. The product was washed with 3 × 30 mL of diethyl ether and 3 × 30 mL of methylene chloride and subsequently dried *in vacuo*: yield 0.30 g (47%). The product is only slightly soluble in acetonitrile, while it is insoluble in methylene chloride, alcohols, and acetone: mp 154 °C dec; IR (KBr, cm^{-1}) 1601 (CO). Anal. Calcd for $C_{33}H_{30}N_4F_6O_8Pd_2S_2$: C, 39.57; H, 3.02; N, 5.59. Found: C, 39.36; H, 3.10; N, 5.68.

Synthesis of PdCl(COC$_7$H$_{10}$COMe)(bpy) (12a). To a cold (−30 °C) solution of 2.59 g (4.7 mmol) [Pd(C_7H_{10}COMe)(bpy)]OTf (**8c**) in 150 mL of acetone was added 6.34 g (108.5 mmol) of sodium chloride. Carbon monoxide (1 atm) was bubbled through the suspension for 2 min after which the reaction mixture was stirred at −30 °C for 1 h. This procedure was repeated seven times. The mixture was diluted with 50 mL of methylene chloride and subsequently filtered through filter aid. After concentrating the filtrate to a few milliliters, 80 mL of pentane were added, and the bright yellow precipitate was collected. Recrystallization was done from methylene chloride/pentane: yield 83%; mp 122 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.0−1.7 (m, 6, nbn), 2.22 (s, 3, COCH_3), 2.47 (s, 1, nbn), 2.60 (d, J = 9.2 Hz, 1, nbn), 3.18 (s, 1, nbn), 4.02 (d, J = 9.2 Hz, 1, nbn), 7.43 (m, 2, bpy), 8.07 (m, 4, bpy), 8.31 (d, J = 4.6 Hz, 1, bpy), 8.87 (d, J = 4.7 Hz, 1, bpy); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 29.00, 29.12 (nbn), 31.46 (CO*C*H_3), 34.98, 38.81, 39.16, 58.64, 67.62 (nbn), 121.69, 122.46, 125.93, 126.60, 139.08, 139.36, 149.20, 151.34, 152.33, 154.50 (bpy); 210.92, 230.63 (*C*O); IR spectrum (KBr, cm^{-1}) 1672, 1710 (CO). Anal. Calcd for $C_{20}H_{21}N_2ClO_2Pd$: C, 51.85; H, 4.57; N, 6.05. Found: C, 51.36; H, 4.50; N, 5.84.

Synthesis of PdI(COC$_7$H$_{10}$COMe)(bpy) (12b). This complex was prepared similarly to **12a** using 20 equiv of sodium iodide, although the insertion procedure was repeated only 4 times: yield 93%; mp 144 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.12 (m, 2, nbn), 1.49 (m, 4, nbn), 2.30 (s, 3, COCH_3), 2.51 (m, 2, nbn), 3.45 (s, br, 1, nbn), 3.96 (d, J = 9.3 Hz, 1, nbn), 7.44 (m, 1, bpy), 7.51 (m, 1, bpy), 7.99 (m, 1, bpy), 8.10 (m, 3, bpy), 8.33 (d, J = 4.6 Hz, 1, bpy), 9.25 (d, J = 5.2 Hz, 1, bpy); ^{13}C NMR (50 MHz, CD_2Cl_2, δ) 28.89, 29.24 (nbn), 32.29 (CO*C*H_3), 35.38, 38.54, 39.37, 58.34, 75.05 (nbn), 122.21, 122.87, 126.12, 126.51, 139.19, 139.28, 150.76, 151.54, 152.34, 154.33 (bpy), 211.37, 299.73 (*C*O); IR spectrum (KBr, cm^{-1}) 1663, 1706 (CO). Anal. Calcd for $C_{20}H_{21}N_2IO_2Pd$: C, 43.30; H, 3.82; N, 5.05. Found: C, 42.75; H, 3.84; N, 4.81.

Alternative Synthesis of 12b. To an ice-cold solution of 0.05 g (0.11 mmol) of **12a** in 25 mL of acetone was added 0.07 g (0.47 mmol) of sodium iodide. The mixture was stirred at 0 °C for 3 h after which the white precipitate was filtered off, and the filtrate was concentrated to a few milliliter. Addition of 50 mL of pentane gave pure orange-colored **12b**, which was dried *in vacuo*: yield 83%.

Synthesis of [Pd(C_7H_{10}COC$_7$H$_{10}$COMe)(bpy)]OTf (13a). This complex was obtained *via* the general alkene insertion procedure: yield 86%; mp 121 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.2−1.9 (m, 10, nbn), 2.00 (s, br, 1, nbn), 2.09 (m, 1, nbn), 2.26 (s, 4, nbn + COCH_3), 2.48 (s, br, 1, nbn), 2.53 (d, J = 6.0 Hz, 1, nbn), 2.62 (d, J = 2.6 Hz, 1, nbn), 2.67 (d, J = 3.5 Hz, 1, nbn), 2.74 (d, J = 5.2 Hz, 1, nbn), 3.02 (d, J = 9.1 Hz, 1, nbn), 3.42 (d, J = 9.1 Hz, 1, nbn), 7.65 (m, 2, bpy), 8.20 (m, 2, bpy), 8.38 (d, J = 5.2 Hz, 1, bpy), 8.50 (m, 3, bpy); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 28.59, 28.75, 29.09, 29.22, 30.45, 35.56, 37.48, 39.39, 40.66, 43.33, 44.25, 52.33, 52.95, 65.32, 70.49 (nbn + CO*C*H_3), 123.34, 124.28, 127.47, 127.57, 140.62, 140.72, 148.45, 150.35, 152.10, 156.48 (bpy), 208.00, 243.39 (*C*O); IR spectrum (KBr, cm^{-1}) 1582, 1708 (CO). Anal. Calcd for $C_{28}H_{31}N_2F_3O_5PdS$: C, 50.12; H, 4.66; N, 4.17. Found: C, 49.96; H, 4.78; N, 4.13.

Synthesis of [Pd(C_7H_8COC$_7$H$_{10}$COMe)(bpy)]OTf (13b). This complex was obtained *via* the general alkene insertion procedure: yield 89%; mp 147 °C dec; ^{1}H NMR (200 MHz, CD_3COCD_3, δ) 1.3−1.8 (m, 8H, nbn), 2.02 (m, 1, nbn), 2.28 (s, 3, COCH_3), 2.32 (m, 2, nbn), 2.55 (m, 1, nbn), 2.75 (m, 2, nbn), 3.13 (m, 1 nbn), 3.40 (m, 2, nbn), 3.75 (m, 1, nbn), 6.33 (m, 2, nbd), 7.88 (m, 2, bpy), 8.35 (m, 2, bpy), 8.65 (m, 2, bpy), 8.78 (m, 2, bpy); ^{13}C NMR (75 MHz, CD_3COCD_3, δ) 28.59 (CO*C*H_3), 35.98, 40.12, 41.65, 45.75, 46.29, 49.10, 50.51, 53.46, 63.67, 65.92, (alkyl), 124.01, 124.89, 128.66, 128.94, 133.53, 135.09, 141.61, 149.55, 152.21, 153.53, 157.58 (alkenyl + pyridyl), 208.17, 243.53 (CO); IR spectrum (KBr, cm^{-1}) 1587, 1698 (CO). Anal. Calcd for $C_{56}H_{58}N_4AgF_6IO_{10}Pd_2S_2$: C, 42.76; H, 3.72; N, 3.56. Found: C, 41.95; H, 3.62; N, 3.48.

Synthesis of [Pd($C_9H_8O_3$COC$_7$H$_{10}$COMe)(bpy)]OTf (13c). This complex was prepared *via* the general alkene insertion procedure but could not be purified: yield 72%; IR spectrum (KBr, cm^{-1}) 1601, 1698, 1778 (CO).

Synthesis of PdI(COC$_7$H$_{10}$COC$_7$H$_{10}$COMe)(bpy) (14). This complex was prepared similarly to **12b**: yield 93%; mp 118 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.07 (d, J = 9.9 Hz, 1, nbn), 1.19 (m, 3,

nbn), 1.57 (m, 8, nbn), 2.27 (m, 4, nbn + $COCH_3$), 2.54 (m, 3, nbn), 2.78 (d, J = 9.3 Hz, 1, nbn), 3.48 (d, J = 9.1 Hz, 2, nbn), 3.99 (s, br, 1, nbn), 7.42 (m, 1, bpy), 7.61 (m, 1, bpy), 8.10 (m, 4, bpy), 8.26 (d, J = 5.0 Hz, 1, bpy), 9.21 (d, J = 4.6 Hz, 1, bpy); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 28.51, 29.02, 29.51, 30.02, 31.23, 35.29, 36.21, 38.43, 39.28, 41.06, 41.30, 53.62, 55.04, 57.40, 63.08, 76.33 (nbn + $COCH_3$), 121.79, 122.43, 126.39, 126.96, 139.12, 139.20, 151.40, 151.80, 152.41, 154.55 (bpy), 210.79, 213.34, 232.73 (CO); IR spectrum (KBr, cm^{-1}) 1669, 1715 (CO). Anal. Calcd for $C_{28}H_{31}N_2IO_3Pd$: C, 49.68; H, 4.62; N, 4.14. Found: C, 47.86; H, 4.67; N, 3.91.

Spin-Saturation Transfer Measurements. Lattice relaxation times were obtained using standard Inversion Recovery methods (11 data points, 90°(180°) pulse width: 8 (16) μs, relaxation delay: 25 s, 8 scans per data point) at sample concentrations of *ca.* 50 mg mL^{-1}. The temperature (± 1 °C) was checked externally against CD_3OD. The spectra for the Forsén–Hoffman experiments[14] were measured using the $(T_d\text{-}\pi/2)_n$ pulse sequence with a presaturation time (T_d) of 25 s, relaxation delay = 25 s, pulse width 4 μs.

X-ray Structure Determination of 8c, 9, and 14. Crystals of **8c**, **9**, and **14**, suitable for X-ray diffraction, were glued to the tip of a glass fiber or sealed in a Lindemann glass capillary (**8c**) and transferred to an Enraf-Nonius CAD4-Turbo diffractometer with rotating anode (Mo Kα radiation, graphite monochromator, λ = 0.710 73 Å). Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of 25 well-centered reflections (SET4) in the range 14.2° < θ < 17.8°, 11.4 < θ < 12.9°, and 9.9° < θ < 13.9° for **8c**, **9**, and **14**, respectively. Reduced-cell calculations did not indicate higher lattice symmetry.[24] Crystal data and details on data collection and refinement are collected in Table 6. Data were corrected for *Lp* effects and for the observed linear decay of the reference reflections. For complexes **8c** and **14** the standard deviations of the intensities, as obtained by counting statistics, were increased according to an analysis of the excess variance of the reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + (pI)^2$ with p = 0.04 and 0.03 for **8c** and **14**, respectively.[25] An empirical absorption/extinction correction was applied for all complexes (DIFABS[26]). The structures were solved by automated Patterson methods and subsequent difference Fourier techniques (SHELXS86[27] for **8c** and DIRDIF-92[28] for **9** and **14**). Complexes **8c** and **14** were refined on F by full-matrix least-squares techniques (SHELX76[29]). Complex **9** was refined on F^2 (SHELXL93[30]); no observance criterium was applied during refinement. Hydrogen atoms were included in the refinement on calculated positions, riding on their carrier atoms. After anisotropic refinement of the non-hydrogen atoms of **9** and introduction of the hydrogen atoms at expected positions, an R-value of 0.093 was obtained. A difference Fourier revealed a large number of residual density peaks (app. 2.4 e $Å^{-3}$) in two symmetry-related channels, running parallel to the b-axis and located at x = 0, z = 3/4 and at x = 1/2, z = 1/4. No discrete solvent model could be refined. The BYPASS procedure,[31] as implemented in the program PLATON,[32] was used to take this electron density into account. A total number of 93.5 electrons were found in the two channels, which had a volume of 205.7 $Å^3$ each. The channels are probably filled with diethyl ether, which was used in crystallization. The non-hydrogen atoms of all three structures were refined with anisotropic thermal parameters. The hydrogen atoms of **8c** were refined with two overall isotropic thermal parameters with values of 0.111(12) and 0.072(4) $Å^2$ for the hydrogen atoms of the methyl group and the other hydrogen atoms, respectively. The hydrogen atoms of **9** were refined with a fixed isotropic thermal parameter amounting to 1.5 or 1.2 times the value of the equivalent isotropic thermal parameter of their carrier atoms, for the methyl hydrogen atoms and the other hydrogen atoms, respectively. The hydrogen atoms of **14** were refined with two overall isotropic thermal parameters with values of 0.18(3) and 0.041(3) $Å^2$ for the hydrogen atoms located in the acetone solvent molecule and the hydrogen atoms in the palladium complex, respectively. The Flack x parameter,[33] derived during the structure-factor calculation of **9**, amounted to 0.50(5), indicating a possible racemic twin. Refinement of a twin model resulted in better $wR2$ values and a component ratio of 0.49(4):0.51. Positional parameters are listed in Tables 7–9 for **8c**, **9**, and **14**, respectively. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography[34] for **9**. Complexes **8c** and **14** were refined using neutral atom scattering factors taken from Cromer and Mann[35] amplified with anomalous dispersion corrections from Cromer and Liberman.[36] Geometrical calculations and illustrations were performed with PLATON;[32] all calculations were performed on a DECstation 5000 cluster.

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Supplementary Material Available: Further details of the structure determinations, including atomic coordinates, bond lengths and angles, and thermal parameters for **8c**, **9**, and **14** (14 pages). [Further details for the structure determinations of **8c** and **14** are available as supplementary material to the preliminary reports (refs 8h and 8l, respectively).]; tables of observed and calculated structure factors (60 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(23) Incorrectly reported in an earlier communication (ref. 8h).
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