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Insertion of Carbon Monoxide and Alkenes in Palladium–Carbon Bonds of Complexes Containing Rigid Bidentate Nitrogen Ligands: The First Example of Isolated Complexes in Stepwise Successive Insertion Reactions on the Way to Polyketones[1]

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Abstract: Facile successive insertion of carbon monoxide and strained alkenes has been observed for both neutral Pd(R)X(Ar-BIAN) and cationic [Pd(R)(MeCN)(Ar-BIAN)]SO_3CF_3 complexes, i.e., complexes containing the rigid bidentate nitrogen ligands bis(arylimino)acenaphthene (Ar-BIAN; Ar = *p*-$MeOC_6H_4$ (*p*-An), *p*-MeC_6H_4 (*p*-Tol), *o,o′*-*i*-$Pr_2C_6H_3$), leading to the formation of new multiple insertion products of the type Pd{CH(R′)CH(R′)C(O)-CH(R′)CH(R′)C(O)R}X(Ar-BIAN). It appears that the rigidly chelating Ar-BIAN ligands have an activating effect on the insertion of CO and alkenes in palladium–carbon bonds as compared to other (bidentate) phosphorus and nitrogen ligands and a stabilizing effect on the Pd–acyl and Pd–alkyl complexes formed. Insertion of carbon monoxide was completed within 1 min (R = Me, X = Cl, I; R = $PhCH_2$, X = Br; R = *p*-MeC_6H_4, X = I), except in the case of RX = *p*-$NO_2C_6H_4CH_2Br$, where insertion required 4 h to go to completion. Insertion of norbornadiene, norbornene, and dicyclopentadiene in the cationic acyl complexes [Pd(C(O)Me)(MeCN)(Ar-BIAN)]SO_3CF_3 occurred instantaneously. Reaction of norbornadiene with the neutral acyl complexes Pd(C(O)Me)Cl(Ar-BIAN) resulted in rapid quantitative insertion, whereas in the case of norbornene and dicyclopentadiene longer reaction times were needed and mixtures of the starting materials and the insertion products were formed. All complexes isolated after alkene insertion have a similar structure, arising from *cis* addition of PdC(O)R to the exo face of the alkene, with the acyl oxygen atom coordinating to the palladium and the chloride or trifluoromethanesulfonate present as anion. After insertion of norbornadiene in the neutral acyl palladium complex, the resulting alkylpalladium compound [Pd(C_7H_8C(O)Me)-(*p*-An-BIAN)] Cl reacted further with carbon monoxide to give the isolable complex Pd(C(O)C_7H_8C(O)Me)Cl(*p*-An-BIAN) (**13a**), whereas the analogous trifluoromethanesulfonate complex did not show any reaction with carbon monoxide. The acyl complexes **13a** reacted again with norbornadiene to yield quantitatively [Pd(C_7H_8C(O)-C_7H_8C(O)Me)(*p*-An-BIAN)]Cl (**14a**), which reacted with $AgSO_3CF_3$ to give [Pd(C_7H_8C(O)C_7H_8C(O)Me)(*p*-An-BIAN)]SO_3CF_3 (**15a**). These new complexes **13–15a**, formed by stepwise successive insertion reactions of carbon monoxide and alkenes, have been isolated and were fully characterized for the first time and constitute a living oligomer system that may insert further molecules of CO and norbornadiene.

Introduction

Transition-metal-catalyzed carbonylation reactions have found wide application, both in synthesis and in industry.[2] One special class of carbonylation reactions concerns the copolymerization of alkenes and carbon monoxide,[3–5] leading to the formation of polyketones, a reaction which is very efficiently catalyzed by complexes of the type PdX_2(L–L) (L–L is a chelating phosphorus or nitrogen ligand, X is a weakly or noncoordinating anion). The reaction is proposed to proceed via a perfectly alternating sequence of carbon monoxide and alkene insertions in palladium–carbon bonds (Scheme 1),[4b,h] An alternative mechanism involving palladium carbene intermediates, explaining the formation of spiroketals as the initial products,[4g,5c] has recently been proposed.[5c]

A lot of experimental[2] and theoretical[6] research has been devoted to insertion of carbon monoxide in metal–carbon bonds, which can be regarded as a fundamental step in the copolymerization reactions. Studies on square-planar 16-electron complexes of palladium(II) or platinum(II) containing phosphine ligands have revealed that insertion of carbon monoxide occurs

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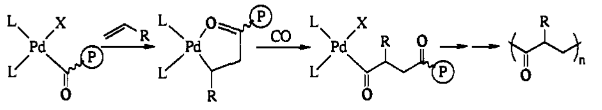
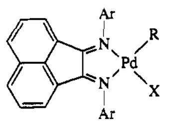
Scheme 1



preferentially from a four-coordinate complex, formed by substitution of a phosphine ligand by CO.[7] However, the carbonylation of complexes with more rigid chelating ligands, such as bidentate N–N or tridentate N–N–N ligands,[8,9] has revealed evidence that other low-energy pathways for insertion of carbon monoxide might also be available. Such mechanisms include insertion from a four-coordinate cationic intermediate formed via dissociation of the halide or from a five-coordinate complex.

Alkenes insert readily into palladium–carbon bonds, as demonstrated by numerous examples of the Heck reaction.[10] Furthermore, a variety of complexes formed by insertion of (strained) alkenes in palladium–acyl bonds has been isolated.[11] From a theoretical study on alkene insertions in platinum–hydride bonds, it appeared that insertion from a four-coordinate intermediate is the preferred reaction pathway.[12] Intramolecular insertions of alkynes and alkenes in palladium–carbalkoxy bonds were shown to proceed via a four-coordinate intermediate,[11a] but intramolecular alkene insertions in platinum–hydride bonds were proposed to occur via a five-coordinate intermediate.[7e] Five-coordinate intermediates might play a role in the intermolecular insertion of alkenes in palladium–acyl bonds, as can be derived from the complex kinetics of the insertion reactions[11c] and the facile insertion of alkenes in palladium–carbon bonds of complexes containing rigidly chelating bidentate and tridentate ligands.[9]

We investigated the insertion of carbon monoxide and alkenes in palladium–carbon bonds of complexes bearing the rigid bidentate nitrogen donor ligands bis(arylimino)acenaphthene (Ar-BIAN) because of the observation that carbon monoxide and alkenes can be incorporated in the organic products of the Pd(Ar-BIAN)-[13] or Pd–phosphine[14]-catalyzed cross coupling reactions of organic halides with organometallic reagents.



Pd(R)X(Ar-BIAN)

As it was shown in stoichiometric studies that the rate of insertion of carbon monoxide in palladium–methyl bonds in a series of Pd(Me)X(P–P) complexes decreased with increasing rigidity of the chelating phosphine,[7f] whereas insertion in complexes with more rigid nitrogen ligands was shown to occur readily,[8,9] we were interested in the influence of the rigid Ar-BIAN ligands on the rate of insertion and the stability of the complexes formed. Because of the observed high reactivity of the Pd(R)X(Ar-BIAN) complexes toward insertion of carbon monoxide and norbornadiene, we focused our attention on successive insertions of these molecules after the insertion of the first molecule of norbornadiene.[15] Elegant work by Brookhart and co-workers has led to the in situ characterization of acyl complexes of the type $[Pd(C(O)\{CH(Ar)CH_2C(O)\}_nMe)(bpy)(CO)]BAr_4$ ($n = 1$–3), formed by successive insertions of CO and 4-*tert*-butylstyrene in cationic acylpalladium complexes.[16] As chloride may, by association and dissociation when required, both facilitate insertion and stabilize the products formed, we have focused on multiple insertion reactions of CO and alkenes by starting from *neutral* acylpalladium complexes, and we describe here the isolation and full characterization of both the acyl- and the alkylpalladium complexes formed after successive CO and alkene insertions, respectively.

Experimental Section

All manipulations were carried out in an atmosphere of dry nitrogen using standard Schlenck techniques. Solvents were dried and distilled before use. ^{1}H NMR spectra were recorded on a Bruker AMX 300 (300.13 MHz) and a Bruker AC 100 (100.13 MHz) spectrometer and ^{13}C NMR spectra on a Bruker AMX 300 spectrometer (75.48 MHz). Chemical shift values are in parts per million relative to TMS as external standard with high-frequency shifts signed positive. ^{19}F NMR spectra were recorded on a Bruker AC 100 spectrometer (94.20 MHz) relative to $CFCl_3$ as external standard. ^{31}P NMR spectra were recorded on a Bruker AMX 300 spectrometer (121.50 MHz) relative to 85% H_3PO_4 as external standard. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. Pd(Me)Cl(COD) (COD = (*Z*,*Z*)-1,5-cyclooctadiene),[17] Ar-BIAN,[18] $PdBr(CH_2C_6H_4\text{-}p\text{-}R)$(Ar-BIAN) (R = H, NO_2),[19] and Pd(*p*-Tol)I(Ar-BIAN)[19] were synthesized according to previously reported procedures.

Pd(Me)Cl(*p*-An-BIAN) (1a). To a solution of 0.30 g of Pd(Me)Cl(COD) (1.13 mmol) in 20 mL of dichloromethane was added 0.48 g of *p*-An-BIAN (1.22 mmol; *p*-An = *p*-$MeOC_6H_4$), and the mixture was stirred at 20 °C. After 1 h, the solution was filtered through Celite filter aid and the residue washed with dichloromethane (2 × 5 mL). The combined filtrates were evaporated to dryness. The product was washed with diethyl ether (3 × 10 mL) and dried in vacuo, yielding 0.55 g of a red solid (89%). Analytically pure samples were obtained by recrystallization from dichloromethane/hexane or by slow evaporation of a solution of the complex in dichloromethane into hexane. Anal. Found (calcd for $C_{27}H_{23}ClN_2O_2Pd$): C, 59.01 (59.03); H, 4.38 (4.22); N, 5.06 (5.10).

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Pd(Me)Cl(*o,o'*-*i*-$Pr_2C_6H_3$-BIAN) (**1b**) was obtained in the same way in 90% yield. Anal. Found (calcd for $C_{37}H_{43}ClN_2Pd$): C, 67.65 (67.58); H, 6.70 (6.59); N, 4.33 (4.26).

Pd(Me)I(*o,o'*-*i*-$Pr_2C_6H_3$-BIAN). To a solution of 0.30 g of Pd(Me)Cl(COD) (1.13 mmol) in 20 mL of dichloromethane were added 0.62 g of *o,o'*-*i*-$Pr_2C_6H_3$-BIAN (1.24 mmol) and 1.69 g of sodium iodide (11.3 mmol), and the mixture was stirred at 20 °C. After 1 h, the solution was filtered through Celite filter aid and the residue washed with dichloromethane (2 × 5 mL). The combined filtrates were evaporated to dryness. The product was washed with diethyl ether (3 × 10 mL) and dried in vacuo, yielding 0.74 g of a red solid (87%). Analytically pure samples were obtained by slow evaporation of a solution of the complex in dichloromethane/methanol (3:1). Anal. Found (calcd for $C_{37}H_{43}IN_2Pd$): C, 59.46 (59.33); H, 5.75 (5.79); N, 3.79 (3.73).

Pd(Me)I(*p*-An-BIAN) was obtained in the same way (91%).

[Pd(Me)(MeCN)(*p*-An-BIAN)]SO_3CF_3 (2a). To a well-stirred solution of 0.27 g of Pd(Me)Cl(*p*-An-BIAN) (0.49 mmol) in 20 mL of dichloromethane and 2 mL of acetonitrile was added 0.15 g of $AgSO_3CF_3$ (0.58 mmol). The mixture was stirred in the dark at 20 °C, and after 1 h the white precipitate was filtered off and the filtrate evaporated to dryness. The product was redissolved in 15 mL of dichloromethane and filtered through Celite filter aid. The residue was extracted with dichloromethane (5 mL), and the combined filtrates were evaporated to about 3 mL. The product was precipitated by the addition of 10 mL of hexane, washed with hexane (2 × 5 mL), and dried in vacuo, yielding 0.30 g of a red solide (87%). Anal. Found (calcd for $C_{30}H_{26}F_3N_3O_5PdS$): C, 51.80 (51.18); H, 3.45 (3.75); N, 5.93 (5.97). ^{19}F NMR ($CDCl_3$): −78.47 ppm.

[Pd(Me)(MeCN)(*o,o'*-*i*-$Pr_2C_6H_3$-BIAN)]SO_3CF_3 (2b) was synthesized in the same way (79%).

[Pd(Me)(CD_3CN)(*p*-Tol-BIAN)]SO_3CF_3 (2c) was synthesized in CD_3CN and analyzed in situ by ^1H NMR spectroscopy.

Pd(C(O)Me)Cl(*p*-An-BIAN) (3a). Method A. Carbon monoxide was bubbled through a glass capillary into a solution of 0.20 g of Pd(Me)Cl(*p*-An-BIAN) (0.36 mmol) in 10 mL of dichloromethane at 20 °C. After 1 min, the reaction flask was closed and the mixture stirred for another 5 min in a CO atmosphere. The solution was filtered through Celite filter aid and the residue washed with dichloromethane (2 × 5 mL). The combined filtrates were evaporated to dryness and the product washed with diethyl ether (2 × 5 mL). After drying of the product in vacuo, 0.17 g of red/brown solid was obtained (81%).

Method B. A solution of 0.20 g of Pd(Me)Cl(*p*-An-BIAN) (0.36 mmol) in 10 mL of dichloromethane was placed in a 200-mL flask connected to a vacuum line. The flask was evacuated and subsequently filled with carbon monoxide to a pressure of 1 bar. This sequence was repeated twice, and then the mixture was stirred 5 min at 20 °C. After that time, the flask was opened and the solution filtered through Celite filter aid. Workup was the same as described above for method A. Analytically pure samples were obtained by recrystallization from chloroform/hexane. Anal. Found (calcd for $C_{28}H_{23}ClN_2O_3Pd$): C, 57.74 (58.25); H, 4.19 (4.02); N, 4.88 (4.85).

Pd(C(O)Me)Cl(*o,o'*-*i*-$Pr_2C_6H_3$-BIAN) (**3b**), Pd(C(O)Me)I(*p*-Tol-BIAN) (**3c**), [Pd(C(O)Me)(*p*-An-BIAN)(S)]SO_3CF_3 (S = CO (**4a**), MeCN (**4a'**)), [Pd(C(O)Me)(*o,o'*-*i*-$Pr_2C_6H_3$-BIAN)(CO)]SO_3CF_3 (**4b**), PdBr(C(O)CH_2Ph)(Ar-BIAN) (Ar = *p*-An (**5a**), *p*-Tol (**5c**)), PdBr(C(O)$CH_2C_6H_4$-*p*-NO_2)(*p*-Tol-BIAN) (**6c**) and Pd(C(O)*p*-Tol)I(*p*-An-BIAN) (**7a**) were obtained in the same way.

3b was recrystallized from dichloromethane/hexane. Anal. Found (calcd for $C_{38}H_{43}ClN_2OPd$): C, 66.21 (66.57); H, 6.50 (6.32); N, 4.38 (4.09).

4a, ^{19}F NMR ($CDCl_3$) −78.59 ppm.

5c, Anal. Found (calcd for $C_{34}H_{27}BrN_2OPd$): C, 60.86 (61.33); H, 4.34 (4.09); N, 4.13 (4.21).

[Pd(C(O)Me)(*p*-An-BIAN)(CO)]SO_3CF_3 (**4a**) was also obtained in the following way. To a solution of 40 mg of **1a** (0.073 mmol) in 0.5 mL of $CDCl_3$ was added 25 mg of $AgSO_3CF_3$ (0.097 mmol), and the mixture was filtered after 5 min. Carbon monoxide was bubbled through the filtrate for 1 min, after which a ^1H NMR spectrum was recorded immediately.

[Pd(C(O)Me)(CD_3CN)(*p*-Tol-BIAN)]SO_3CF_3 (**4c'**) was obtained by the reaction of **3c** with $AgSO_3CF_3$ in CD_3CN and analyzed in situ by ^1H NMR.

[Pd(C(O)Me)(*p*-An-BIAN)(PPh_3)]SO_3CF_3 (4a''). To a solution of a mixture of **4a** and **4a'** (50 mg, about 0.069 mmol) in 5 mL of dichloromethane was added 20 mg of PPh_3 (0.076 mmol), and the mixture was stirred at 20 °C. After 5 min, the solvent was evaporated and the product washed with diethyl ether (2 × 3 mL) and dried in vacuo.

[Pd(C_7H_8C(O)Me)(*p*-An-BIAN)]Cl (8a). Norbornadiene (41 μL, 0.40 mmol) was added to a solution of 0.21 g of Pd(C(O)Me)Cl(*p*-An-BIAN) (**3a**) (0.36 mmol) in 10 mL of dichloromethane at 20 °C. The solution was stirred at 20 °C and after 30 min evaporated to dryness. The product was washed with 5 mL of diethyl ether and dried in vacuo, yielding 0.22 g of a dark red solid (91%). In similar ways were synthesized (reaction times in parentheses) [Pd(C_7H_8C(O)Me)(*o,o'*-*i*-$Pr_2C_6H_3$-BIAN)]Cl (**8b**, 2 h), [Pd(C_7H_8C(O)Me(Ar-BIAN)]SO_3CF_3 (Ar = *p*-An (**9a**), *o,o'*-*i*-$Pr_2C_6H_3$ (**9b**), 10 min), [Pd(C_7H_{10}C(O)Me)(*p*-An-BIAN)]SO_3CF_3 (**10a**, 10 min), [Pd($C_{10}H_{12}$C(O)Me)(*p*-An-BIAN)]SO_3CF_3 (**11a**, 10 min), [Pd(C_7H_8C(O)Et)(*p*-An-BIAN)]Cl (**12a**, 30 min), and [Pd(C_7H_{10}C(O)Me)(*p*-An-BIAN)]Cl (2 h). C_7H_{10} = norbornene, $C_{10}H_{12}$ = dicyclopentadiene.

9a, ^{19}F NMR ($CDCl_3$): −78.41 ppm.

[Pd(C_7H_8C(O)Me)(Ar-BIAN)]SO_3CF_3 (**9a**) was also obtained by a reaction of 31.8 mg of **8a** (0.047 mmol) with 20.3 mg of $AgSO_3CF_3$ (0.09 mmol) in 0.5 mL of $CDCl_3$. After being stirred for 30 min at 20 °C in the dark, the mixture was filtered and the product identified by ^1H NMR, without isolation.

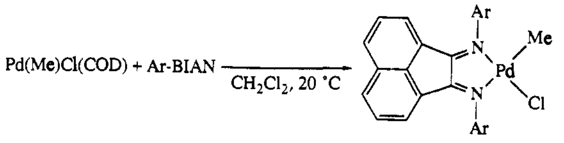
Pd(C(O)C_7H_8C(O)Me)Cl(*p*-An-BIAN) (13a). Carbon monoxide was bubbled through a solution of 0.18 g of [Pd(C_7H_8C(O)Me)(*p*-An-BIAN)]Cl (**8a**) (0.27 mmol) in 10 mL of dichloromethane for 1 min and the mixture stirred under CO during 5 min at 20 °C. After that time the solution was filtered through Celite filter aid, the residue was washed with dichloromethane (5 mL), and the filtrates were evaporated to dryness. The product was washed with diethyl ether (5 mL) and dried in vacuo, giving 0.15 g of a brown product (80%). Anal. Found (Calcd for $C_{36}H_{31}ClN_2O_4Pd$): C, 61.78 (61.99); H, 4.59 (4.48); N, 4.15 (4.02).

[Pd(C_7H_8C(O)C_7H_8C(O)Me)(*p*-An-)BIAN)]Cl (14a). To a solution of 0.11 g of Pd(C(O)C_7H_8C(O)Me)Cl(*p*-An-BIAN) (**13a**) (0.16 mmol) in 10 mL of dichloromethane was added 18 μL of norbornadiene (0.18 mmol), and the mixture was stirred at 20 °C. After 30 min, the solvent was evaporated, and the product washed with diethyl ether (5 mL) and dried in vacuo, giving a red product (0.11 g, 87%).

[Pd(C_7H_8C(O)C_7H_8C(O)Me)(*p*-An-BIAN)]SO_3CF_3 (15a). To a solution of 56.7 mg of **14a** (0.072 mmol) in 10 mL of dichloromethane was added 21.0 mg of $AgSO_3CF_3$ (0.082 mmol), and the mixture was stirred at 20 °C in the dark. After 15 min, the mixture was filtered through Celite filter aid and the solution evaporated to dryness. The product was washed with diethyl ether (5 mL) and dried in vacuo, yielding 60 mg of a dark red product (93%). Anal. Found (calcd for $C_{44}H_{39}F_3N_2O_7PdS$): C, 58.29 (58.51); H, 4.31 (4.35); N, 2.96 (3.10).

Results

Synthesis of the Starting Organopalladium Complexes. Methylpalladium chloride complexes **1** were synthesized starting from Pd(Me)Cl(COD) (eq 1; COD = (*Z,Z*)-1,5-cyclooctadiene), similar to the reported methylpalladium complexes with bidentate P–P, P–N, and N–N and tridentate N–N–N ligands.[7f,g,8b,9] The facile high-yield synthesis of Pd(Me)Cl(COD) makes this route preferable to the one via [Pd(Me)(μ-Cl)(SMe_2)]$_2$.[20]



(1)

1a, Ar = *p*-$MeOC_6H_4$;
1b, Ar = *o,o'*-*i*$Pr_2C_6H_3$

The corresponding methylpalladium iodide complexes were obtained from Pd(Me)Cl(COD) by carrying out the substitution reaction in the presence of an excess sodium iodide. Pd(Me)I(*p*-Tol-BIAN) (**1c**) obtained in this way was identical to the complex obtained by oxidative addition of iodomethane to zerovalent Pd(*p*-Tol-BIAN)(alkene) complexes.[19]

Cationic complexes of the type [Pd(Me)(Ar-BIAN)(S)]SO_3CF_3 (S = solvent molecule) (**2**) were obtained by the reaction of the corresponding halide complexes with silver trifluoromethanesulfonate (eq 2).

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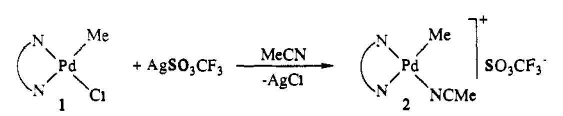
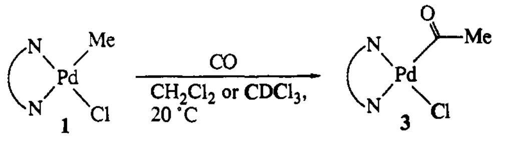
[20] Byers, P. K.; Canty, A. J.; Engelhardt, L. M.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1986**, 1731.



(2)

These complexes were either prepared in situ (S = CD_3CN, acetone-d_6, or $CDCl_3$) or isolated from dichloromethane/acetonitrile (S = CH_3CN). Attempted isolation from noncoordinating solvents such as dichloromethane and chloroform led to considerable decomposition. The dehalogenation reaction is reversible, as the neutral complexes **1** are regenerated quantitatively upon reaction of the cationic complexes **2** with the appropriate sodium halide.

Insertion of Carbon Monoxide. All methylpalladium complexes **1** reacted rapidly with carbon monoxide to give the corresponding acetylpalladium complexes **3** (eq 3).

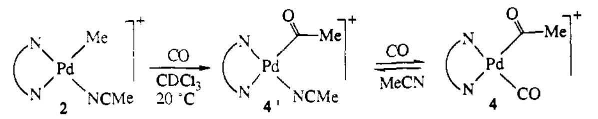


(3)

The reactions were completed within 1 min under ambient conditions in chloroform or dichloromethane, i.e., 20 °C and 1 bar CO pressure, either by bubbling CO gas through a glass capillary[21a] into a solution of the palladium complex or by evacuation followed by admission of CO into the reaction flask on a vacuum line.

The insertion of carbon monoxide is reversible, but decarbonylation occurs much more slowly. When a solution of Pd(C(O)-Me)Cl(*p*-An-BIAN) (**3a**) (*p*-An = *p*-anisyl = *p*-$MeOC_6H_4$) was refluxed in dichloromethane, after 1.5 h 75% unreacted **3a** and 25% of the decarbonylated Pd(Me)Cl(*p*-An-BIAN) (**1a**) were present.

Reaction of the cationic complexes [Pd(Me)(MeCN)(*p*-An-BIAN)]SO_3CF_3 (**2a**) with carbon monoxide resulted in the formation of two products (eq 4). Bubbling carbon monoxide through a solution of **2a** during 3–5 min led to the formation of [Pd(C(O)Me)(*p*-An-BIAN)(CO)]SO_3CF_3 (**4a**)[21b] and free acetonitrile. This product was also obtained from the reaction of carbon monoxide with [Pd(Me)(*p*-An-BIAN)]SO_3CF_3, prepared in situ from **1a** and $AgSO_3CF_3$ in $CDCl_3$ in the absence of acetonitrile. Conversely, short reaction times of **2a** with CO in $CDCl_3$ (10–30 s) or reaction in dichloromethane followed by evaporation to isolate the product led to the formation of a mixture of [Pd(C(O)Me)(*p*-An-BIAN)(CO)]SO_3CF_3 (**4a**) and [Pd-(C(O)Me)(MeCN)(*p*-An-BIAN)]SO_3CF_3 (**4a′**, major product).



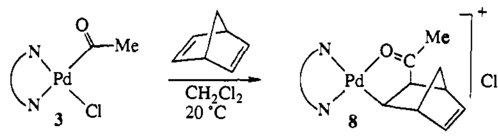
(4)

In solution **4a′** was obtained as the only complex when an excess of acetonitrile (ca. 20 equiv) was added to a $CDCl_3$ solution of a mixture of **4a** and **4a′**. The analogous complex [Pd(C(O)-Me)(CD_3CN)(*p*-Tol-BIAN)]SO_3CF_3 (**4c′**) was obtained via dehalogenation of the acyl complex **3c** with silver trifluoromethanesulfonate in CD_3CN and studied in situ. As compared to their neutral counterparts **3**, the cationic complexes **4** undergo decarbonylation in the solid state more readily, i.e., drying in vacuo for several hours or storage at 20 °C for several days resulted in formation of methylpalladium complexes together with decomposition products. In coordinating solvents (acetonitrile or acetone), complex **4c′** was rather stable toward decarbonylation (no trace of Pd–Me after 20 h at 20 °C). Reaction of a mixture of the cationic acyl complexes **4a** and **4a′** with 1 equiv of triphenylphosphine gave [Pd(C(O)Me)(*p*-An-BIAN)(PPh_3)]SO_3CF_3 (**4a″**) as the only product, even in the presence of a large excess of acetonitrile (50 equiv).

Insertion of carbon monoxide in benzyl–palladium and *p*-tolyl–palladium bonds in Pd(Ar-BIAN) complexes occurred within 15 min, yielding quantitatively the acyl complexes PdBr(C(O)CH_2-Ph)(Ar-BIAN) (**5a**, Ar = *p*-An; **5c**, Ar = *p*-Tol) and Pd(C(O)-*p*-Tol)I(*p*-An-BIAN) (**7a**), respectively. On the contrary, PdBr($CH_2C_6H_4$-*p*-NO_2)(*p*-Tol-BIAN) reacted much more slowly, and conversion to the acyl complex PdBr(C(O)$CH_2C_6H_4$-*p*-NO_2)(*p*-Tol-BIAN) (**6c**) was only completed after 4 h (the conversion was 5% after 5 min and 62% after 90 min). These results are in agreement with a migration of the organic group to the coordinated carbon monoxide.[6,22] Use of a metallic needle to bubble CO gas through a solution of PdBr($CH_2C_6H_4$-*p*-NO_2)-(*p*-Tol-BIAN) gave complete conversion to **6c** within 5 min.[21a] Reaction of PdBr(C(O)CH_2Ph)(Ar-BIAN) (**5a,c**) with $AgSO_3CF_3$ in the presence or in the absence of acetonitrile gave no cationic acylpalladium complex, but instead [Pd(η^3-CH_3Ph)(Ar-BIAN)]SO_3CF_3 was formed, which was identical to the reaction product obtained from PdBr(CH_2Ph)(Ar-BIAN) and $AgSO_3CF_3$.[19]

Insertion of Strained Alkenes in Acyl–Palladium Bonds. Reaction of neutral and cationic acylpalladium complexes Pd-(C(O)Me)Cl(*p*-An-BIAN) (**3a**) and [Pd(C(O)Me)(*p*-An-BIAN)-(S)]SO_3CF_3 (**4a**) with strained alkenes led to the insertion of these alkenes in the acyl–palladium bond, similar to previously reported insertion reactions.[9,11]

Reaction with norbornadiene (eq 5) led to the rapid quantitative formation of the insertion products [Pd(C_7H_8C(O)Me)(*p*-An-BIAN)]X (**8a**, X = Cl; **9a**; X = SO_3CF_3; 100% conversion within 3 min for **3a** and instantaneous for **4a** at 20 °C). Norbornene and dicyclopentadiene reacted instantaneously with the cationic complex **4a** to give quantitatively the insertion complexes [Pd-(C_7H_{10}C(O)Me)(*p*-An-BIAN)]SO_3CF_3 (**10a**) and [Pd(C_{10}-H_{12}C(O)Me)(*p*-An-BIAN)]SO_3CF_3 (**11a**), respectively. However, reaction of the neutral acylpalladium complex **3a** with norbornene and dicyclopentadiene gave mixtures of the starting acyl- and the alkene-inserted complexes, and no further conversion was achieved (63:37 and 47:53, respectively). Furthermore, the reactions were much slower as compared to norbornadiene insertion reactions (about 1 h at 20 °C before no further alkene insertion occurred).[23] The analogous *o,o′*-*i*-$Pr_2C_6H_3$-BIAN complexes **3,4b** reacted with norbornadiene to give the insertion complexes **8,9b**, but the reaction of the neutral complex **3b** was much slower as compared to that of **3a** (50% conversion after 20 min at 20 °C and 100% converion within 1 h).



(5)

Norbornadiene also readily reacted with the propionyl complex Pd(C(O)Et)Cl(*p*-An-BIAN), giving quantitatively the insertion complex [Pd(C_7H_8C(O)Et)(*p*-An-BIAN)]Cl (**12a**) within 5 min. Interestingly, reaction of Pd(C(O)Et)Cl(*p*-An-BIAN) with

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(21) (a) The increased rate of CO insertion when a metallic needle was used was observed before[9] and might be caused by the presence of catalytic amounts of metal carbonyl or Lewis acid species in solution. Promotion of CO insertion in a Ru–Me bond by $Ru(CO)_4(PR_3)$, $ZnCl_2$, and H^+ has been published: Kraakman, M. J. A.; de Klerk-Engels, B.; de Lange, P. P. M.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1992**, *11*, 3774. (b) Similar species containing a chelating diphosphine have recently been identified: Tóth, I.; Elsevier, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 10388-10389.

(22) (a) Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101. (b) Ozawa, F.; Yamamoto, A. *Chem. Lett.* **1981**, 289.

(23) During the insertion of norbornene and dicyclopentadiene, there was no evidence for the formation of significant amounts of other products, e.g., arising from decarbonylation. The reason for the higher reactivity of norbornadiene is unclear. Coordination of the second double bond seems unlikely, as in that case insertion from the *endo* face of the alkene is expected. Probably the ring strain of the alkene is an important factor, similar to previously reported observations.[11b]

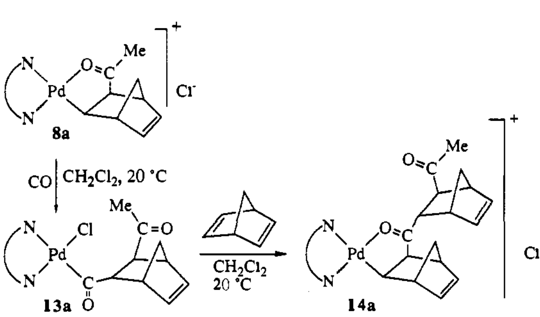
Table 1. ^{1}H NMR Data of Selected Acyl- and Alkylpalladium Insertion Complexes[a]

	H_3	H_4	H_5	$H_{9,10}$	H_{12}	H_{13}	$H_{14,17}$	$H_{15,16}$	H_{18}	H_{19}	H_{21}
1a[b]	6.67 d (7.3) 7.1 m (5 H)	7.50 pst 7.44 pst	8.06 d (8.4) 8.03 d (8.4)	7.1 m (5 H) 7.4 m (4 H)	3.93 s 3.91 s						
3a[c]	6.8 vbr	7.47 pst	8.04 d (8.3)	7.27 br 7.03 d (8.6)	3.88 s						
8a	7.18 d (7.2)	7.54 pst	8.14 d (8.3)	7.38 d 7.13 d (8.8)	3.94 s	2.00 dd (6.2,1.9)	3.00 s 2.38 s	5.96 dd (5.2,2.8) 5.48 dd (5.2,3.0)	1.66 d 1.28 d (9.0)	2.47 d (6.2)	2.53 s
9a	6.80 d (7.3) 7.69 d (7.3)	7.53 pst 7.50 pst	8.15 d (8.3) 8.13 d (8.1)	*d*	3.94 s 3.93 s	1.91 dd (5.7,1.9)	3.07 s 2.35 s	6.02 dd (5.0,2.6) 5.47 dd (5.0,2.9)	1.53 d 1.26 d (9.4)	2.50 d (5.7)	2.42 s
10a	6.77 d (7.3) 7.68 d (7.2)	7.58 pst 7.53 pst	8.13 pst	*e*	3.93 s 3.92 s	2.44 dd (6.0,1.2)	2.38 br 1.61 s	1.51 m 1.21 m 0.95 m 0.49 m	1.63 d 1.15 d (9.9)	2.71 d (6.0)	2.31 s
11a[f]	6.51 d (7.3) 7.73 d (7.2)	7.58 pst	8.14 pst	*f*	3.92 s	2.43 d (5.9)	3.07 br 1.70 s	1.2 m 0.68 br	1.86 d 1.45 d (9.8)	2.65 d (5.9)	2.27 s
13a	6.65 br 7.1 m (5 H)	7.46 br	8.04 d (8.2)	7.3 br (4 H) 7.1 br (5 H)	3.87 s	*g*	3.00 s 2.86 s	6.13 dd (5.5,3.0) 6.05 dd (5.5,3.0)	0.79 d 0.66 d (9.0)	*g*	2.10 s
14a	7.18 d (7.1)	7.49 pst	8.11 d (8.2)	7.31 d 7.08 d (8.8)	3.88 s	1.84 dd (5.8,1.7)	3.05 s 2.20 s	5.95 dd (5.3,2.9) 5.40 dd (5.3,3.1)	1.39 d 1.18 d (9.2)	2.38 d (5.8)	*h*

[a] Recorded at 300.13 MHz in $CDCl_3$ at 20 °C, unless noted otherwise, *J* in parentheses. See Table 2 for the adopted numbering scheme (s = singlet, d = doublet, dd = doublet of doublets, pst = pseudotriplet, m = multiplet, br = broad, v = very). [b] 0.91 s, PdMe. [c] 2.23 s, PdC(O)Me. [d] 7.60 d (7.9 Hz; 1 H), 7.48 d (8.9 Hz; 2 H), 7.36 dd (8.7, 2.3 Hz; 1 H), 7.22 dd (8.3, 2.3 Hz, 1 H), 7.11 d (8.9 Hz; 3 H), $H_{9,10}$. [e] 7.50 d (8.8 Hz; 2 H), 7.31 dd (8.5, 2.8 Hz; 1 H), 7.23 dd (8.7, 2.4 Hz; 1 H), 7.18 dd (8.7, 2.4 Hz; 1 H), 7.11 d (8.8 Hz; 3 H), $H_{9,10}$. [f] 7.5 m (4 H), H_4, H_{9-13}; 7.1–7.2 m (6 H), $H_{9,10}$. Cyclopentene ring: 5.63 m, 5.56 m, =CH; 2.5 s, CH_2. Signals of the minor isomer (34%): 6.63 d (7.2 Hz), H_3; 3.93 s, H_{12}; 2.28 s, H_{21}; 1.95 d (9.8 Hz), H_{18}; 2.62 s, CH_2 (cyclopentene ring). [g] 4.04 (8.9 Hz), $H_{13,19}$, the other signal is overlapped by H_{12}. [h] Signals of the $C_7H_8C(O)Me$ moiety which is *not* part of the palladacycle (numbers are marked by a prime): $H_{13'}$ overlapped by H_{12}; 3.33 s, 3.05 s, $H_{14',17'}$; 6.28 dd (5.5, 3.2 Hz), 6.03 dd (5.5, 2.7 Hz), $H_{15',16'}$; 1.41 s (2 H), $H_{18'}$; 2.48 d (4.2 Hz), $H_{19'}$; 2.09 s, C(O)*Me*.

norbornene and dicyclopentadiene produced mixtures of the acyl- and the alkene-inserted complexes in the same ratio (63:37 and 45:55, respectively)[23] as observed in the reaction of the acetyl complex Pd(C(O)Me)Cl(*p*-An-BIAN) with these alkenes.

Successive Insertion Reactions of CO and Norbornadiene in $PdC_7H_8C(O)Me$ Entities. Reaction of the norbornadiene-inserted complexes [Pd($C_7H_8C(O)Me$)(*p*-AN-BIAN)]Cl (**8a**) with carbon monoxide led to the facile insertion of a second CO molecule to give the isolable acyl complex Pd(C(O)$C_7H_8C(O)Me$)Cl(*p*-An-BIAN) (**13a**) (eq 6), which is similar to the in situ characterized [Pd(C(O)CH(Ar)$CH_2C(O)Me$)(bpy)(CO)]BAr_4 as an intermediate in the Pd-catalyzed copolymerization of CO and 4-*tert*-butylstyrene[16] and the recently reported ionic analogue [Pd(C(O)$C_7H_{10}C(O)Me$)(bpy)]SO_3CF_3.[34]



(6)

In contrast to the ready insertion of carbon monoxide in the cationic complex **8a** with a chloride anion, the corresponding trifluoromethanesulfonate complex **9a** is completely inert toward insertion of a second CO molecule. Insertion of CO after alkene insertion has also been observed as a secondary reaction after the reaction of norbornene with Pd(C(O)Me)Cl($Ph_2P(CH_2)_3PPh_2$),[11h] but **13a** provides the first isolated complex obtained by insertion of a second molecule of CO after insertion of an alkene in an acyl–palladium bond, which is fully characterized by IR, ^{1}H, and ^{13}C NMR spectroscopy and microanalysis (vide infra). The newly formed acyl complex **13a** reacted again with strained alkenes: when employing norbornadiene, quantitative formation of the insertion product [Pd($C_7H_8C(O)C_7H_8C(O)Me$)(*p*-An-BIAN)]Cl (**14a**) readily occurred (eq 6), whereas partial conversion was observed when norbornene was used (38%), similar to the reactions of the neutral acyl complex **3a** with norbornene.[23] The analogous complex [Pd($C_7H_8C(O)C_7H_8C(O)Me$)(*p*-An-BIAN)]SO_3CF_3 (**15a**) has been obtained by the reaction of **14a** with $AgSO_3CF_3$.

Spectroscopic Characterization of the Methyl- and Acylpalladium Complexes 1–7. The methyl- and acylpalladium complexes **1–3** were isolated and fully characterized, whereas the cationic acyl complexes **4** were studied in situ by spectroscopic techniques (Tables 1 and 2 and S1–S3 in the supplementary material). All neutral complexes Pd(Me)Cl(Ar-BIAN) **1** show the characteristic Pd–Me resonance in the area 0.8–0.9 ppm in ^{1}H NMR and 4.2–4.7 ppm in ^{13}C NMR, while the cationic complexes [Pd(Me)(MeCN)(Ar-BIAN)]SO_3CF_3 **2** give Pd–Me resonances at somewhat lower frequencies, in agreement with earlier observations.[24] The methyl resonance of coordinated acetonitrile (2.28 (**2a**) and 2.08 ppm (**2b**)) is observed at higher frequency than that of free acetonitrile (2.00 ppm). Remarkably, for the complexes [Pd(Me)(MeCN)(Ar-BIAN)]SO_3CF_3, the CN stretching frequency is absent in IR. Unfortunately, no IR data were reported

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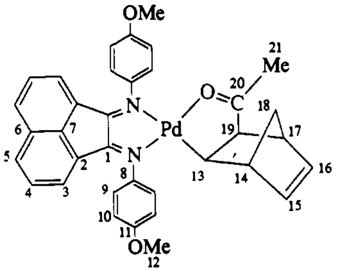
[24] Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1990**, *393*, 299.

Table 2. ^{13}C NMR Data of Selected Acyl and Alkyl Insertion Complexes[a] (Adopted numbering scheme is shown below)



	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	$C_{14/17}$	$C_{15/16}$	C_{18}	C_{19}	C_{20}	C_{21}
1a[b]	n.o.	127.6 126.9	125.5 125.1	129.0	131.5 131.0	131.9	144.6	140.2 139.0	115.5 114.7	124.3 123.2	159.7 159.2	56.1 56.2							
3a[c]	n.o.	126.8	125.4	129.0	131.5	131.7	n.o.	144.5	115.2	123.1	159.6	56.1							
8a	170.7	126.0	125.7	129.2	132.7	131.8	146.0	138.8	115.5	123.9	160.2	56.3	50.0	48.8 47.0	135.6 134.2	45.9	62.9	236.0	28.8
9a	176.1 166.5	126.3 125.8	126.4 125.4	129.3 129.2	133.1 132.3	131.9	146.0	138.6 138.4	116.9 115.4 115.3	124.4	160.9 160.2	56.3	49.2	47.3 46.8	123.5 122.3	44.6	62.0	238.7	28.3
10a	175.5 165.8	126.5 125.9	126.3 125.3	129.3 129.2	133.0 132.2	131.9	145.6	139.0 138.7	115.9 115.5 115.3	124.3 123.9 123.5	160.7 160.1	56.4 56.3	57.2	43.8 42.2	29.5 28.6	36.9	71.6	239.9	28.0
11a[d]	176.5 165.8	126.5 125.7	126.6 125.5	129.4 129.3	133.4 132.6	131.7	145.6	138.7 138.3	115.2	124.7	160.5 159.8	56.6 56.5	53.8	*d*	*d*	39.4	67.8	242.1	28.4
13a	171.2	127.1	125.8	129.0	131.8	131.7	144.7	n.o.	115.2	124.0	159.6	56.1	55.0	44.7 43.6	139.1 137.2	43.9	62.4	*e*	31.8
14a[f]	175.6 165.2	126.2 125.6	126.3 125.2	129.3	133.0 132.6	131.7	144.7	138.8 138.0	115.8 115.3	123.6	160.5 159.5	56.5	*f*	*f*	135.1 134.7	46.2	63.8	241.2	*f*

[a] Recorded at 75.48 MHz in $CDCl_3$ at 20 °C, unless noted otherwise (n.o. = not observed). [b] 4.7, PdMe. [c] 223.4, Pd*C*(O)Me; 33.8; PdC(O)*Me*. [d] 49.3, 47.6, 46.5, 42.4, C_{14-17}. Signals of the cyclopentene ring: 123.4, 123.0, =CH; 31.5, CH_2. The minor isomer shows additional resonances at 176.1, C_1; 130.6, C_4; 133.2, C_5; 116.6, 115.3, C_9; 159.7, C_{11}; 56.7, C_{12}; 241.0, C_{20}; 28.5, C_{21}. [e] 222.0, Pd*C*(O)R; 210.1, R*C*(O)Me. [f] Recorded at –40 °C; the signals of the norbornadiene moiety which is *not* part of the five-membered palladacycle are indicated by a prime: 50.8, 50.2, 50.0, 49.6, 47.7, 46.9, $C_{13,14,17}$ and $C_{13',14',17'}$; 138.7, 138.6, $C_{15',16'}$; 44.8, $C_{18'}$; 62.7, $C_{19'}$; 208.7, $C_{20'}$; 29.7, C(O)*Me*.

for other cationic *cis*-Pd^{II}(MeCN) complexes containing bisphosphines,[7f,g] bpy,[24] and tmeda.[25]

The formation of the acyl complexes Pd(C(O)Me)Cl(Ar-BIAN) **3** after reaction of the methyl complexes **1** with carbon monoxide is evident from the high-frequency shift of the methyl resonance from 0.8–0.9 to 2.2–2.5 ppm in ^{1}H NMR, the observation of a CO stretching frequency in IR (1710–1730 cm^{-1}), and resonances of the CO (ca. 220 ppm) and methyl groups (ca. 35 ppm) in ^{13}C NMR spectroscopy. These data agree well with those reported for other *cis*-acetylpalladium complexes[7f,g,8a,b,9a] and those for Pd(C(O)Me)Cl(*p*-Tol-BIAN) obtained via oxidative addition of acetyl chloride to Pd(*p*-Tol-BIAN)(dimethyl fumarate).[19]

For the cationic [Pd(C(O)Me)(S)(Ar-BIAN)]SO_3CF_3 complexes (**4**, S = CO; **4′**, S = MeCN), similar observations were made. Pure samples for microanalysis could not be obtained, because drying in vacuo or storage at 20 °C for prolonged periods resulted in decomposition. IR spectroscopy of **4a** reveals two CO stretching frequencies at 2120 and 1725 cm^{-1}, characteristic of a terminal Pd*CO*[7b,g,26] and a Pd*C*(*O*)R moiety, and indicates that the trifluoromethanesulfonate anion is not coordinated to palladium.[27,28] For **4a′**, the presence of the inserted CO at 1725 cm^{-1} and noncoordinating trifluoromethanesulfonate appears, whereas the CN stretching frequency of acetonitrile is not observed. The difference with the analogous [Pd(C(O)Me)(MeCN)$(PPh_3)_2$]BF_4, which shows ν(CN) at 2240–2282 cm^{-1},[11c] might arise from the different geometries of both complexes (*cis*-N–N vs *trans*-P_2).

The coordination of the phosphine in [Pd(C(O)Me)(*p*-An-BIAN)(PPh_3)]SO_3CF_3 (**4a″**) is clear from the observed resonance at 27.4 ppm in ^{31}P NMR. In IR, a Pd*C*(*O*)Me signal is observed at 1705 cm^{-1}, and in ^{1}H NMR the methyl resonance has shifted to 1.69 ppm, in agreement with literature values for complexes with C(O)Me and PPh_3 ligands in *cis* positions.[17f,11c] This shift to low frequency must be ascribed to the anisotropic shielding of the methyl group by one of the phenyl rings of the phosphine.

Spectroscopic Characterization of the Alkene-Inserted Products 8–12. The complexes formed after insertion of norbornadiene, norbornene, and dicyclopentadiene (**8–11**) were characterized by ^{1}H and ^{13}C NMR and IR spectroscopy (Tables 1 and 2 and S1–S3 of the supplementary material). The complexes are too unstable in the solid state to allow outside microanalysis. The ^{1}H NMR spectra for the insertion products **8–11** show a well-defined pattern for the inserted alkene, and from the coupling constants $^3J(H_{13}–H_{19})$, which are in the range 5.6–6.7 Hz, *cis* addition of PdC(O)Me to the *exo* face of the alkene can be concluded.[11c]

Formation of the *exo* product is in agreement with the geometries found for the insertion products of norbornene with [Pd(C(O)Me)(MeCN)$(PPh_3)_2$]BF_4[11c] and of dicyclopentadiene with [Pd(C(O)Me)(MeCN)(bpy)]SO_3CF_3,[11g] which were determined by X-ray crystallography. There is no evidence for the formation of a nortricyclenyl complex **8**, **9**, as was observed for the reaction of norbornadiene with Pd(C(O)Me)Cl($Ph_2P(CH_2)_3PPh_2$).[11h] The acyl oxygen atom is coordinated to the palladium, forming a five-membered palladacycle, in agreement with previous observations,[11c,f–h] as can be derived from the CO stretching frequency at 1600 cm^{-1} in IR,[29] the carbonyl resonance at approximately 240 ppm in ^{13}C NMR, and the methyl resonance at about 2.4 ppm in ^{1}H NMR. The presence of trifluo-

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(25) de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907.

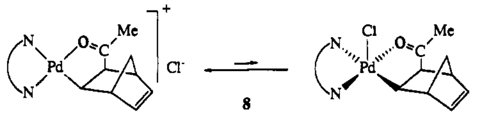
(26) (a) Usón, R.; Forniés, J.; Tomás, M.; Menjón, B. *Organometallics* **1985**, *4*, 1912. (b) Cinellu, M. A.; Gladiali, S.; Minghetti, G. *J. Organomet. Chem.* **1989**, *363*, 401.

(27) (a) Dedert, P. L.; Thompson, J. S.; Ibers, J. A.; Marks, T. J. *Inorg. Chem.* **1982**, *21*, 969. (b) Lawrence, G. A. *Chem. Rev.* **1986**, *86*, 17.

(28) van Asselt, R.; Rijnberg, E.; Elsevier, C. J., *Organometallics*, in press.

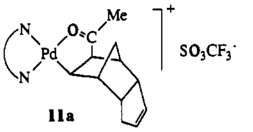
(29) The CO stretching frequency at 1600 cm^{-1} coincides with a C=C stretching frequency of the Ar-BIAN ligand, but the increased intensity of the signal after alkene insertion leaves no doubt that this signal represents a CO stretching frequency.

romethanesulfonate as an anion, not coordinated to palladium, appears from IR.[27,28] Furthermore, for complexes **8**,**9** the observed chemical shift difference of approximately 0.5 ppm for the remaining alkene protons ($H_{15,16}$) of the norbornadiene moiety is characteristic for an inserted norbornadiene that is part of a five-membered palladacycle.[30] The presence of chloride as an anion which is not coordinated to palladium in a fifth coordination position (eq 7) appears from the equivalent conductance of 80,9 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ for **8b** in dichloromethane, whereas the equivalent conductances for the neutral precursors **1b** and **3b** were 3.3 and 3.4 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$, respectively.

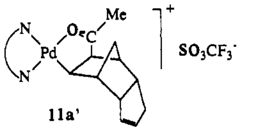


(7)

Insertion of norbornadiene and norbornene leads to the formation of only one isomer in all cases (complexes **8**–**10**), but after insertion of dicyclopentadiene two isomers of **11a** are formed in a ratio of 2:1 which differ in the position of the double bond in the five-membered cyclopentene ring. There is no evidence for any reaction of the acylpalladium complex **4a** at this double bond, indicating complete regioselectivity of the insertion reaction.



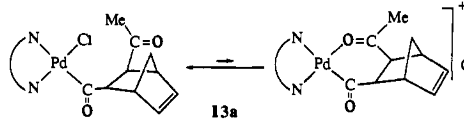
11a



11a'

The complexes **8** and **9** obtained from the insertion of norbornadiene in neutral Pd(C(O)Me)Cl(Ar-BIAN) (**3**) and cationic [Pd(C(O)Me)(Ar-BIAN)(S)]SO_3CF_3 (**4**,**4'**) complexes, respectively, are thus very similar, and the chloride complex **8a** could easily be converted to the trifluoromethanesulfonate complex **9a** by reaction with $AgSO_3CF_3$. A major difference in the behavior of the chloride (**8**) and trifluoromethanesulfonate (**9**) complexes appears from the fluxional behavior in ^1H NMR: the chloride complexes **8** are in fast exchange at 20 °C and give one averaged signal for protons on both halves of the ligand, whereas the trifluoromethanesulfonate complexes **9** are in slow exchange at 20 °C, resulting in the observation of separate signals for protons on both halves of the ligand. Furthermore, because of the inequivalence above and below the coordination plane, the *p*-anisyl substituents on the imine N-atom, which are oriented out of the coordination plane,[18c] give rise to a complex set of resonances. The fluxional behavior of the chloride complexes **8** is slowed down upon cooling: at −40 °C, the *p*-An-BIAN complex **8a** is still in fast exchange (some broadening is observed in the aromatic region), whereas complex **8b**, with the larger *o*,*o'*-*i*-$Pr_2C_6H_3$-BIAN ligand, is in the limit of slow exchange at −40 °C, which appears from the observation of two doublets for H_5 (8.26 (J = 8.5 Hz), 8.22 ppm (J = 8.6 Hz)) and H_3 (6.70 (J = 7.1 Hz), 6.62 ppm (J = 7.2 Hz)), two multiplets for CH (*i*-Pr) (3.3 (2 H), 2.9 ppm (2 H)) and CH_3 (*i*-Pr) (1.3 (13 H, +H_{18}), 0.9 ppm (12 H)). The norbornadiene pattern does not change upon cooling for both **8a** and **8b**. These results are in agreement with a site exchange of the C,O-coordinated acetylnorbornene moiety, aided by coordination of the anion to palladium.

Spectroscopic Characterization of the Multiple Insertion Products 13–15. Formation of Pd(C(O)C_7H_8C(O)Me)Cl(*p*-An-BIAN) (**13a**) from the insertion of CO in the alkyl–palladium bond of **8a** is clear from the observed high-frequency shift of H_{13} from 2.00 to 3.9–4.0 ppm. From ^1H NMR (methyl resonance (H_{21}) at 2.10 ppm and the alkene protons $H_{15/16}$ at 6.13 and 6.05 ppm) and ^{13}C NMR (two carbonyl resonances at 222.0 and 210.1 ppm, comparable to the observed resonances for [Pd(C(O)CH(Ar)CH_2C(O)Me)(bpy)(CO)]BAr_4[16]), formation of a neutral complex can be derived, i.e., coordination of chloride to palladium and no formation of a six-membered palladacycle via coordination of the acyl oxygen atom (eq 8). In agreement with this structure, the complex has a low equivalent conductance of 5.8 $\Omega^{-1}\cdot cm^{-2}\cdot mol^{-1}$ and shows in IR a broad resonance at 1699 cm^{-1}, due to two overlapping CO stretching frequencies.



(8)

The complex [Pd(C_7H_8C(O)C_7H_8C(O)Me)(*p*-An-BIAN)]Cl (**14a**), formed after reaction of **13a** with norbornadiene, was characterized by IR, ^1H, and ^{13}C NMR spectroscopy. The observed coupling constant $^3J(H_{13}–H_{19})$ of 5.8 Hz in ^1H NMR reveals that the insertion occurs via *cis* addition of PdC(O)R to the exo face of norbornadiene, similar to the monoinsertion complexes **8**–**12**. ^1H and ^{13}C NMR revealed the presence of two distinct inserted norbornadiene moieties. One is part of a five-membered palladacycle formed by coordination of the acyl oxygen to palladium, as is clear from ^1H NMR ($H_{15/16}$ at 5.95 and 5.40 ppm), ^{13}C NMR (CO at 241.2 ppm), and IR (ν(CO) = 1598 cm^{-1}). The other norbornadiene is not part of a palladacycle and resembles the pendant norbornadiene moiety of complex **13a** (methyl (H_{21}) at 2.09 ppm, $H_{15/16}$ at 6.28 and 6.03 ppm in ^1H NMR; CO at 208.7 ppm in ^{13}C NMR; ν(CO) at 1703 cm^{-1} in IR). These results clearly rule out formation of an eight-membered palladacycle via coordination of the carbonyl oxygen of the C(O)Me group to palladium, in agreement with the expectation that eight-membered metallacycles are thermodynamically less favorable than five-membered rings. The presence of two different carbonyl carbon groups in **14a** was unequivocally derived from the ^{13}C NMR data [Pd(C_7H_8^{13}C(O)C_7H_8^{13}C(O)Me)(*p*-An-BIAN)]Cl, formed when ^{13}C-labeled carbon monoxide was used. Furthermore, in IR the CO stretching frequencies of the ^{13}C(O)-labeled complex are observed at 1660 and 1550 cm^{-1}, and the found ratios $\nu(^{13}CO)/\nu(^{12}CO)$ of 0.98 and 0.97 agree well with the expected value of 0.98. Unfortunately, no correct analytical data could be obtained, as the complex **14a** has only limited stability in the solid state as well as in solution. However, anion exchange with $AgSO_3CF_3$ resulted in conversion to the analogous complex [Pd(C_7H_8C(O)C_7H_8C(O)Me)(*p*-An-BIAN)]SO_3CF_3 (**15a**), which was stable enough to allow us to obtain analytical data.

Discussion

Insertion of Carbon Monoxide and Alkenes. From mechanistic studies on the insertion of carbon monoxide in square-planar organopalladium(II) and -platinum(II) complexes it is known that insertion from a four-coordinate intermediate is preferable to insertion from a five-coordinate intermediate.[7] For complexes containing monodentate or flexible bidentate (phosphine) ligands, insertion of CO from an intermediate formed via dissociation of one of the phosphines is the preferred pathway. However, the facile insertion of CO in alkyl–palladium bonds of complexes containing the rigid Ar-BIAN ligands, from which dissociation of one of the coordinating N-atoms is unlikely, suggests that low-energy pathways via other routes are also available. Possible

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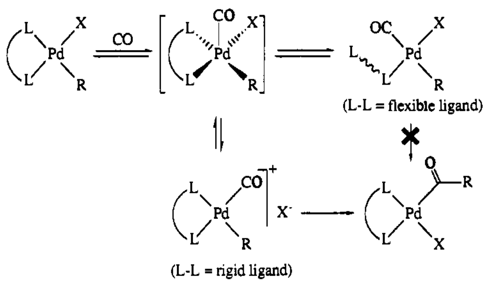
(30) This large difference is chemical shift between H_{15} and H_{16} after norbornadiene insertion is possibly due to the rigidity of this moiety imposed by the chelating C,O coordination, leading to different chemical environments, whereas in the case of more flexible monodentate C(O)C_7H_8C(O)Me moieties, as in **13a**, the chemical environments of H_{15} and H_{16} are more alike (on average). The reason for the large differences in chemical shift of $C_{15,16}$ between complexes **8a** and **9a** is unclear: probably in the cationic complex **9a** there is some interaction of the double bond with palladium or there is a slight distorsion (possibly on the way to a nortricyclenyl complex) in the acetylnorbornene moiety.

Scheme 2



routes include insertion from a five-coordinate intermediate or from a four-coordinate intermediate formed via loss of the halide, which is aided by the approach or the precoordination of carbon monoxide. It must be noted here that the chloride might remain in the neighborhood of the palladium in the cationic complex, which can be expected in solvents like chloroform and dichloromethane, making the difference between a five-coordinate and a cationic four-coordinate complex very small. Similar mechanisms can be assumed for the insertion of alkenes in acyl–palladium bonds, as evidence for insertion of alkenes in metal–carbon and metal–hydrogen bonds from both four-coordinate[11a,12] and five-coordinate[7c] intermediates has been presented.

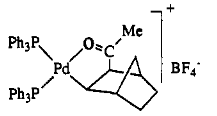
The rate of insertion of carbon monoxide in methyl–palladium bonds and of alkenes in acyl–palladium bonds is higher for palladium complexes containing Ar-BIAN ligands than for complexes containing (di)phosphine ligands. For complexes with the bidentate phosphine ligands $Ph_2P(CH_2)_nPPh_2$ ($n = 2$–4), the rate of CO and alkene insertion decreased in the order $n = 4 \approx 3 \gg 2$, i.e., with increasing ligand rigidity.[7f,11h] However, the high reactivity toward insertion reactions of complexes containing rigid Ar-BIAN ligands suggests that the flexibility of the ligands, which was reported to be important for the creation of open coordination sites and facilitation of the insertion reaction by modification of the L–Pd–L angle,[6c,7,12] is not an important prerequisite for the Pd(Ar-BIAN) complexes. The activating effect of the Ar-BIAN ligand can be ascribed to its rigidity, which disables dissociation of one ligating N-atom, which would in turn lead to the formation of products in a "thermodynamic sink" or to decomposition: in the case of flexible bidentate ligands, preferential dissocation of the coordinating atom *trans* to the organic ligand is expected, leading to the formation of a complex which cannot undergo the insertion reaction (Scheme 2). In the case of rigid bidentate ligands, dissociation of the ligand *trans* to the organic group is prohibited and the only alternative is dissociation of the halide, generating a *cis* complex which can undergo insertion (Scheme 2). Although halide dissociation is expected to be a slow process due to the small *trans* influence of the Ar-BIAN ligand, it represents the only viable route (apart from a mechanism through five-coordinate species) to account for our results. Furthermore, the σ-donor capacities of the Ar-BIAN ligand, leading to a more positive polarization of the carbonyl C-atom,[7g,21] and the greater accessibility of the palladium center, as compared to Pd–bis(phosphine) complexes, are expected to be favorable for the insertion process.

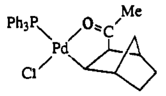
The facile insertion of CO and alkenes in the cationic methyl- and acylpalladium complexes **2** and **4**, respectively, can be ascribed to the increased accessibility of the palladium center combined with less back-bonding to CO or alkene and concomitant lower activation energy for their transfer as compared to the neutral analogues **1** and **3**.[11c] The weak coordination of acetonitrile to palladium is reflected in the formation of $[Pd(C(O)Me)(Ar\text{-}BIAN)(CO)]SO_3CF_3$ in solution upon reaction of **2** with carbon monoxide and was also observed in the reaction of cationic $[PtMe_3(p\text{-}Tol\text{-}BIAN)]SO_3CF_3$ complexes with acetonitrile.[28]

Neutral acylpalladium complexes **3** containing rigid Ar-BIAN ligands are rather stable and decarbonylation is slow, in contrast to analogous complexes containing more flexible bidentate phosphine and nitrogen ligands.[7f,8b] The slow rate of decarbonylation might be due to the greater thermodynamic stability of the acyl complexes **3** as compared to the alkyl complexes **1**. Alternatively, the absence of low-energy pathways for decarbonylation via N or Cl dissociation to create empty coordination sites, due to the rigidity and the low *trans* influence of the Ar-BIAN ligands, is expected to play an important role. In this case, the equilibrium of halide dissociation lies completely to the side of the neutral starting acyl complex **3**, whereas in the case of the reverse CO insertion reaction, excess CO is present thereby shifting the equilibrium toward the complex $[Pd(R)(Ar\text{-}BIAN)(CO)]^+Cl^-$. The kinetic stabilization of acylpalladium complexes by rigid ligands is also apparent from the observations made for complexes containing tridentate ligands: complexes with the rigid terpy ligand were stable toward decarbonylation at 20 °C,[8b] whereas complexes with the more flexible $2,6\text{-}(Me_2NCH_2)_2$-pyridine ligand decarbonylated at 20 °C.[8c] The stabilizing effect of rigid ligands on (labile) organometallic intermediates, as compared to more flexible ligands, was also reflected by the fact that they retard decomposition of triorganopalladium(IV) complexes[28,31] and cationic triorganoplatinum(IV) complexes in solution.[28]

Rigid Ar-BIAN ligands do not only facilitate CO insertion in palladium–carbon bonds and stabilize the acylpalladium complexes formed but also activate the acyl complexes to undergo alkene insertion reactions, as can be derived from the observed reactivity toward insertion of strained alkenes of both neutral Pd(C(O)Me)Cl(Ar-BIAN) (**3**) and cationic $[Pd(C(O)Me)(MeCN)(Ar\text{-}BIAN)]SO_3CF_3$ (**4**) palladium complexes. As opposed to the reactivity of the neutral acylpalladium(Ar-BIAN) complexes **3**, no insertion was observed for the neutral complexes Pd(C(O)(Me)I(bpy) or Pd(C(O)Me)I(tmeda) (tmeda = *N,N,N′,N′*-tetramethylethylenediamine),[32] whereas cationic $[Pd(C(O)Me)(MeCN)(bpy)]SO_3CF_3$ underwent insertion of strained alkenes.[11g,34]

Another aspect of the use of rigid chelating ligands is that insertion of strained alkenes in both neutral and cationic complexes yields the same type of products **8** and **9**, which only differ in the counterion, as was also observed in the insertion of alkenes in acetyl–palladium bonds of complexes containing the chelating diphosphine $Ph_2P(CH_2)_3PPh_2$. On the contrary, reaction of norbornene with cationic palladium complexes containing monodentate phosphine ligands resulted in the formation of $[Pd(C_7H_{10}C(O)Me)(PPh_3)_2]BF_4$, similar to **10a**, whereas the neutral $Pd(C(O)Me)Cl(PPh_3)_2$ reacted with norbornene via loss of coordinated phosphine, giving a neutral monophosphine complex $Pd(C_7H_{10}C(O)Me)Cl(PPh_3)$.[11c]





Successive Insertion Reactions of CO and Alkenes. The activating effect of the rigid Ar-BIAN ligands on insertion reactions has allowed us to study for the first time stepwise the

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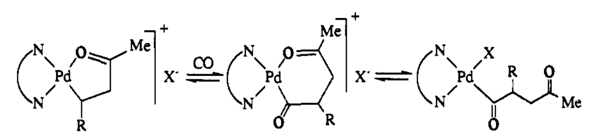
(31) Byers, P. K.; Canty, A. J.; Honeyman, R. T.; Watson, A. A. *J. Organomet. Chem.* **1989**, *363*, C22.

(32) This difference in reactivity is not due to the halide, as the iodide complex Pd(C(O)Me)I(*p*-An-BIAN) shows the same reactivity toward strained alkenes as the chloride analogue **3a**.

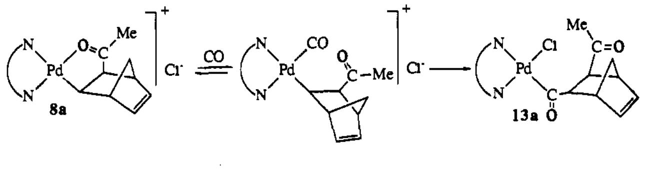
(33) The reaction can be monitored by IR spectroscopy. After CO insertion a (broad) signal is observed at about 1700 cm^{-1}, whereas two signals are observed at about 1600 and 1700 cm^{-1} after alkene insertion.

(34) After submission of this paper, a communication appeared in which the synthesis of (ionic) complexes $Pd(\{C(O)C_7H_{10}\}_nC(O)Me)X(bpy)$ (X = Cl, I) and $[Pd\{C_7H_{10}C(O)\}_nMe)(bpy)]SO_3CF_3$ ($n = 1,2$) and an X-ray crystal structure of $Pd(\{C(O)C_7H_{10}\}_2C(O)Me)I(bpy)$ were reported: Markies, B A.; Verkerk, K. A. N.; Rietveld, M. H. P.; Boersma, J.; Kooijman, H.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1993**, 1317.

Scheme 3



Scheme 4



CO/alkene copolymerization via successive insertion of CO and alkenes in palladium–carbon bonds by starting from neutral acylpalladium complexes. In situ spectroscopic characterization of acyl complexes of the type [Pd{(C(O)CH(Ar)CH$_2$}$_n$C(O)Me)(bpy)(CO)]BAr$_4$ (n = 1–3) formed via multiple insertion reactions has been reported,[16] but here the isolation and full characterization of both acyl- and alkylpalladium complexes containing alternating CO and alkene units formed after each insertion have been exemplified. As no reaction was observed for the norbornadiene-inserted complex [Pd(C$_7$H$_8$C(O)Me)(*p*-An-BIAN)]SO$_3$CF$_3$ (**9a**) with carbon monoxide, it is evident that the chloride anion is important for the stabilization of the acyl complex [Pd(C(O)C$_7$H$_8$C(O)Me)Cl(*p*-An-BIAN)] (**13a**).

After the insertion of carbon monoxide in the five-membered palladacycle of **8**,**9a**, a free coordination site or a six-membered palladacycle is formed (Scheme 3), which are both expected to result from thermodynamically unfavorable processes. Occupation of the empty coordination site by the chloride anion leads to an overall exothermic reaction and formation of **13a**, whereas in the case of the noncoordinating anion SO$_3$CF$_3$, insufficient energy of stabilization is provided and the overall insertion reaction remains endothermic. A similar mechanism has been proposed for the insertion of carbon monoxide after reaction of norbornene with Pd(C(O)Me)Cl(Ph$_2$P(CH$_2$)$_3$PPh$_2$), which was observed as a side reaction.[11h]

Another possible explanation invokes coordination of CO with concomitant opening of the five-membered palladacycle, from which the insertion of CO is aided by the chloride anion (Scheme 4), similar to the observations made for palladium and platinum complexes containing a cyclometalated tridentate N–N–C ligand (LH = 6-PhCH(Me)-bpy): [M(L)(S)]BF$_4$ complexes (M = Pd, Pt; S = solvent) did not give any CO insertion, whereas PdCl(L) underwent CO insertion under higher CO pressure.[26b]

The acyl complex **13a** reacted quantitatively with norbornadiene to give an isolated alkyl complex containing alternating inserted CO and alkene units, i.e., [Pd(C$_7$H$_8$C(O)C$_7$H$_8$C(O)Me)(*p*-An-BIAN)]Cl (**14a**) (eq 6). The isolation and characterization of the new complexes **13a** and **14a**, formed via successive CO and alkene insertion reactions, provide direct evidence for the stepwise chain growth in palladium-catalyzed CO/alkene copolymerization.[4b,h] The analytical data of the analogous complex [Pd(C$_7$H$_8$C(O)C$_7$H$_8$C(O)Me)(*p*-An-BIAN)]SO$_3$CF$_3$ (**15a**) showed unequivocally the insertion of two CO and two norbornadiene moieties, which is further supported by spectroscopic data of the complexes and a ^{13}C(O)-labeled analogue of **14a**. The complexes **14a** showed further reaction with CO and alkenes, but the complexity of the ^{1}H NMR spectra made assignment difficult.[33] Furthermore, after the second alkene insertion, further insertions are expected to proceed alike, and the basic idea of stepwise chain growth of the CO/alkene copolymer is demonstrated by our results.

The activating effect of the Ar-BIAN ligands on the insertion reactions gave us the opportunity to use neutral acylpalladium complexes for the stepwise insertions of norbornadiene and CO. Furthermore, the stabilizing effect due to the rigidity of the Ar-BIAN ligands and the presence of the chloride anion has allowed us to isolate and fully characterize both acyl- and alkylpalladium complexes formed after successive insertion reactions. It must be noted that successive insertion reactions were not observed for complexes [Pd(C$_7$H$_8$C(O)Me)(*p*-An-BIAN)]SO$_3$CF$_3$ (**9a**), whereas catalytic copolymerization is carried out by using palladium complexes with weakly coordinating anions.[4,5] However, this seeming discrepancy can be explained by the different conditions of the catalytic reactions as compared to our stoichiometric conditions. The high CO pressure might lead to an increased rate of carbonylation of **9a**, and, in the presence of a large excess of alkene relative to palladium, the formed acylpalladium complex analogous to **13a** is trapped by reaction with alkene, thereby making the reaction exothermic and driving the copolymerization.

Conclusion

Neutral and cationic organopalladium complexes containing the rigid bidentate nitrogen ligands Ar-BIAN undergo facile (successive) insertion of carbon monoxide and strained alkenes. The facile insertion of carbon monoxide and norbornadiene, especially in the neutral complexes Pd(C(O)Me)Cl(Ar-BIAN) **3**, is surprising in view of earlier observations that insertion rates for comparable Pd–diphosphine complexes decreased with increasing ligand rigidity[7f,11h] and the observed unreactivity of analogous Pd(C(O)Me)I(bpy) and Pd(C(O)Me)I(tmeda) complexes toward alkenes.[11g] The rigidity of the nitrogen ligand plays an important role in the increased reactivity toward insertion by preventing dissociation of one of the coordinating N-atoms and thereby forcing dissociation of the halide, as it was shown that complexes with other bidentate chelating nitrogen ligands such as bpy were less reactive toward carbon monoxide and alkenes.[9a] Furthermore, the good σ-donor capacity of Ar-BIAN and the accessibility of the palladium center in the presented complexes, as compared to those bearing sterically crowding phosphine or nitrogen ligands, will facilitate the insertion reactions.

The activating effect of the rigid Ar-BIAN ligands on insertion of CO and alkenes in palladium–carbon bonds and the availability of pure complexes [Pd(C$_7$H$_8$C(O)Me)(*p*-An-BIAN)]Cl (**8a**) allowed us to investigate stepwise the successive CO and alkene insertion reactions by starting from neutral alkylpalladium complexes. After each separate insertion step, both acyl- and alkyl-palladium complexes of the type PdC(O)CH(R′)CH(R′)C(O)Me and Pd(CH(R′)CH(R′)C(O)CH(R′)CH(R′)C(O)Me, containing alternating CO and alkene units, have been isolated and fully characterized. These observations provide direct evidence for the mechanism of copolymerization via alternating insertion of CO in alkyl–palladium and of alkenes in acyl–palladium bonds.[4] Furthermore, the isolation of a living oligomer and its ability to undergo further insertions of CO and norbornadiene demonstrates the utility and aptness of rigid bidentate nitrogen ligands in both stabilizing and activating organopalladium systems.

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Supplementary Material Available: Listing of ^{1}H NMR (Table S1), ^{13}C NMR (Table S2), and IR (Table S3) spectroscopic data for the complexes **1–14**, which are not included in Tables 1 and 2 (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.