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


Published in: Journal of the American Chemical Society

DOI: 10.1021/ja00082a020

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (http://dare.uva.nl)
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)SF CF complexes, i.e., complexes containing the rigid bidentate nitrogen ligands bis(arylino)acenaphthene (Ar-BIAN); Ar = p-MeOC6H4, p-Tol, o,o'-i-PrC6H3, X = Cl, I; R = PhCH2, X = Br; R = p-MeC6H4, X = I, except in the case of RX = p-N02C6H4CH2Br, 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)SCF reacted 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 Pd(COR) 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(C7H8C(O)C7H8C(O)Me)(p'-An-BIAN) Cl reacted further with carbon monoxide to give the isocarbonyl complex Pd(C(O)C6H4CH2C(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(O)C6H4CH2C(O)Me)(p-An-BIAN)Cl (14a), which reacted with AgSO3CF3 to give Pd(C7H8C(O)C6H4C(O)Me)(p-An-BIAN)SO3CF3 (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. One special class of carbonylation reactions concerns the copolymerization of alkenes and carbon monoxide, leading to the formation of polyketones, a reaction which is very efficiently catalyzed by palladium-carbon bonds (Scheme 1). An alternative mechanism involving palladium carbene intermediates, explaining the formation of spiroketals as the initial products, has recently been proposed.

A lot of experimental and theoretical 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...
Scheme 1

preferentially from a four-coordinate complex, formed by substitution of a phosphine ligand by CO. However, the carbonation of complexes with more rigid chelating ligands, such as bidentate N-N or tridentate N-N-N ligands, 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. Furthermore, a variety of complexes formed by insertion of (strained) alkenes in palladium–acyl bonds has been isolated. 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. Intramolecular insertions of bidentate nitrogen donor ligands to palladium carbon bonds of complexes containing rigidly chelating bidentate and tridentate ligands.

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) or Pd-phosphine-catalyzed cross coupling reactions of organic halides with organometallic reagents.

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, whereas insertion in complexes with more rigid nitrogen ligands was shown to occur readily. 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 successful insertions of these molecules after the insertion of the first molecule of norbornadiene. Elegant work by Brookhart and co-workers has led to the in situ characterization of acyl complexes of the type [Pd(CO)(CH$_2$)C(O)(Me)(bpy)-(CO)]BAr$_4$ (n = 1–3), formed by successive insertions of CO and 4-tert-butylystyrene in catonic acyl palladium complexes. As chloride may, by association and dissociation when required, 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 alkyl-palladium complexes formed after successive CO and alkene insertions, respectively.

Experimental Section

All manipulations were carried out in an atmosphere of dry nitrogen using standard Schlenk 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. $^1$H NMR spectra were recorded on a Bruker AC 100 spectrometer (94.20 MHz) relative to CFCl$_3$ as external standard. $^1$H NMR spectra were recorded on a Bruker AMX 300 spectrometer (121.50 MHz) relative to 85% H$_3$PO$_4$ 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(CO)(COD) = (Z,Z)-1,5-cyclooctadiene), $^{17}$ Ar-BIAN, $^{18}$ PdBr(C$_2$H$_4$)H-p-(Ar-BIAN) (R = H, NO$_2$) and Pd(p-Tol)(Ar-BIAN) were synthesized according to previously reported procedures. $^{19}$ Pd-p-Tol-(Ar-BIAN) was a solution of 0.30 mmol of Pd-p-Tol-CI (1.13 mmol) in 20 mL of dichloromethane was added 0.48 g of p-An(1.22 mmol; p-An = p-MeOC$_6$H$_4$) 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 x 5 mL). The combined filtrates were evaporated to dryness. The product was washed with diethyl ether (3 x 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$_x$H$_y$Cl$_z$O$_w$Pd$_3$): C, 59.01 (59.03); H, 4.38 (4.22); N, 5.06 (5.10).

Dichloromethane was added 20 mg of PPh₃ (0.076 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 the complex in dichloromethane/methanol (3:1). Anal. Found (calcd for C₃₇H₄₃ClN₂O₇Pd): C, 66.21 (66.57); H, 6.50 (6.32); N, 4.38 (4.21).

Pd(Me)(C₇H₄(0)Me)(p-An-BIAN) (7a). To a solution of 40 mg of Pd(Me)(C₇H₄(0)Me)(p-An-BIAN) (0.16 mmol) in 10 mL of dichloromethane was added 20.3 mg of AgSO₃CF₃ (0.097 mmol), and the mixture was stirred at 20 °C. After 15 min, the mixture 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 (5 mL) and dried in vacuo, yielding 0.15 g of a brown product (80%). Anal. Found (calcd for C₃₇H₂₇BrN₂O₇PdS): C, 58.29 (58.51); H, 4.31 (4.35); N, 2.96 (3.10).

Pd(C(0)Me)(C₇H₈C(0)Me)(p-An-BIAN) (13a). To a solution of 0.11 g of Pd(C(0)Me)(C₇H₈C(0)Me)(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(0)Me)(C₇H₈C(0)Me)(p-An-BIAN)(S)SO₃CF₃ (15a). To a solution of 56.7 mg of 14a (0.072 mmol) in 10 mL of dichloromethane was added 21.0 mg of AgSO₃CF₃ (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 C₃₇H₂₇BrN₂O₇PdS): C, 58.29 (58.51); H, 4.31 (4.35); N, 2.96 (3.10).

Results

Synthesis of the Starting Organopalladium Complexes. Methylenediphosphine chloride complexes 1 were synthesized starting from Pd(Me)(CICOD) (eq 1; COD = (Z,Z)-1,5-cyclooctadiene), similar to the reported methylenediphosphine complexes with bidentate P-P, P-N, and N-N and tridentate N-N-N ligands. The facile high-yield synthesis of Pd(Me)(CICOD) makes this route preferable to the one via [Pd(Me)(µ-Cl)(SM)2]₂.²⁰

Pd(Me)(CICOD) + Ar-BIAN

CH₂C≡CH, 20 °C

1a, Ar = MeOC₆H₄
1b, Ar = o,o′-i-Pr₂C₆H₄

The corresponding methylenediphosphine iodide complexes were obtained by adding Pd(Me)(CICOD) by carrying out the substitution reaction in the presence of an excess sodium iodide. Pd(Me)(C₄H₄ ar-BIAN) (1e) obtained in this way was identical to the complex obtained by oxidative addition of iodomethane to zerovalent Pd(p-Tol-BIAN)(alkene) complexes. Cationic complexes of the type [Pd(Me)(Ar-BIAN)(S)SO₃CF₃ (S = solvent molecule) (2) were obtained by the reaction of the corresponding halide complexes with silver trifluoromethanesulfonate (eq 2).

Ordinating solvents such as dichloromethane and chloroform led re-figatively upon reaction of the cationic complexes. The reactions were completed within 1 min under ambient evacuation followed by admission of CO into the reaction flask reversibly, as the neutral complexes are regenerated quanti-tatively upon reaction of the cationic complexes with the compatible sodium halide. Insertion of Carbon Monoxide. All methylpalladium complexes reacted rapidly with carbon monoxide to give the corresponding acetyl palladium complexes (eq 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 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 decarbo-nylation occurs much more slowly. When a solution of Pd(C(O)-Me)Cl(p-An-BIAN) (3a) (p-An = p-anisyl = p-MeOCH2C6H4) 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)2(MeCN)(p-An- BIAN)]SO3CF3 (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)]SO3CF3 (4a) and free acetonitrile. This product was also obtained from the reaction of carbon monoxide with [Pd(Me)2(p-An-BIAN)]SO3CF3 prepared in situ from 1a and AgSO3CF3 in CdCl3 in the absence of acetonitrile. Conversely, short reaction times of 2a with CO in CdCl3 (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)]SO3CF3 (4a) and [Pd(C(O)Me)(MeCN)(p-An-BIAN)]SO3CF3 (4a′, major product).

In solution 4a was obtained as the only complex when an excess of acetonitrile (ca. 20 equiv) was added to a CdCl3 solution of a mixture of 4a and 4a′. The analogous complex [Pd(C(O)-Me)( CdCl3)](p-Tol-BIAN)]SO3CF3 (4c′) was obtained via dehalogenation of the acyl complex 3c with silver trifluoro- methanesulfonate in CdCl3 and studied in situ. As compared to their neutral counterparts 3a, 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)(PPh3)]SO3- CF3 (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(An-BIAN) complexes occurred within 15 min, yielding quantitatively the acyl complexes PdBr(C(O)CH2-Ph)(An-BIAN) (5a, 5b, 5c) and Pd(C(O)-tol-Tol-BIAN) (7a, respectively. On the contrary, PdBr(C6H5CH2-NO2)(p-Tol-BIAN) reacted much more slowly, and conversion to the acyl complex PdBr(C6H5CH2-CH2-C6H4-NO2)(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. Use of a metallic needle to bubble CO gas through a solution of PdBr(C6H5CH2-CH2-C6H4-NO2)(p-Tol-BIAN) gave complete conversion to 6c within 5 min. Reaction of PdBr(C6H5CH2-Ph)(An-BIAN) (5a,c) with AgSO3- CF3 in the presence or in the absence of acetonitrile gave no cationic acylpalladium complex, but instead [Pd(C7H8-CH3-Ph)(An-BIAN)]SO3CF3 was formed, which was identical to the reaction product obtained from PdBr(C6H5CH2-Ph)(An-BIAN) and AgSO3- CF3.

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)SO3CF3 (4a) with strained alkenes led to the insertion of these alkenes in the acyl–palladium bond, similar to previously reported insertion reactions.11 Reaction with norbornadiene (eq 5) led to the rapid quantitative formation of the insertion products [Pd(C7H8C(O)Me)(p-An- BIAN)]X (8a, X = Cl; 8a, X = SO3CF3; 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- (C7H8C(O)Me)(p-An-BIAN)]SO3CF3 (10a) and [Pd(C7H8- H2C(O)Me)(p-An-BIAN)]SO3CF3 (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). The analogous 0,0′-t-PrC6H4-2-BIAN complexes 3b reacted with norbornene to give the insertion complexes 8b, 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% conversion within 1 h). Norbornadiene also readily reacted with the propionyl complex Pd(C(O)Et)Cl(p-An-BIAN), giving quantitatively the insertion complex [Pd(C7H8C(O)Et)(p-An-BIAN)]Cl (12a) within 5 min. Interestingly, reaction of Pd(C(O)Et)Cl(p-An-BIAN) with

---

(21) (a) The increased rate of CO insertion when a metallic needle was used was observed before 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)2(Pr3)2, ZnCl2, and H+ has been published: Kraakman, M. J. A.; de Klerk-Engels, B.; de Lange, P. P. M.; Vrieze, K.; Simons, W. J. J.; Spek, A. L. Organometallics 1992, 1, 3774. (b) Similar species containing a chelating diphosphate have recently been identified: Tóth, I.; Elsevier, C. J. J. Am. Chem. Soc. 1993, 115, 10388-10389.


(23) (a) 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.15
norbornene and dicyclopentadiene produced mixtures of the acyl- and the alkene-inserted complexes in the same ratio (63:37 and 9.8, respectively) as observed in the reaction of the acetyl complex Pd(C=O)Cl(Ph2P(CH2)3-PPPh2),11b 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, 1H, and 13C 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(C7H8C(O)C7H8C(O)Me)2Cl(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(C7H8C(O)C7H8C(O)Me)2Cl(p-An-BIAN)]SO3CF3 (15a) has been obtained by the reaction of 14a with Ag2SO3CF3.

**Table 1.** 1H NMR Data of Selected Acyl- and Alkylpalladium Insertion Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>H3</th>
<th>H4</th>
<th>H5</th>
<th>H9,10</th>
<th>H12</th>
<th>H13,17</th>
<th>H15,16</th>
<th>H18</th>
<th>H19</th>
<th>H21</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a†</td>
<td>6.67 d (7.3)</td>
<td>7.50 pst (8.4)</td>
<td>8.06 d (9)</td>
<td>7.1 m (10)</td>
<td>7.1 m (11)</td>
<td>5.96 dd (12)</td>
<td>1.66 d (13)</td>
<td>2.47 d (14)</td>
<td>2.53 s</td>
<td></td>
</tr>
<tr>
<td>3a ‡</td>
<td>6.8 vbr (7.3)</td>
<td>7.44 ppt (8.3)</td>
<td>8.03 d (9)</td>
<td>7.4 m (10)</td>
<td>7.4 m (11)</td>
<td>5.48 dd (12)</td>
<td>1.28 d (13)</td>
<td>2.53 d (14)</td>
<td>2.50 s</td>
<td></td>
</tr>
<tr>
<td>8a</td>
<td>7.18 d (7.2)</td>
<td>7.54 pst (8.3)</td>
<td>8.14 d (9)</td>
<td>7.38 d (10)</td>
<td>7.13 d (11)</td>
<td>2.00 dd (12)</td>
<td>3.00 s (13)</td>
<td>5.96 dd (14)</td>
<td>1.66 d (15)</td>
<td></td>
</tr>
<tr>
<td>9a</td>
<td>6.80 d (7.3)</td>
<td>7.53 pst (8.3)</td>
<td>8.15 d (9)</td>
<td>7.1 m (10)</td>
<td>3.94 s (11)</td>
<td>1.91 dd (12)</td>
<td>3.07 s (13)</td>
<td>5.48 dd (14)</td>
<td>1.53 d (15)</td>
<td></td>
</tr>
<tr>
<td>10a</td>
<td>6.77 d (7.3)</td>
<td>7.58 pst (8.3)</td>
<td>8.13 pst (9)</td>
<td>7.38 d (10)</td>
<td>3.94 s (11)</td>
<td>2.44 dd (12)</td>
<td>2.38 br (13)</td>
<td>1.51 m (14)</td>
<td>1.63 d (15)</td>
<td></td>
</tr>
<tr>
<td>11a ‡</td>
<td>6.51 d (7.3)</td>
<td>7.53 pst (8.3)</td>
<td>7.38 d (9)</td>
<td>7.13 d (10)</td>
<td>3.94 s (11)</td>
<td>2.44 dd (12)</td>
<td>2.38 br (13)</td>
<td>1.51 m (14)</td>
<td>1.63 d (15)</td>
<td></td>
</tr>
<tr>
<td>13a</td>
<td>6.65 br (7.1)</td>
<td>7.46 br (8.2)</td>
<td>7.3 br (9)</td>
<td>7.1 br (10)</td>
<td>7.1 br (11)</td>
<td>3.87 s (12)</td>
<td>3.00 s (13)</td>
<td>6.13 dd (14)</td>
<td>0.79 d (15)</td>
<td></td>
</tr>
<tr>
<td>14a</td>
<td>7.18 d (7.1)</td>
<td>7.49 pst (8.2)</td>
<td>8.11 d (9)</td>
<td>7.31 d (10)</td>
<td>7.06 d (11)</td>
<td>3.88 s (12)</td>
<td>1.84 dd (13)</td>
<td>2.05 s (14)</td>
<td>1.39 d (15)</td>
<td></td>
</tr>
</tbody>
</table>

* Recorded at 300.13 MHz in CDCl3 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). † 0.91 s, PdMe2. ‡ 2.23 s, Pd(CO)2Me. 3.76 s. 7.00 ppm. Remarkably, for the complexes [Pd(C7H8C(O)C7H8C(O)Me)2Cl(p-An-BIAN)]Cl(8a) the signal is overlapped by H2. 4 Signals of the C=CH2/CO/Me moiety which is not part of the palladacycle (numbers are marked by a prime): H23 overlapped by H21; 3.33 s, 3.05 s, H14,15; 6.28 dd (3.5, 3.2 Hz), 6.03 dd (5.5, 2.7 Hz), H15,16; 1.41 s (2 H), H19; 2.48 d (4.2 Hz), H19; 2.09 s, C(O)Me2.

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)MeCl(Ph2P(CH2)3-PPPh2),11b 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, 1H, and 13C 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(C7H8C(O)C7H8C(O)Me)2Cl(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(C7H8C(O)C7H8C(O)Me)2Cl(p-An-BIAN)]SO3CF3 (15a) has been obtained by the reaction of 14a with Ag2SO3CF3.

**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 1H NMR and 4.2–4.7 ppm in 13C NMR, while the cationic complexes [Pd(Me)Cl(MeCN)(Ar-BIAN)]SO3CF3 2 give Pd–Me resonances at somewhat lower frequencies, in agreement with earlier observations.24 The methyl resonance of coordinated acetoni trile (2.28 (2a) and 2.08 ppm (2b)) is observed at higher frequency than that of free acetone triate (2.00 ppm). Remarkably, for the complexes [Pd(Me)Cl(MeCN)(Ar-BIAN)]SO3CF3, the CN stretching frequency is absent in IR. Unfortunately, no IR data were reported.

for other cationic cis-PdII(MeCN) complexes containing bishosphines.74,27 byp,26 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 methy resonance from 0.8–0.9 to 2.2–2.5 ppm in 1H 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 13C NMR spectroscopy. These data agree well with those reported for other cis-acyl palladacycles and for Pd(C(O)Me)(MeCN)(PPh3)2BF411c and of dicyclopentadiene cis positions.11d,11e 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 8–11. The complexes formed after insertion of norbornadiene, norbornene, and dicyclopentadiene (8–11) were characterized by 1H and 13C 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 1H NMR spectra for the insertion products 8–11 show a well-defined pattern for the inserted alkene, and from the coupling constants J(H13–H19), which are in the range 5.6–6.7 Hz, cis addition of Pd(C(O)Me) to the exo face of the alkene can be concluded.11c

The coordination of the phosphine in [Pd(C(O)Me)(p-An-BIAN)(PPh3)]SO2CF3 (4a') is clear from the observed resonance at 27.4 ppm in 31P NMR. In IR, a Pd(C(O)Me) signal is observed at 1705 cm–1, and in 1H NMR the methyl resonance has shifted to 1.69 ppm, in agreement with literature values for complexes with C(O)Me and PPh ligands in cis positions.19,11c 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.

Table 2. 13C NMR Data of Selected Acyl and Alkyl Insertion Complexes (Adopted numbering scheme is shown below)

<table>
<thead>
<tr>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
<th>C9</th>
<th>C10</th>
<th>C11</th>
<th>C12</th>
<th>C13</th>
<th>C14/17</th>
<th>C15/16</th>
<th>C18</th>
<th>C19</th>
<th>C20</th>
<th>C21</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>n.o.</td>
<td>127.6</td>
<td>125.5</td>
<td>129.0</td>
<td>131.5</td>
<td>131.9</td>
<td>144.6</td>
<td>140.2</td>
<td>115.5</td>
<td>124.3</td>
<td>159.7</td>
<td>56.1</td>
<td>46.9, c13,14,17</td>
<td>c13,,14',17'; 138.7, 138.6, 139.1, 44.8, c18,19; 62.7, c19; 208.7, c20; 29.7, C(0)Me.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>n.o.</td>
<td>126.9</td>
<td>125.1</td>
<td>131.0</td>
<td>139.0</td>
<td>114.7</td>
<td>123.2</td>
<td>159.2</td>
<td>159.6</td>
<td>50.0</td>
<td>48.8</td>
<td>135.6</td>
<td>45.9</td>
<td>62.9</td>
<td>236.0 28.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8a</td>
<td>170.7</td>
<td>126.0</td>
<td>125.7</td>
<td>129.2</td>
<td>132.7</td>
<td>131.8</td>
<td>146.0</td>
<td>138.8</td>
<td>115.5</td>
<td>123.9</td>
<td>160.2</td>
<td>160.2</td>
<td>46.8</td>
<td>122.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9a</td>
<td>176.1</td>
<td>126.3</td>
<td>126.4</td>
<td>129.3</td>
<td>133.1</td>
<td>131.9</td>
<td>146.0</td>
<td>138.6</td>
<td>116.9</td>
<td>124.4</td>
<td>160.9</td>
<td>160.3</td>
<td>42.2</td>
<td>28.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10a</td>
<td>176.5</td>
<td>125.5</td>
<td>126.3</td>
<td>129.3</td>
<td>133.0</td>
<td>131.9</td>
<td>145.6</td>
<td>139.0</td>
<td>115.9</td>
<td>124.3</td>
<td>160.7</td>
<td>56.4</td>
<td>57.2</td>
<td>43.8</td>
<td>29.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11a</td>
<td>176.5</td>
<td>126.5</td>
<td>126.6</td>
<td>129.4</td>
<td>133.4</td>
<td>131.7</td>
<td>145.6</td>
<td>138.7</td>
<td>115.2</td>
<td>124.7</td>
<td>160.5</td>
<td>56.6</td>
<td>53.8</td>
<td>44.7</td>
<td>39.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15a</td>
<td>171.2</td>
<td>127.1</td>
<td>125.8</td>
<td>129.0</td>
<td>131.8</td>
<td>131.7</td>
<td>144.7</td>
<td>138.6</td>
<td>115.2</td>
<td>124.0</td>
<td>159.6</td>
<td>56.1</td>
<td>55.0</td>
<td>44.7</td>
<td>39.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14a</td>
<td>175.6</td>
<td>126.2</td>
<td>126.3</td>
<td>129.3</td>
<td>133.0</td>
<td>131.7</td>
<td>144.7</td>
<td>138.8</td>
<td>115.8</td>
<td>123.6</td>
<td>160.5</td>
<td>56.5</td>
<td>46.2</td>
<td>63.8</td>
<td>241.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16a</td>
<td>152.5</td>
<td>125.6</td>
<td>125.2</td>
<td>132.6</td>
<td>138.0</td>
<td>115.3</td>
<td>139.5</td>
<td>134.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Recorded at 75.48 MHz in CDCl3 at 20 °C, unless noted otherwise (n.o. = not observed). a 4.7, PdMe* 223.4, Pd(C(O)Me) 33.8; Pd(C(O)Me)Cl(p-An-BIAN)

(1) The PdC(0)Me signal is observed 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)(PPh3)]S03CF3, which shows v(CN) at 2120 ppm, is clear from the observed resonance at 27.4 ppm in 31P NMR. In IR, a Pd(C(O)Me) signal is observed at 1705 cm–1, and in 1H NMR the methyl resonance has shifted to 1.69 ppm, in agreement with literature values for complexes with C(O)Me and PPh ligands in cis positions.19,11c 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 8–11. The complexes formed after insertion of norbornadiene, norbornene, and dicyclopentadiene (8–11) were characterized by 1H and 13C 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 1H NMR spectra for the insertion products 8–11 show a well-defined pattern for the inserted alkene, and from the coupling constants J(H13–H19), which are in the range 5.6–6.7 Hz, cis addition of Pd(C(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)(PPh3)]BF4,10d and of dicyclopentadiene with [Pd(C(O)Me)(MeCN)(bpy)]SO2CF318c 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(Ph3P(H2)2-PPh3).11b The acyl oxygen atom is coordinated to the palladium, forming a five-membered palladacycle, in agreement with previous observations.11c,24 as can be derived from the CO stretching frequency at 1600 cm–1 in IR,29 the carbonyl resonance at approximately 240 ppm in 13C NMR, and the methyl resonance at about 2.4 ppm in 1H NMR. The presence of trifluoro-
romethanesulfonate as an anion, not coordinated to palladium, appears from IR.\textsuperscript{27,28} Furthermore, for complexes 8, 9 the observed chemical shift difference of approximately 0.5 ppm for the remaining alkene protons (H\textsubscript{15,16}) of the norbornadiene moiety is characteristic for an inserted norbornadiene that is part of a five-membered palladacycle.\textsuperscript{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}cm^{-1} 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}cm^{-1} mol^{-1}, respectively.

Insertion of norbornadiene and norborne 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.

The complexes 8 and 9 obtained from the insertion of norbornadiene in neutral Pd(C(O)(OMe)Cl(2-Ar-BIAN)) (3) and cationic Pd(C(O)(OMe)(2-Ar-BIAN)(Si)SO\textsubscript{2}CF\textsubscript{3} (4a, 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\textsubscript{2}CF\textsubscript{3}. A major difference in the behavior of the chloride (8) and trifluoromethanesulfonate (9) complexes appears from the fluxional behavior in \textsuperscript{1}H 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-ansyl substituents on the imine N-atom, which are oriented out of the coordination plane,\textsuperscript{28} 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 \(\sigma_{\text{NS}}\) of \(\text{Pr}_{2}C_{5}H_{7}\)-BIAN ligand, is in the limit of slow exchange at −40 °C, which appears from the observation of two doublets for H\textsubscript{2} (8.26 (J = 8.5 Hz), 8.22 ppm (J = 8.6 Hz)) and H\textsubscript{1} (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\textsubscript{1} (i-Pr) (1.3 (13 H, +H\textsubscript{1}), 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 acetyl norborne moiety, aided by coordination of the anion to palladium.

(8b)

\[ \text{Insertion of CO and Alkenes on the Way to Polyketones} \]

The complex [Pd(C\textsubscript{5}H\textsubscript{4}C(0)C\textsubscript{7}H\textsubscript{5}C(O)(OMe)(p-An-BIAN))]Cl (14a), formed after reaction of 13a with norborne, was characterized by IR, \textsuperscript{1}H, and \textsuperscript{13}C NMR spectroscopy. The observed coupling constant \(J(H_{15}-H_{16})\) of 5.8 Hz in \textsuperscript{1}H NMR reveals that the insertion occurs via \textit{cis} addition of Pd(CO)R to the exo face of norborne, similar to the monoinsertion complexes 8-12. \textsuperscript{1}H and \textsuperscript{13}C NMR revealed the presence of two distinct inserted norborne moieties. One is part of a five-membered palladacycle formed by coordination of the acyl oxygen to palladium, as is clear from \textsuperscript{1}H NMR (H\textsubscript{15,16} at 5.95 and 5.40 ppm), \textsuperscript{13}C NMR (CO at 241.2 ppm), and IR (\(\nu(CO) = 1598 \text{ cm}^{-1}\)). The other norborne moiety is not part of a palladacycle and resembles the pendant norborne moiety of complex 13a (methyl (H\textsubscript{2}) at 2.09 ppm, H\textsubscript{15,16} at 6.28 and 6.03 ppm in \textsuperscript{1}H NMR; CO at 208.7 ppm in \textsuperscript{13}C NMR; \(\nu(CO) = 1703 \text{ cm}^{-1}\)).

The complexes [Pd(C\textsubscript{5}H\textsubscript{4}C(0)C\textsubscript{7}H\textsubscript{5}C(O)(OMe)(p-An-BIAN))]Cl (14a), formed after reaction of 13a with norborne, was characterized by IR, \textsuperscript{1}H, and \textsuperscript{13}C NMR spectroscopy. The observed coupling constant \(J(H_{15}-H_{16})\) of 5.8 Hz in \textsuperscript{1}H NMR reveals that the insertion occurs via \textit{cis} addition of Pd(CO)R to the exo face of norborne, similar to the monoinsertion complexes 8-12. \textsuperscript{1}H and \textsuperscript{13}C NMR revealed the presence of two distinct inserted norborne moieties. One is part of a five-membered palladacycle formed by coordination of the acyl oxygen to palladium, as is clear from \textsuperscript{1}H NMR (H\textsubscript{15,16} at 5.95 and 5.40 ppm), \textsuperscript{13}C NMR (CO at 241.2 ppm), and IR (\(\nu(CO) = 1598 \text{ cm}^{-1}\)). The other norborne moiety is not part of a palladacycle and resembles the pendant norborne moiety of complex 13a (methyl (H\textsubscript{2}) at 2.09 ppm, H\textsubscript{15,16} at 6.28 and 6.03 ppm in \textsuperscript{1}H NMR; CO at 208.7 ppm in \textsuperscript{13}C NMR; \(\nu(CO) = 1703 \text{ cm}^{-1}\)).

These results clearly rule out formation of an eight-membered palladacycle via coordination of the carbonyl oxygen of the C(OMe) 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 \textsuperscript{13}C NMR data [Pd(C\textsubscript{5}H\textsubscript{4}C(0)C\textsubscript{7}H\textsubscript{5}C(O)(OMe)(p-An-BIAN))]Cl, formed when \textit{13}C-labeled carbon monoxide was used. Furthermore, in IR the CO stretching frequencies of the \textsuperscript{13}C(O)-labeled complex are observed at 1660 and 1550 cm\textsuperscript{-1}, and the found ratios \(\nu(13CO)/\nu(12CO)\) 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\textsubscript{2}CF\textsubscript{3} resulted in conversion to the analogous complex [Pd(C\textsubscript{5}H\textsubscript{4}C(0)C\textsubscript{7}H\textsubscript{5}C(O)(OMe)(p-An-BIAN))]SO\textsubscript{2}CF\textsubscript{3} (15a), which was stable enough to allow us to obtain analytical data.

\textbf{Discussion}

\textit{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.\textsuperscript{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 bond 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
which can be expected in solvents like chloroform and dichloromethane. The effect of the Ar-BIAN ligand can be ascribed to its rigidity, which cannot undergo the insertion reaction (Scheme 2). In the case of flexible bidentate ligands, dissociation of the ligand to the organic group is prohibited and the only alternative is decomposition: in the case of rigid bidentate ligands, dissociation of the coordinating atom is expected, leading to the formation of a complex which only differ in the counterion, as was also observed in the insertion of alkenes in acetyl-palladium bonds containing the chelating diphosphine ligands. The activating effect of the rigid Ar-BIAN ligands is expected to play an important role. In this study, the equilibrium of halide dissociation lies completely to the side of the neutral starting acyl complex, whereas in the case of the reverse CO insertion reaction, excess CO is present thereby shifting the equilibrium toward the complex. 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, whereas complexes with the more flexible 2,6-(Me2NCH=)2-pyridine ligand decarbonylated at 20 °C. 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 and cationic triorganoplatinum(IV) complexes in solution.

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 alkynes of both neutral Pd(C(O)Me)Cl(Ar-BIAN) (3) and cationic [Pd(C(O)Me)(MeCN)(Ar-BIAN)]SO2CF3 (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'-tetramethylethlenediamine), whereas cationic [Pd(C(O)(Me)(MeCN)(bpy)]SO2CF3 underwent insertion of strained alkynes.

Another aspect of the use of rigid chelating ligands is that insertion of strained alkynes 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 ligands. On the contrary, reaction of norbornene with cationic palladium complexes containing monodentate phosphine ligands resulted in the formation of [Pd(C7H10(C(O)(Me)(PPh3)][BF4], similar to 10a, whereas the neutral Pd(C(O)(Me)Cl(PPh3)2 reacted with norbornene via loss of coordinated phosphine, giving a neutral monophosphine complex Pd(C7H10(C(O)(Me)Cl(PPh3).11c

**Scheme 2**

![Scheme 2](image)

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...
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)C2H4C(O)Me)-(bpy)(CO)]][Ar-BIAN](n = 1–3) formed via multiple insertion reactions has been reported, but here the isolation and full characterization of both acyl- and alkylpalladium complexes containing alternating CO and alkene units after each insertion have been exemplified. As no reaction was observed for the norbornadiene-inserted complex [Pd(C2H4C(O)Me)(p-An-BIAN)]SO3CF3 (13a) with carbon monoxide, it is evident that the chloro anion is important for the stabilization of the acyl complex [Pd(C(O)-C2H4C(O)Me)p-An-BIAN]Cl (13a).

After the insertion of carbon monoxide in the five-membered palladacycle of 8a, 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 nocoordinating anion SO3CF3, 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 norbornadiene with Pd(C(O)Me)Cl(PH3/P(CH3)3PPh3), 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 chloro anion (Scheme 4), similar to the observations made for palladium and platinum complexes containing a cyclometalated tridentate N–N–C ligand (LH = 6-PhCH2(Me)-bpy): [M(L)(S)]BF4 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(C2H4C(O)C2H4C(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 The analytical data of the analogous complex [Pd(C2H4C(O)C2H4C(O)Me)(p-An-BIAN)]SO3CF3 (15a) showed unequivocally the insertion of two CO and two norbornadiene moieties, which is further supported by spectroscopic data of the complexes and a 13C-labeled analogue of 14a. The complexes 14a showed further reaction with CO and alkenes, but the complexity of the 2H NMR spectra made assignment difficult.31 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(C2H4C(O)Me)(p-An-BIAN)]SO3CF3 (9a), whereas catalytic copolymerization is carried out by using palladium complexes with weakly coordinating anions.4b 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 rigidity7b,11h and the observed unreactivity of analogous Pd(C(O)Me)(bpy) and Pd(C(O)Me)(tmdea) complexes toward alkenes.11b 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(C2H4C(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 Pd(C(O)CH(R)C(0)CH(R)-C(O)Me) and Pd(CH(R)2CH(R)C(0)CH(R)C(0)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 complexes.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.

Acknowledgment. We thank Prof. Dr. P. W. N. M. van Leeuwen and Dr. E. Drent (Koninklijke/Shell Laboratorium Amsterdam) for helpful discussions and the Netherlands Foundation of Chemical Research (SON) and the Netherlands Organization of Scientific Research (NWO) for financial support (to R. v. A.).

Supplementary Material Available: Listing of 1H NMR (Table S1), 13C 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.