Stepwise Successive Insertion of Carbon Monoxide and Allenes into Palladium−Carbon Bonds of Complexes Containing the Rigid Bidentate Nitrogen Ligand Bis(*p*-anisylimino)acenaphthene

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Propadiene, 3-methyl-1,2-butadiene (DMA), and 2,4-dimethyl-2,3-pentadiene (TMA) reacted via migratory insertion with both neutral and ionic Pd(R)X(*p*-An-BIAN) (R = Me (**1**), C(O)-Me (**2**); X = Cl (**a**), SO_3CF_3 (**b**)) complexes, containing the rigid nitrogen ligand bis(*p*-anisylimino)acenaphthene (*p*-An-BIAN), resulting in the novel and stable allylpalladium complexes Pd(η^3-C_3H_4R)X(*p*-An-BIAN) (R = Me (**3**), C(O)Me (**6**)), Pd(η^3-C_5H_8R)X(*p*-An-BIAN) (R = Me (**4**), C(O)Me (**7**)), and Pd(η^3-$C_7H_{12}R$)X(*p*-An-BIAN) (R = Me (**5**), C(O)Me (**8**)), respectively (X = Cl (**a**), SO_3CF_3 (**b**)). The neutral complexes **6a** and **7a** reacted with carbon monoxide to form the acylpalladium complexes Pd(C(O)C_3H_4C(O)Me)Cl(*p*-An-BIAN) (**9**) and Pd(C(O)C_5H_8C(O)Me)Cl(*p*-An-BIAN) (**10**), respectively, while the analogous trifluoromethanesulfonate complexes **6b** and **7b** were completely inert toward CO. Complexes **9** and **10** reacted again with propadiene and DMA, respectively, to yield the allylpalladium complexes Pd(η^3-C_3H_4C(O)C_3H_4C(O)Me)Cl(*p*-An-BIAN) (**11**) and Pd(η^3-C_5H_8C(O)C_5H_8C(O)Me)Cl(*p*-An-BIAN) (**12**), respectively. Also insertion of norbornadiene in complex **10** was possible, yielding the ionic complex [Pd(C_7H_8C(O)C_5H_8C(O)Me)(*p*-An-BIAN)]Cl (**13a**), which reacted with $AgSO_3CF_3$ to give [Pd(C_7H_8C(O)C_5H_8C(O)Me)(*p*-An-BIAN)]SO_3CF_3 (**13b**). The novel complexes **9**−**12** are the first isolated and fully characterized complexes formed by successive insertion reactions of carbon monoxide and allenes, while **13a** is the first isolated complex containing a metal-bonded ter-oligomer of carbon monoxide, an allene, and norbornadiene. The X-ray crystal structure of **7a** has been determined and shows a distorted square pyramidal geometry in which the BIAN ligand is bonded to the palladium center in an unusual asymmetric fashion (Pd−N(1) = 2.144(7) Å; Pd−N(2) = 2.600(8) Å).

Introduction

The insertion of unsaturated molecules like carbon monoxide, alkenes, alkynes, and allenes into metal−carbon bonds is a very important step in many transition metal catalyzed processes.[1−4] Two very interesting, recently developed examples in which a palladium-based catalyst is used are the alkoxy carbonylation of alkynes[5] and in particular the copolymerization of carbon monoxide and alkenes, resulting in the formation of polyketones.[6−14] The most favored mechanism of this copolymerization proceeds via successive stepwise insertion reactions of carbon monoxide and the alkene into palladium−carbon bonds. To explain the sometimes observed formation of spiroketals, Consiglio *et al.* proposed an alternative mechanism involving palladium−carbene intermediates,[10] but very recently Sen *et al.* showed that spiroketals can be formed from polyketones.[13]

Although much is known about the CO/alkene copolymerization,[6−13] relatively little is known about the alternating insertion of CO and alkenes on a metal center. Elegant work of Brookhart *et al.* has resulted in the *in situ* characterization of acyl complexes of the

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(1) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986.

(2) Tkatchenko, I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8.

(3) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(4) Cazes, B. *Pure Appl. Chem.* **1990**, *62*, 1867.

(5) Drent, E.; Arnoldy, P.; Budzelaar, P. H. M. *J. Organomet. Chem.* **1993**, *455*, 247.

(6) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235.

(7) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1982**, *104*, 3520.

(8) Lai, T.-W.; Sen, A. *Organometallics* **1984**, *3*, 866.

(9) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303.

(10) Batistini, A.; Consiglio, G. *Organometallics* **1992**, *11*, 1766.

(11) Brookhart, M.; Rix, F. C.; DeSimone, J. M.; Barborak, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 5894.

(12) Bartolini, S.; Carfagna, C.; Musco, A. *Macromol. Rapid Commun.* **1995**, *16*, 9.

(13) Jiang, Z.; Sen, A. *J. Am. Chem. Soc.* **1995**, *117*, 4455.

(14) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663.

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type [Pd(C(O)[CH(Ar)CH$_2$C(O)]$_n$Me)(bpy)(CO)]BAr$_4$ (n = 1−3), formed via successive insertion of CO and 4-*tert*-butyl styrene into ionic acylpalladium complexes.[11] Very recently Brookhart also succeeded in the *in situ* characterization of [Pd(C(O)Me)(phen)(C$_2$H$_4$)]BAr$_4$ and [Pd(Me)(phen)(CO)]BAr$_4$, two believed key intermediates in the palladium(II) mediated CO/ethene copolymerization.[15] Boersma *et al.* reported a sequential insertion of CO and norbornene, starting from the neutral methyl complex Pd(Me)X(bpy) (X = I, Cl).[16,17] However, varying the anion with each step was required to accomplish this sequential insertion. Elsevier *et al.* reported a sequential insertion of CO and norbornadiene, also starting from a neutral palladium methyl complex but without the need of varying the anion. By starting from the complex Pd(Me)Cl(*p*-An-BIAN), bearing the rigid bidentate nitrogen ligand bis(*p*-anisylimino)acenaphthene (*p*-An-BIAN), metal-bonded co-oligomers up to [Pd(C$_7$H$_8$C(O)C$_7$H$_8$C(O)Me)(*p*-An-BIAN)]Cl could be isolated and fully characterized.[18,19] The stability and reactivity of the acyl- and alkylpalladium intermediates were attributed to the rigidity of the BIAN ligand, which is able to stabilize otherwise labile organometallic intermediates.[20]

At this point, we wanted to study whether the stability and reactivity of complexes containing the BIAN ligand would also facilitate co-oligomerization of CO and other unsaturated molecules than strained alkenes. We have chosen to turn our attention to allenes, since it is known that α-diimine ligand containing palladium complexes are able to catalyze the copolymerization of allenes and CO.[21] Furthermore, it has been shown very recently that the electrophilic central carbon atom of allenes reacts in a fast and clean fashion with the nucleophilic R group of complexes of the type Pd(R)X(L) (R = alkyl, acyl; X = Cl, Br, BF$_4$; L = bidentate, tridentate nitrogen ligand).[22,23] Here we describe the isolation and full characterization of novel acyl-, allyl-, and alkylpalladium complexes, formed after successive CO, allene, and norbornadiene insertions, respectively.

Experimental Section

General Comments. All manipulations were carried out in an atmosphere of purified dry nitrogen by using standard Schlenk techniques. Solvents were dried and stored under nitrogen. Carbon monoxide 99.5% was purchased from Hoek-Loos and propadiene from Air Products, which were used without further purification. *p*-An-BIAN[24] and Pd(R)X(*p*-An-BIAN) (R = Me (**1**), C(O)Me (**2**); X = Cl (**a**), SO$_3$CF$_3$ (**b**))[19] were prepared according to the literature. The allylpalladium dimers [Pd(η^3-C$_3$H$_4$R)Cl]$_2$, [Pd(η^3-C$_5$H$_8$R)Cl]$_2$, and [Pd(η^3-C$_7$H$_{12}$R)Cl]$_2$ were prepared by the reaction of Pd(R)Cl(COD) (R = Me, C(O)Me; COD = 1,5-cyclooctadiene) with propadiene, 3-methyl-1,2-butadiene (dimethylallene, DMA), and 2,4-dimethyl-2,3-pentadiene (tetramethylallene, TMA), respectively.[25] All other starting chemicals were used as commercially obtained. Silver trifluoromethanesulfonate was stored under nitrogen in the dark. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 300 spectrometer (300.13 and 75.48 MHz, respectively). Chemical shifts are in ppm relative to TMS as external standard. ^{19}F NMR spectra were recorded on a Bruker AC 100 spectrometer (94.20 MHz) at 20 °C, relative to CFCl$_3$ as external standard. IR spectra were obtained on a Bio-Rad FTS-7 spectrophotometer. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

Neutral Allylpalladium Complexes 3a−8a. Method A. Propadiene was bubbled for 1 min through a solution of Pd(Me)Cl(*p*-An-BIAN) (**1a**) (219.7 mg, 0.40 mmol) in 25 mL of dichloromethane. In the case of DMA and TMA 0.44 mmol (1.1 equiv) was added. After being stirred at 20 °C for 16 h in the case of propadiene and DMA and for 3 days in the case of TMA the dark red solution was evaporated to dryness and the product was washed with diethyl ether (2 × 20 mL) and dried in vacuo. The products could be isolated in high yields (88−97%).

In the same way were synthesized by the reaction of Pd(C(O)Me)Cl(*p*-An-BIAN) (**2a**) with propadiene, DMA, and TMA (reaction times and yields in parentheses) Pd(η^3-C$_3$H$_4$C(O)Me)Cl(*p*-An-BIAN) (**6a**, 15 min, 95%), Pd(η^3-C$_5$H$_8$C(O)Me)Cl(*p*-An-BIAN) (**7a**, 15 min, 90%), and Pd(η^3-C$_7$H$_{12}$C(O)Me)Cl(*p*-An-BIAN) (**8a**, 16 h, 87%), respectively.

Method B. To a solution of [Pd(η^3-C$_3$H$_4$Me)Cl]$_2$ (39.4 mg, 0.10 mmol) in 20 mL of dichloromethane was added *p*-An-BIAN (86.3 mg, 0.22 mmol). After being stirred at 20 °C for 5 min, the solution was evaporated and the residue was washed with diethyl ether (2 × 20 mL) and dried in vacuo, resulting in Pd(η^3-C$_3$H$_4$Me)Cl(*p*-An-BIAN) (**3a**) (0.18 mmol, 90%).

Complexes **4a**−**8a** were synthesized from the corresponding allylpalladium dimers in the same way (86−92%).

3a. MS: found, m/z = 554 (calcd for C$_{30}$H$_{27}$N$_2$O$_2$Pd, 554). No correct microanalysis was obtained, probably due to the presence of a small amount of [Pd(η^3-C$_3$H$_4$Me)Cl]$_2$.

4a. Anal. Found (calcd for C$_{32}$H$_{31}$ClN$_2$O$_2$Pd): C, 62.01 (62.25); H, 5.05 (5.06); N, 4.49 (4.54).

5a. Anal. Found (calcd for C$_{34}$H$_{35}$ClN$_2$O$_2$Pd): C, 62.95 (63.26); H, 5.47 (5.47); N, 4.40 (4.34).

6a. IR (KBr): 1692 cm^{-1}, ν(CO). Anal. Found (calcd for C$_{31}$H$_{27}$ClN$_2$O$_3$Pd): C, 60.18 (60.30); H, 4.35 (4.41); N, 4.62 (4.54).

7a. IR (KBr): 1690 cm^{-1}, ν(CO). Anal. Found (calcd for C$_{33}$H$_{31}$ClN$_2$O$_3$Pd): C, 61.26 (61.40); H, 4.83 (4.84); N, 4.38 (4.34).

8a. IR (KBr): 1700 cm^{-1}, ν(CO). MS: found, m/z = 638 (calcd for C$_{35}$H$_{35}$N$_2$O$_3$Pd, 638). No correct microanalysis was obtained, probably due to the presence of a small amount of [Pd(η^3-C$_7$H$_{12}$C(O)Me)Cl]$_2$.

Ionic Allylpalladium Complexes 3b−8b. Method A. To a solution of Pd(Me)Cl(*p*-An-BIAN) (**1a**) (82.4 mg, 0.15 mmol) in a mixture of 20 mL of dichloromethane and 1 mL of acetonitrile was added AgSO$_3$CF$_3$ (43.7 mg, 0.17 mmol). After the solution was stirred for 1 min in the dark at 20 °C propadiene was bubbled through for 1 min or in the case of DMA and TMA 0.17 mmol (1.1 equiv) was added. After being

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[15] Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137.

[16] 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.

[17] Markies, B. A.; Kruis, D.; Rietveld, M. H. P.; Verkerk, K. A. N.; Boersma, J.; Kooijman, H.; Lakin, M. T.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1995**, *117*, 5263.

[18] van Asselt, R.; Gielens, E. E. C. G.; Rülke, R. E.; Elsevier, C. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1203.

[19] van Asselt, R.; Gielens, E. E. C. G.; Rülke, R. E.; Vrieze, K.; Elsevier, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 977.

[20] van Asselt, R.; Rijnberg, E.; Elsevier, C. J. *Organometallics* **1994**, *13*, 706.

[21] Drent, E. Neth. Appl. 1988, 88/1168; *Chem. Abstr.* **1990**, *113*, 24686f.

[22] Rülke, R. E.; Kliphuis, D.; Elsevier, C. J.; Fraanje, J.; Goubitz, K.; van Leeuwen, P. W. N. M.; Vrieze, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1817.

[23] Rülke, R. E. *Insertion Reactions with Novel Palladium Complexes;* Dutch PhD Thesis; University of Amsterdam: Amsterdam, The Netherlands, 1995; pp 103−128.

[24] van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; Benedix, R. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 88.

[25] Ankersmit, H. A.; Veldman, N.; Spek, A. L.; Eriksen, K.; Goubitz, K.; Vrieze, K.; van Koten, G. *Inorg. Chim. Acta*, in press.

stirred for 10 min in the dark at 20 °C, the red solution was evaporated to dryness. After addition of 20 mL of dichloromethane the solution was filtered through Celite filter aid. The residue was extracted with dichloromethane (5 mL), and the combined filtrates were evaporated to dryness. The product was washed with diethyl ether (2 × 20 mL) and dried in vacuo, giving **3b**−**5b** in yields varying from 65 to 85%.

Method B. To a solution of $[Pd(\eta^3\text{-}C_3H_4Me)Cl]_2$ (24.4 mg, 0.062 mmol) in a mixture of 25 mL of dichloromethane and 1 mL of acetonitrile were added $AgSO_3CF_3$ (36.0 mg, 0.14 mmol) and *p*-An-BIAN (54.9 mg, 0.14 mmol). After being stirred for 15 min in the dark at 20 °C, the solution was evaporated to dryness. After addition of 20 mL of dichloromethane the solution was filtered through Celite filter aid. The residue was extracted with dichloromethane (5 mL), and the combined filtrates were evaporated to dryness. The residue was washed with diethyl ether (2 × 20 mL) and dried in vacuo, giving $[Pd(\eta^3\text{-}C_3H_4Me)(p\text{-An-BIAN})]SO_3CF_3$ (**3b**) (0.11 mmol, 85%).

Complexes **4b** (70%) and **5b** (76%) were synthesized from the corresponding allylpalladium dimers in the same way.

Method C. To a solution of **3a**−**5a** (0.05 mmol) in a mixture of 25 mL of dichloromethane and 1 mL of acetonitrile was added $AgSO_3CF_3$ (0.06 mmol, 1.2 eq.). After being stirred for 10 min in the dark at 20 °C, the solution was evaporated to dryness. After addition of 20 mL dichloromethane the solution was filtered through Celite filter aid. The residue was extracted with dichloromethane (5 mL), and the combined filtrates were evaporated to dryness. The product was washed with diethyl ether (2 × 20 mL) and dried in vacuo, giving **3b**−**5b** in virtually quantitative yields.

With the same methods $[Pd(\eta^3\text{-}C_3H_4C(O)Me)(p\text{-An-BIAN})]SO_3CF_3$ (**6b**), $[Pd(\eta^3\text{-}C_5H_8C(O)Me)(p\text{-An-BIAN})]SO_3CF_3$ (**7b**), and $[Pd(\eta^3\text{-}C_7H_{12}C(O)Me)(p\text{-An-BIAN})]SO_3CF_3$ (**8b**) were synthesized.

3b. IR (KBr): 1265, 1152, 1032, 638 cm^{-1}, $\nu(SO_3CF_3)$. ^{19}F NMR ($CDCl_3$): −78.5 ppm. Anal. Found (calcd for $C_{31}H_{27}F_3N_2O_5PdS$): C, 52.75 (52.96); H, 3.95 (3.87); N, 4.04 (3.98).

4b. IR (KBr): 1269, 1151, 1031, 637 cm^{-1}, $\nu(SO_3CF_3)$. ^{19}F NMR ($CDCl_3$): −78.6 ppm. Anal. Found (calcd for $C_{33}H_{31}F_3N_2O_5PdS$): C, 54.08 (54.21); H, 4.35 (4.28); N, 3.88 (3.83).

5b. IR (KBr): 1263, 1165, 1030, 638 cm^{-1}, $\nu(SO_3CF_3)$. ^{19}F NMR ($CDCl_3$): −78.3 ppm. Anal. Found (calcd for $C_{35}H_{35}F_3N_2O_5PdS$): C, 55.26 (55.38); H, 4.74 (4.65); N, 3.58 (3.69).

6b. IR (KBr): 1701 cm^{-1}, $\nu(CO)$; 1252, 1153, 1030, 637 cm^{-1}, $\nu(SO_3CF_3)$. ^{19}F NMR ($CDCl_3$): −78.6 ppm. Anal. Found (calcd for $C_{32}H_{27}F_3N_2O_6PdS$): C, 52.42 (52.58); H, 3.88 (3.73); N, 3.94 (3.83).

7b. IR (KBr): 1701 cm^{-1}, $\nu(CO)$; 1263, 1152, 1030, 637 cm^{-1}, $\nu(SO_3CF_3)$. ^{19}F NMR ($CDCl_3$): −78.7 ppm. Anal. Found (calcd for $C_{34}H_{31}F_3N_2O_6PdS$): C, 54.02 (53.80); H, 4.12 (4.12); N, 3.73 (3.69).

8b. IR (KBr): 1707 cm^{-1}, $\nu(CO)$; 1264, 1155, 1031, 638 cm^{-1}, $\nu(SO_3CF_3)$. ^{19}F NMR ($CDCl_3$): −78.7 ppm. Anal. Found (calcd for $C_{36}H_{35}F_3N_2O_6PdS$): C, 54.78 (54.93); H, 4.55 (4.48); N, 3.59 (3.56).

$Pd(C(O)C_3H_4C(O)Me)Cl(p\text{-An-BIAN})$ (9). A solution of $Pd(\eta^3\text{-}C_3H_4C(O)Me)Cl(p\text{-An-BIAN})$ (**6a**) (168.2 mg, 0.26 mmol) in 20 mL of dichloromethane was brought into a 100 mL stainless-steel autoclave, and CO was introduced up to 50 bar. After the solution was stirred at 20 °C for 2 h, the pressure was released and the solution was filtered through Celite filter aid. The residue was extracted with dichloromethane (5 mL), and the combined filtrates were evaporated to dryness. The product was washed with diethyl ether (2 × 20 mL) and dried in vacuo, yielding a dark brown product (0.24 mmol, 93%). IR (KBr): 1701, 1686 cm^{-1}, $\nu(CO)$. Anal. Found (calcd for $C_{32}H_{27}ClN_2O_4Pd$): C, 59.38 (59.55); H, 4.41 (4.22); N, 4.30 (4.34).

$Pd(C(O)C_5H_8C(O)Me)Cl(p\text{-An-BIAN})$ (10) was obtained from $Pd(\eta^3\text{-}C_5H_8C(O)Me)Cl(p\text{-An-BIAN})$ (**7a**) in the same way by using 25 bar of CO (83%). IR (KBr): 1699, 1677 cm^{-1}, $\nu(CO)$. Anal. Found (calcd for $C_{34}H_{31}ClN_2O_4Pd$): C, 60.51 (60.63); H, 4.61 (4.64); N, 4.21 (4.16).

$Pd(\eta^3\text{-}C_3H_4C(O)C_3H_4C(O)Me)Cl(p\text{-An-BIAN})$ (11). Through a solution of $Pd(C(O)C_3H_4C(O)Me)Cl(p\text{-An-BIAN})$ (**9**) (42.7 mg, 0.066 mmol) in 25 mL of dichloromethane, propadiene was bubbled for 1 min. After being stirred at 20 °C for 15 min, the dark red solution was evaporated to dryness and the product was washed with diethyl ether (2 × 20 mL). After being dried in vacuo, a red solid was obtained (0.050 mmol, 76%). IR (KBr): 1696, 1675 cm^{-1}, $\nu(CO)$. Anal. Found (calcd for $C_{35}H_{31}ClN_2O_4Pd\cdot CH_2Cl_2$): C, 56.79 (56.12); H, 4.51 (4.32); N, 3.74 (3.64).

$Pd(\eta^3\text{-}C_5H_8C(O)C_5H_8C(O)Me)Cl(p\text{-An-BIAN})$ (12) was obtained from $Pd(C(O)C_5H_8C(O)Me)Cl(p\text{-An-BIAN})$ (**10**) in the same way (83%). IR (KBr): 1700, 1685 cm^{-1}, $\nu(CO)$. Anal. Found (calcd for $C_{39}H_{39}ClN_2O_4Pd$): C, 62.74 (63.16); H, 5.45 (5.30); N, 3.89 (3.78).

$[Pd(C_7H_8C(O)C_5H_8C(O)Me)(p\text{-An-BIAN})]Cl$ (13a). Norbornadiene (2.5 μL, 0.024 mmol) was added to a solution of $Pd(C(O)C_5H_8C(O)Me)Cl(p\text{-An-BIAN})$ (**10**) (15.3 mg, 0.023 mmol) in 20 mL of chloroform at 20 °C. After 30 min the solution was evaporated to dryness and the product was washed with diethyl ether (2 × 20 mL) and dried in vacuo, giving a red product (0.015 mmol, 67%), which was too unstable in the solid state to allow outside microanalysis. IR (KBr): 1605 cm^{-1} (br), $\nu(CO)$.

$[Pd(C_7H_8C(O)C_5H_8C(O)Me)(p\text{-An-BIAN})]SO_3CF_3$ (13b). To a solution of $[Pd(C_7H_8C(O)C_5H_8C(O)Me)(p\text{-An-BIAN})]Cl$ (**13a**) (23.0 mg, 0.030 mmol) in a mixture of 20 mL of dichloromethane and 1 mL of acetonitrile was added $AgSO_3CF_3$ (8.5 mg, 0.033 mmol), and the mixture was stirred in the dark at 20 °C. After 15 min, the mixture was evaporated to dryness. After addition of 20 mL of dichloromethane the solution was filtered through Celite aid and the residue was extracted with dichloromethane (5 mL). The combined filtrates were evaporated to dryness and the product was washed with diethyl ether (2 × 20 mL) and dried in vacuo, yielding a dark red product (0.017 mmol, 57%). IR (KBr): 1600 cm^{-1} (br), $\nu(CO)$; 1252, 1155, 1031, 637 cm^{-1}, $\nu(SO_3CF_3)$. ^{19}F NMR ($CDCl_3$): −78.5 ppm. Anal. Found (calcd for $C_{42}H_{39}F_3N_2O_7PdS\cdot 1.5CH_2Cl_2$): C, 51.86 (51.90); H, 4.29 (4.21); N, 2.77 (2.78).

Structure Determination and Refinement of 7a. A red rod-shaped crystal of **7a** was mounted on top of a glass fiber (using the inert-oil technique) and transferred to the cold nitrogen stream of an Enraf-Nonius CAD4T diffractometer for data collection at 150 K (rotating anode, 60 kV, 100 mA, monochromated Mo Kα radiation, ω-scan mode). Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with $9.92 < \theta < 13.83°$. The unit cell parameters were checked for the presence of higher lattice symmetry.[26] A total of 5476 reflections were collected and merged into an unique dataset of 4988 reflections. Data were collected for *Lp*, for a linear decay (8.8%) of the three intensity control reflections during the 14.5 h of X-ray exposure time, and for absorption (using the DIFABS[27] method; correction range 0.665−1.302). The structure was solved with Patterson methods (DIRDIF[28]) and subsequent difference Fourier analyses. Refinement on F^2 with all unique reflections was carried out by full-matrix least-squares techniques. The dichloromethane solvate molecule is disordered over two locations in a 0.105(5):0.895(5) ratio. Hydrogen atoms were introduced on calculated positions and included in the refine-

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(26) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.

(27) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(28) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF Program System. Technical report of the Crystallography Laboratory*; University of Nijmegen: Nijmegen, The Netherlands, 1992.

Table 1. Crystal and Refinement Data for $Pd(\eta^3\text{-}C_5H_8C(O)Me)Cl(p\text{-An-BIAN})$ (7a)

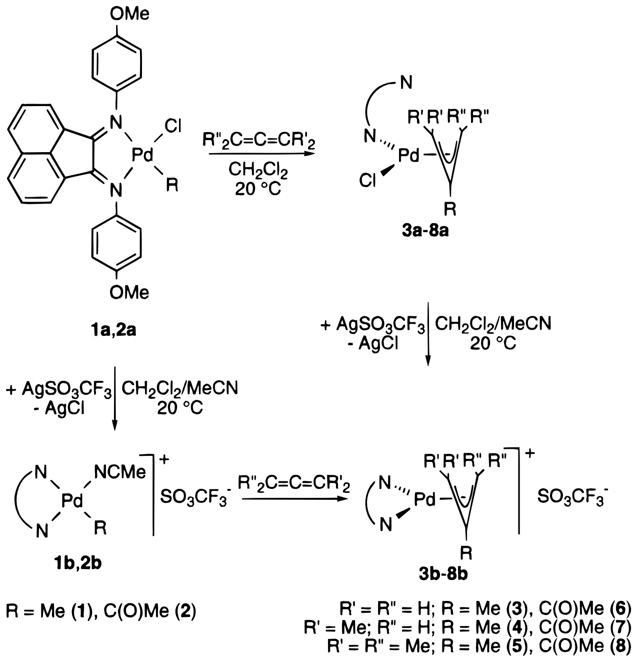
(a) Crystal Data	
formula	$C_{33}H_{31}ClN_2O_3Pd \cdot CH_2Cl_2$
M_r	730.43
cryst system	monoclinic
space group	$P2_1/c$ (No. 14)
a−c (Å)	16.3463(9), 10.8381(8), 19.609(2)
β (deg)	114.19(1)
V (Å^3)	3169.1(5)
Z	4
D_{calcd} (g·cm^{-3})	1.531
$F(000)$	1488
μ (cm$^{-1)}$	8.8
cryst size (mm)	0.10 × 0.13 × 0.42
(b) Data Collection	
θ_{min}, θ_{max}	1.14, 24.00
radiation	Mo Kα (graphite-monochrom), 0.710 73 Å
$\Delta\omega$ (deg)	$0.83 + 0.35 \tan \theta$
hor and vert aperture (mm)	$3.00 + 1.50 \tan \theta$, 4.00
ref reflns	$\bar{2}\bar{1}6$, $\bar{3}\bar{2}\bar{1}$, $\bar{4}\bar{0}\bar{2}$
data set	h, −18 to 17; k, −12 to 0; l, −22 to 0
tot. data	5476
tot. unique data	4988
obsd data	4557 $[Fo^{2\,>} -1.0\sigma(F_o^2)]$
(c) Refinement	
no. of reflns and params	4557, 421
weighting scheme	$w = 1.0/[\sigma^2(F_o^2) + (0.0395P)^2]$
final $R1$, w$R2$, S	0.0689, 0.1287, 0.992
$(\Delta/\sigma)_{av}$ and max in final cycle	0.000, 0.003

ment riding on their carrier atoms. All non-hydrogen atoms, except the minor disorder chloride atoms, were refined with anisotropic thermal parameters; hydrogen atoms with isotropic thermal parameters related to the U_{eq} of the carrier atoms. Weights were introduced in the final refinement cycles; convergence was reached at $R1 = 0.0689$ and $wR2 = 0.1287$. A final difference Fourier analysis shows no features outside the range −0.51 to 0.61 e/Å^3. Crystal data and numerical details of the structure determination are given in Table 1. Neutral atom scattering factors and anomalous dispersion factors were taken from the ref 29. All calculations were performed with SHELXL93[30] and the PLATON[31] package (geometrical calculations and illustrations) on a DEC-5000 cluster.

Results

Insertion of Allenes into Alkyl− and Acyl−Palladium Bonds. The reaction of the neutral palladium complexes Pd(R)Cl(*p*-An-BIAN) (R = Me (**1a**), C(O)Me (**2a**)) and the *in situ* synthesized ionic complexes $[Pd(R)(p\text{-An-BIAN})NCMe]SO_3CF_3$ (R = Me (**1b**), C(O)Me (**2b**)) with allenes led to insertion of the latter into the Pd−R bond. Similar to previously reported allene insertion reactions, the insertion takes place via migration of the R group to the central most electrophilic carbon atom of the allene.[22,23,32−36] As expected, in the case of the ionic complexes **1b** and **2b** allene insertion resulted in ionic allylpalladium complexes. In contrast, allene insertion into the Pd−R bond of the complexes **1a** and **2a** resulted in the formation of neutral allylpalladium complexes (Scheme 1).

Scheme 1



Reaction with propadiene, 3-methyl-1,2-butadiene (dimethylallene, DMA), and 2,4-dimethyl-2,3-pentadiene (tetramethylallene, TMA) with **1a** led to the formation of the insertion products $Pd(\eta^3\text{-}C_3H_4Me)Cl(p\text{-An-BIAN})$ (**3a**), $Pd(\eta^3\text{-}C_5H_8Me)Cl(p\text{-An-BIAN})$ (**4a**), and $Pd(\eta^3\text{-}C_7H_{12}Me)Cl(p\text{-An-BIAN})$ (**5a**), respectively. Complexes **3a** and **4a** were formed in high yields within 16 h, and complex **5a** was formed within 72 h. The reactions of propadiene and DMA with **2a** were much faster compared to the reactions of these allenes with **1a**. The allene insertion products $Pd(\eta^3\text{-}C_3H_4C(O)Me)Cl(p\text{-An-BIAN})$ (**6a**) and $Pd(\eta^3\text{-}C_5H_8C(O)Me)Cl(p\text{-An-BIAN})$ (**7a**) were formed quantitatively within 2 min. Insertion of TMA proceeded much slower, and only after 16 h a complete conversion of **2a** to $Pd(\eta^3\text{-}C_7H_{12}C(O)Me)Cl(p\text{-An-BIAN})$ (**8a**) was observed. Both complexes **1b** and **2b** reacted instantaneously with propadiene, DMA, and TMA to form the ionic complexes $[Pd(\eta^3\text{-}C_3H_4Me)(p\text{-An-BIAN})]SO_3CF_3$ (**3b**), $[Pd(\eta^3\text{-}C_5H_8Me)(p\text{-An-BIAN})]SO_3CF_3$ (**4b**), $[Pd(\eta^3\text{-}C_7H_{12}Me)(p\text{-An-BIAN})]SO_3CF_3$ (**5b**), $[Pd(\eta^3\text{-}C_3H_4C(O)Me)(p\text{-An-BIAN})]SO_3CF_3$ (**6b**), $[Pd(\eta^3\text{-}C_5H_8C(O)Me)(p\text{-An-BIAN})]SO_3CF_3$ (**7b**), and $[Pd(\eta^3\text{-}C_7H_{12}C(O)Me)(p\text{-An-BIAN})]SO_3CF_3$ (**8b**). All ionic allylpalladium complexes could also be obtained in high yields by the reaction of the corresponding halide complexes with $AgSO_3CF_3$.

The reaction of the allylpalladium dimers $[Pd(\eta^3\text{-}C_3H_4R)Cl]_2$, $[Pd(\eta^3\text{-}C_5H_8R)Cl]_2$, and $[Pd(\eta^3\text{-}C_7H_{12}R)Cl]_2$ (R = Me, C(O)Me) with 2 equiv of *p*-An-BIAN also led to the formation of the allylpalladium complexes **3a**, **4a**, **5a**, **6a**, **7a**, and **8a**, respectively (Scheme 2).

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[29] *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

[30] Sheldrick, G. M. *SHELLXL93. Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Federal Republic of Germany, 1993.

[31] Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

[32] Stevens, R. R.; Shier, G. D. *J. Organomet. Chem.* **1970**, *21*, 495.

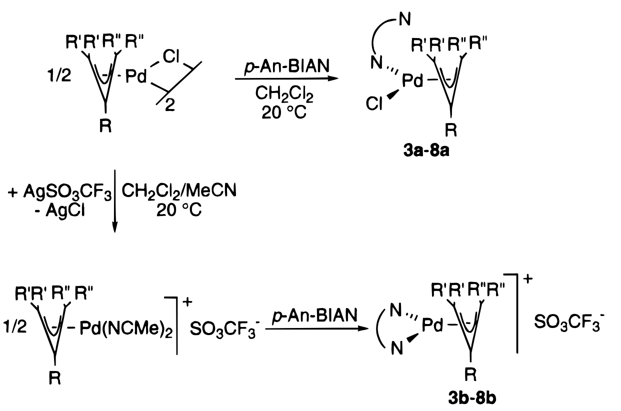
[33] Chrisholm, M. H.; Clark, H. C.; Hunter, D. H. *J. Chem. Soc., Chem. Commun.* **1971**, 809.

[34] Chrisholm, M. H.; Johns, W. S. *Inorg. Chem.* **1975**, *14*, 1189.

[35] Clark, H. C.; Milne, C. R. C.; Wong, C. S. *J. Organomet. Chem.* **1977**, *136*, 265.

[36] De Felice, V.; Cucciolito, M. E.; De Renzi, A.; Ruffo, F.; Tesauro, D. *J. Organomet. Chem.* **1995**, *493*, 1.

Scheme 2



R' = R" = H; R = Me (**3**), C(O)Me (**6**)
R' = Me; R" = H; R = Me (**4**), C(O)Me (**7**)
R' = R" = Me; R = Me (**5**), C(O)Me (**8**)

These reactions occurred instantaneously and, as has been described earlier for other Pd(allyl)(Ar-BIAN),[37] Pd(allyl)(DAB),[38] and Pd(allyl)(Pyca)[39] complexes, in some cases in solution equilibria existed. In the case of **3a**, **4a**, **5a**, and **8a** equilibria with the corresponding allylpalladium dimer and free *p*-An-BIAN were observed, as could be derived from the presence of signals attributable to the dimer and free *p*-An-BIAN in the ^{1}H NMR spectra of **3a**, **4a**, **5a**, and **8a** (10, 13, 33, and 21%, respectively, of the corresponding allylpalladium dimer at 20 °C). Addition of 2 equiv of $AgSO_3CF_3$ before the addition of 2 equiv of *p*-An-BIAN to the corresponding dimer resulted in the formation of the ionic complexes **3b**−**8b** (Scheme 2). The allylpalladium complexes **3a**−**8b** were as a solid as well in solution stable at 20 °C for several weeks and were fully characterized (*vide infra*). Crystals of **7a** suitable for X-ray diffraction were obtained by slow evaporation of a solution of **7a** in dichloromethane at 4 °C.

X-ray Crystal Structure of Pd(η^3-$C_5H_8C(O)Me$)Cl(p-An-BIAN) (7a). The molecular structure of Pd(η^3-$C_5H_8C(O)Me$)Cl(*p*-An-BIAN) (**7a**) with the adopted numbering scheme is shown in Figure 1. Selected bond distances and angles are reported in Table 2.

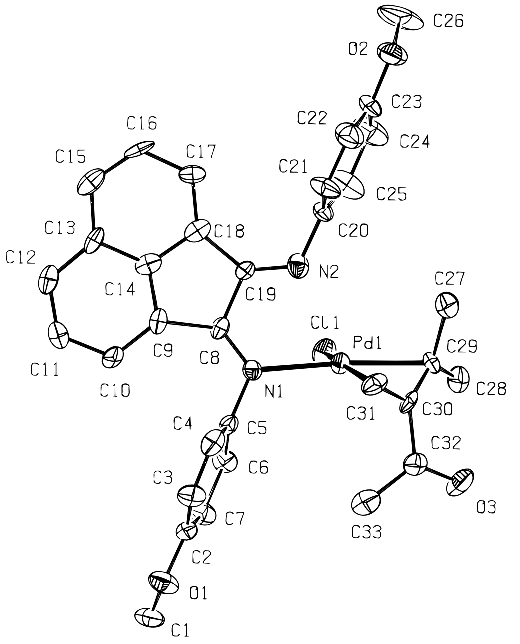


Figure 1. ORTEP drawing (50% probability level) and adopted numbering scheme of Pd(η^3-$C_5H_8C(O)Me$)Cl(*p*-An-BIAN) (**7a**). Hydrogen atoms and CH_2Cl_2 have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Pd(η^3-$C_5H_8C(O)Me$)Cl(*p*-An-BIAN) (7a)

Bond Distances			
Pd(1)−Cl(1)	2.405(3)	C(30)−C(31)	1.409(12)
Pd(1)−N(1)	2.144(7)	C(30)−C(32)	1.510(13)
Pd(1)−N(2)	2.600(8)	C(32)−C(33)	1.508(15)
Pd(1)−C(29)	2.174(9)	O(3)−C(32)	1.218(12)
Pd(1)−C(30)	2.060(9)	N(1)−C(5)	1.439(12)
Pd(1)−C(31)	2.127(10)	N(1)−C(8)	1.272(11)
C(27)−C(29)	1.521(14)	N(2)−C(19)	1.260(11)
C(28)−C(29)	1.481(13)	N(2)−C(20)	1.443(12)
C(29)−C(30)	1.425(13)	C(8)−C(19)	1.512(12)
Bond Angles			
Cl(1)−Pd(1)−N(1)	92.2(2)	C(29)−C(30)−C(31)	120.3(7)
N(1)−Pd(1)−C(31)	100.8(3)	C(30)−C(32)−C(33)	119.8(8)
Cl(1)−Pd(1)−C(29)	96.8(2)	C(30)−C(32)−O(3)	119.4(9)
N(1)−Pd(1)−N(2)	69.8(3)	C(27)−C(29)−C(30)	119.3(8)
Pd(1)−C(30)−C(32)	118.1(6)	C(28)−C(29)−C(30)	122.8(8)

The geometry of **7a** can be described as distorted square pyramidal, with the nitrogen atom N(1), the chloride atom Cl(1), and the terminal allyl carbon atoms C(29) and C(31) positioned on the basal sites and the second nitrogen atom N(2) occupying the apical site. The allyl ligand is bonded almost symmetrically to the palladium center (2.174(9) and 2.127(10) Å for Pd(1)−C(29) and Pd(1)−C(31), respectively). The BIAN ligand is coordinated in an asymmetric fashion: N(1) is at bonding distance from the palladium center (Pd(1)−N(1) = 2.144(7) Å), while N(2) is at a nonbonding distance (Pd(1)−N(2) = 2.600(8) Å). Since the palladium atom lies 0.210(1) Å above the plane defined by N(1), Cl(1), and the barycenter of the allyl triangle, the geometry of **7a** can be seen as intermediate between square planar and square pyramidal.[40] An almost identical coordination fashion has been observed earlier for the 2,9-dimethyl-1,10-phenanthroline ligand in Pd(η^3-C_5H_9)Cl(dmfen)[41] and Pt(CO)I_2(dmfen).[42] All other distances and angles are as expected. The allyl triangle makes an angle of 104(1)° with regard to the plane defined by Pd(1), N(1), Cl(1), and the barycenter of the allyl triangle, which is comparable with those found for other α-diimine ligand containing allylpalladium complexes, *e.g.* 107.3(6)° for [Pd(η^3-$C_7H_{12}C(O)Me$)(bpy)]SO_3CF_3,[22] 106.5(8)° for Pd(η^3-C_5H_9)Cl(dmfen),[41] and 109.4° for [Pd(η^3-C_3H_4Me)(bpy)]SO_3CF_3.[43] Also the palladium−carbon distances of 2.174(9), 2.060(9), and 2.127(10) Å

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[37] van Asselt, R.; Vrieze, K.; Elsevier, C. J. *J. Organomet. Chem.* **1994**, *480*, 27.

[38] Crociani, B.; Boschi, T.; Uguagliati, P. *Inorg. Chim. Acta* **1981**, *48*, 9.

[39] Crociani, B.; Di Bianca, F.; Giovenco, A.; Boschi, T. *Inorg. Chim. Acta* **1987**, *127*, 169.

[40] The distance of the palladium atom from the plane defined by N(1), Cl(1) and the barycenter of the allyl triangle found in **7a** (0.210(1) Å) lies in between the value for an ideal square planar geometry (0 Å) and the calculated value for an ideal square pyramidal geometry (about 1.1 Å).

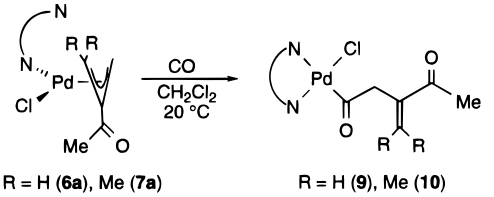
[41] Hansson, S.; Norrby, P.-O.; Sjögren, M. P. T.; Åkermark, B.; Cucciolito, M. E.; Giardano, F.; Vitagliano, A. *Organometallics* **1993**, *12*, 4940.

[42] Fanizzi, F. P.; Maresca, L.; Natile, G.; Lanfranchi, M.; Tiripicchio, A.; Pacchioni, G. *J. Chem. Soc., Chem. Commun.* **1992**, 333.

[43] Albinati, A.; Kunz, R. W.; Ammann, C. J.; Pregosin, P. S. *Organometallics* **1991**, *10*, 1800.

for Pd(1)−C(29), Pd(1)−C(30), and Pd(1)−C(31), respectively, are within the expected values for allylpalladium complexes. The α-diimine plane of the BIAN ligand is roughly planar (torsion angle N(1)−C(8)−C(19)−N(2) = −2.9(12)°) and makes a dihedral angle of 83.0(5)° with the plane defined by Pd(1), N(1), Cl(1), and the barycenter of the allyl triangle. The angles between the plane of the acenaphthene backbone and the aromatic substituents on the nitrogen atoms are 77.3(4) and 77.8(4)°, which is larger than found for free *p*-Tol-BIAN (55−60°)[24] but smaller than the angles observed for Pd(Me)Cl(*o,o′*-*i*$Pr_2C_6H_3$-BIAN) (about 84°),[24] in which two ortho isopropyl substituents are present on the aromatic groups.

Successive Insertion of CO and Allenes. The reaction of complexes **6a** and **7a** with carbon monoxide resulted in the insertion of CO into the allyl−palladium bond to give the acylpalladium complexes Pd(C(O)C_3H_4C(O)Me)Cl(*p*-An-BIAN) (**9**) and Pd(C(O)C_5H_8C(O)Me)Cl(*p*-An-BIAN) (**10**), respectively (eq 1). The presence of methyl substituents on the terminal allyl carbon atoms has a remarkable influence on this CO insertion. Thus a CO pressure of 50 bar was required for a complete conversion of **6a**, while for the conversion of **7a**, which contains two methyl substituents on one terminal allyl carbon atom, a CO pressure of 25 bar was sufficient for a complete conversion. In contrast to **6a** and **7a**, complex **8a**, in which there are two methyl substituents on each of the terminal allyl carbon atoms, was even completely inert toward CO; after 18 h under a CO pressure of 50 bar at 20 °C no reaction was observed. As observed for **8a**, complex **5a** did not react with CO (50 bar, 18 h). Similar to complexes **6a** and **7a**, complexes **3a** and **4a** reacted with CO to form the CO insertion products Pd(C(O)C_3H_4Me)Cl(*p*-An-BIAN) and Pd(C(O)C_5H_8Me)Cl(*p*-An-BIAN), respectively, but in contrast to **6a** and **7a** a complete conversion was not possible (50 and 60% conversion after 24 h under 50 bar of CO for **3a** and **4a**, respectively). Also because of immediate decarbonylation upon releasing the CO pressure, these CO insertion products could not be isolated nor characterized.

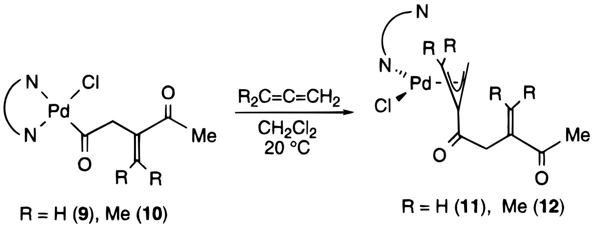


(1)

The nature of the anion in the allylpalladium complexes also plays an important role in the CO insertion reaction. The ionic complexes **3b**−**8b** did not undergo CO insertion under 50 bar of CO at 20 °C, and only slow decomposition resulting in palladium blackening was observed.

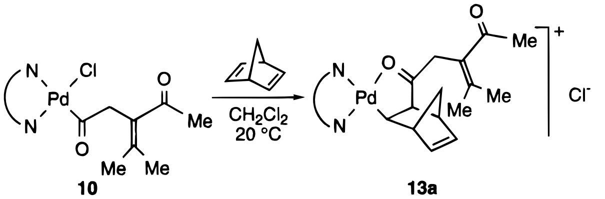
The CO insertion into the allyl−palladium bond of **6a** and **7a** is a reversible reaction. In solution, decarbonylation of the acyl complexes **9** and **10** took place, resulting in the re-formation of **6a** and **7a**, respectively, without decomposition (complete decarbonylation after 16 h for **9** and 2 days for **10** in dichloromethane at 20 °C or within 1 h for **9** and within 2 h for **10** in refluxing dichloromethane). Abstraction of the chloride ion from **9** and **10** by addition of $AgSO_3CF_3$ accelerated the decarbonylation reaction and led to the immediate formation of **6b** and **7b**, respectively. In the solid state both complexes **9** and **10** were much more stable toward decarbonylation (no trace of complexes **6a** and **7a**, respectively, after 20 h in vacuo).

The acylpalladium complexes **9** and **10** reacted rapidly and almost quantitatively with propadiene and DMA, resulting in the formation of the novel allylpalladium complexes Pd(η^3-C_3H_4C(O)C_3H_4C(O)Me)Cl(*p*-An-BIAN) (**11**) and Pd(η^3-C_5H_8C(O)C_5H_8C(O)Me)Cl(*p*-An-BIAN) (**12**), respectively (eq 2). Complexes **11** and **12** are the first isolated and fully characterized complexes, obtained via successive CO and allene insertion reactions.



(2)

Complex **10** also reacted with the strained alkene norbornadiene resulting in formation of the insertion product [Pd(C_7H_8C(O)C_5H_8C(O)Me)(*p*-An-BIAN)]Cl (**13a**) (eq 3). In contrast to all other performed insertion reactions and to the insertion reaction of norbornadiene into the acyl−palladium bond of Pd(C(O)Me)Cl(*p*-An-BIAN),[19] dichloromethane is not a proper solvent for this reaction as the insertion is very slow and unselective, resulting in several uncharacterized norbornadiene insertion products, together with the decarbonylation product **7a**. However, carrying out the reaction in chloroform allowed one to obtain the desired norbornadiene insertion product **13a** quantitatively. The difference in reactivity between norbornadiene and DMA was examined by a competition experiment. When a mixture of 1 equiv of norbornadiene and 1 equiv of DMA was added to a solution of **10** in $CDCl_3$ at 20 °C, an almost exclusive formation of **12** (>99%) and virtually no formation of **13a** (<1%) was observed in the ^1H NMR spectrum of the reaction solution, indicating that the insertion reaction of norbornadiene is much slower than the insertion of DMA in complex **10** .

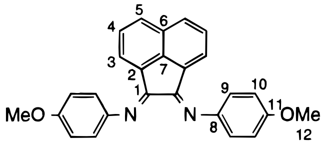


(3)

Norbornadiene also reacted with complex **9** resulting in the insertion product [Pd(C_7H_8C(O)C_3H_4C(O)Me)(*p*-An-BIAN)]Cl, but because of the relative fast decarbonylation of **9** only a mixture of the norbornadiene insertion product and **6a** could be obtained, while the norbornadiene insertion product could not be isolated nor characterized. The complex [Pd(C_7H_8C(O)C_5H_8C(O)Me)(*p*-An-BIAN)]SO_3CF_3 (**13b**) has been obtained by reacting **13a** with 1 equiv of $AgSO_3CF_3$.

The complexes **11**, **12**, and **13a** all showed further reactivity toward CO and allenes/norbornadiene, but

Table 3. ^{1}H NMR Data (δ) for Complexes 3−13[a]



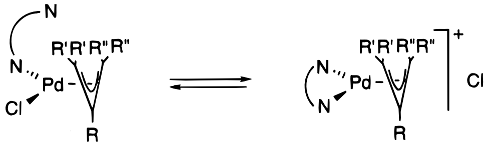
	H$_3$	H$_4$	H$_5$	H$_{9,10}$	H$_{12}$	other signals
3a	7.22 d (7.3)	7.45 pst	8.00 d (8.3)	7.50 d (8.8), 7.06 d (8.8)	3.92 s	3.2 br, H$_{syn,anti}$; 1.96 s, Me
3b	7.29 d (7.3)	7.53 pst	8.10 d (8.3)	7.48 d (8.7), 7.11 d (8.7)	3.94 s	3.44 s, H$_{syn}$; 3.37 s, H$_{anti}$; 2.15 s, Me
4a	7.11 d (7.4)	7.44 pst	7.99 d (8.3)	7.44 d (8.4), 7.07 d (8.4)	3.92 s	3.41 br, H$_{syn}$; 3.30 br, H$_{anti}$; 1.91 s, Me; 1.06 s, Me$_{syn}$, 1.04 s, Me$_{anti}$
4b	*b*	7.52 pst	8.09 d (8.2)	7.40 d (8.5), 7.15 d (8.5)	3.95 s	3.63 s, H$_{syn}$; 3.49 s, H$_{anti}$; 2.07 s, Me; 1.19 s, Me$_{syn}$; 0.72 s, Me$_{anti}$
5a	6.93 d (7.3)	7.46 pst	8.03 d (8.3)	7.35 d (8.7), 7.12 d (8.7)	3.93 s	1.85 s, Me; 1.49 s, Me$_{syn}$; 0.98 s, Me$_{anti}$
5b	6.89 d (7.3)	7.52 pst	8.09 d (8.3)	7.26 d (8.9), 7.18 d (8.9)	3.96 s	1.92 s, Me; 1.53 s, Me$_{syn}$; 0.83 s, Me$_{anti}$
6a	7.33 d (7.3)	7.47 pst	8.00 d (8.2)	7.47 d (8.8), 7.04 d (8.8)	3.91 s	3.3 br, H$_{syn,anti}$; 2.19 s, C(O)Me
6b	7.26 d (7.2)	7.52 pst	8.09 d (8.1)	7.51 br, 7.09 d (8.8)	3.94 s	3.93 s, H$_{syn}$; 3.78 s, H$_{anti}$; 2.31 s, C(O)Me
7a	7.20 d (7.3)	7.43 pst	7.98 d (8.3)	7.49 d (8.6), 7.03 d (8.6)	3.90 s	3.4 br, H$_{syn,anti}$; 2.14 s, C(O)Me; 1.23 s, Me$_{syn}$; 0.95 s, Me$_{anti}$
7b	7.08 d (7.3)	7.52 pst	8.08 d (8.3)	7.45 d (8.9), 7.13 d (8.9)	3.94 s	3.84 d (2.6), H$_{syn}$; 3.61 d (2.6), H$_{anti}$; 2.40 s, C(O)Me; 1.27 s, Me$_{syn}$; 0.70 s, Me$_{anti}$
8a	7.00 d (7.1)	7.42 pst	7.97 d (8.3)	7.44 d (8.8), 7.06 d (8.8)	3.91 s	2.34 s, C(O)Me; 1.49 s, Me$_{syn}$; 1.04 s, Me$_{anti}$
8b	6.88 d (7.3)	7.51 pst	8.07 d (8.3)	7.33 br, 7.15 d (8.6)	3.93 s	2.35 s, C(O)Me; 1.57 s, Me$_{syn}$; 0.66 s, Me$_{anti}$
9	6.67 d (6.5)[b]	7.50 pst, 7.43 pst	8.08 d (7.7), 8.06 d (7.7)	7.24 m, 7.00 m	3.86 s	6.04 s, =CH;[d] 5.61 s, =CH;[e] 3.95 s, CH$_2$; 2.21 s, C(O)Me
10[c,f]	6.55 d (6.8)[b]	7.50 pst, 7.43 pst	8.06 d (8.4), 8.03 d (8.4)	7.27 m, 7.03 m	3.87 s	1.89 s, C(O)Me; 1.73 s, =CMe;[g] 1.28 s, =CMe[h]
11	7.33 d (7.2)	*i*	8.00 d (8.2)	7.46 d (8.8), 7.04 d (8.8)	3.91 s	6.06 s, =CH;[d] 5.64 s, =CH;[e] 3.51 s, CH2; 3.4 br, H$_{syn,anti}$; 2.31 s, C(O)Me
12	7.18 d (7.3)	*i*	7.98 d (8.3)	7.46 d (8.7), 7.03 d (8.7)	3.90 s	3.57 s, CH$_2$; 3.3 br, H$_{syn,anti}$; 2.15 s, C(O)Me; 1.96 s, Me$_{syn}$; 1.60 s, Me$_{anti}$; 1.27 s, =CMe;[g] 0.96 s, =CMe[h]
13a[f,j]	7.02 d (6.2)	7.52 pst	8.12 d (8.3)	7.35 d (8.8), 7.09 d (8.8)	3.93 s	2.22 s, C(O)Me; 1.97 s, Me$_{syn}$; 1.79 s, Me$_{anti}$
13b[k]	7.65 d (7.2), 6.82 d (7.2)	7.58 pst, 7.51 pst	8.14 d (7.3), 8.11 d (7.3)	7.45 d (8.8), 7.08 d (8.8) 7.34 m 7.17 m	3.96 s, 3.95 s	3.76 d (18.5), C*H*H; 3.69 d (18.5), CH*H*; 2.16 s, C(O)Me; 2.00 s, =CMe;[g] 1.79 s, =CMe[h]

[a] Recorded at 300.13 MHz in CDCl$_3$ at 20 °C, unless noted otherwise, J (Hz) in parentheses (s = singlet, d = doublet, dd = doublets of doublet, pst = pseudotriplet, m = multiplet, br = broad). [b] Signal of (other) H$_3$ is overlapping with signal of H$_{9,10}$. [c] Recorded at −40 °C. [d] Olefinic proton *cis* to C(O)Me. [e] Olefinic proton *trans* to C(O)Me. [f] Signal of CH$_2$ is overlapping with signal of H$_{12}$. [g] Me group *cis* to C(O)Me. [h] Me group *trans* to C(O)Me. [i] Signal of H$_4$ is overlapping with signals of H$_{9,10}$. [j] Signals of C$_7$H$_8$ moiety: 5.95 dd (5.3, 2.8 Hz), =CH; 5.56 dd (5.3, 3.2 Hz), =CH; 3.07/2.45 s, CHC=; 2.40 d (6.6 Hz), CHC(O)R; 2.07 dd (6.6, 1.5 Hz), Pd−CH; 1.82 d (9.1 Hz), C*H*H; 1.35 d (9.1 Hz), CH*H*. [k] Signals of C$_7$H$_8$ moiety: 6.03 dd (5.4, 2.9 Hz), =CH; 5.46 dd (5.4, 3.2 Hz), =CH; 3.17/2.29 s, CHC=; 2.58 d (5.8 Hz), CHC(O)R; 2.02 dd (5.8, 1.5 Hz), Pd−CH; 1.60 d (9.3 Hz), C*H*H; 1.32 d (9.3 Hz), CH*H*.

due to the complexity of the NMR spectra the characterization of the products was very difficult.

Spectroscopic Characterization of Complexes 3−8. The allylpalladium complexes **3**−**8**, formed by insertion reactions of allenes into palladium−carbon bonds, were isolated and characterized by ^{1}H and ^{13}C NMR (Tables 3 and 4, respectively) and IR spectroscopy. Selected compounds were also characterized by ^{19}F NMR and mass spectroscopy and microanalysis.

Formation of the allyl complexes **3**−**8** is clear from the observed *syn* and *anti* methyl and proton signals in the ^{1}H NMR spectra and, in the case of **6**−**8**, the low-frequency shift of the ^{13}CO resonance from 223.4 ppm for **2a**[19] to about 200 ppm in the ^{13}C NMR. Complexes **6**−**8** all show in the IR a CO stretching frequency in the region 1690−1700 cm^{-1}, which is in agreement with those reported for other (allyl-2-acetyl)palladium compounds.[22] The trifluoromethanesulfonate complexes **3b**−**8b** all show in the ^{19}F NMR one resonance at about −79 ppm, and in the IR all expected vibrations of the trifluoromethanesulfonate group are observed. The absence of SO stretching frequencies in the region 1200−1250 cm^{-1} and above 1300 cm^{-1} indicates that the trifluoromethanesulfonate group is not coordinated to the palladium center.[20] The high equivalent conductivities for **3b**−**8b** (in the range of 25−45 Ω^{-1} cm^2 mol^{-1}) in dichloromethane at 20 °C are in agreement with an ionic structure. Although the molecular structure of **7a** clearly shows the presence of a neutral complex, in which the chloride is coordinated (*vide supra*), in solution an equilibrium between the neutral and an ionic structure, in which the chloride is dissociated, may be present for complexes **3a**−**8a** (eq 4). The observed



(4)

3a-8a

equivalence of the *syn* and *anti* protons on one end of the allyl moiety of complexes **7a**,**b** in the ^{1}H NMR upon adding an equimolar amount of **7a** to a solution of **7b**

Table 4. ^{13}C NMR Data (δ) for Complexes 3−13[a]

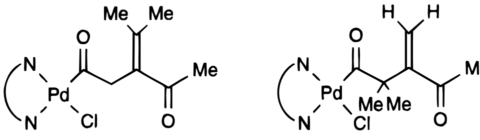
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	allyl[b]	other signals
3a	167.5	127.1	125.3	128.9	131.8	131.8	144.8	142.6	115.4	122.7	159.4	56.3	130.7, 62.1	24.0, Me
3b	171.8	126.1	126.1	129.3	132.7	132.1	146.9	142.3	115.8	123.2	160.3	56.5	136.7, 64.6	24.4, Me
4a	168.1	127.1	125.7	129.0	131.9	131.8	145.5	142.2	115.6	122.2	159.3	56.4	123.2, 85.3, 60.9	24.7, Me; 23.2/21.6, Me$_{syn,anti}$
4b	n.o.	126.2	126.3	129.4	132.7	132.0	146.6	141.5	116.0	122.6	160.0	56.5	127.3, 87.3, 63.6	24.3, Me; 22.3/21.8, Me$_{syn,anti}$
5a	170.6	126.3	126.4	129.3	132.6	131.8	145.7	141.0	115.9	121.6	159.3	56.4	118.0, 86.1	27.5/26.3, Me$_{syn,anti}$; 19.9, Me
5b	171.7	126.2	126.5	129.4	132.7	131.8	146.1	140.8	116.0	121.7	159.5	56.4	118.7, 86.8	27.3/26.1, Me$_{syn,anti}$; 19.9, Me
6a	163.9	128.1	124.7	128.5	130.9	131.7	143.4	142.5	115.3	122.3	159.1	56.1	111.2, 56.4	196.0, *C*(O)Me; 25.9, C(O)*Me*
6b	171.0	125.1	125.2	128.3	131.8	131.1	146.1	141.4	114.8	122.2	159.2	55.5	123.1, 63.1	194.9, *C*(O)Me; 26.0, C(O)*Me*
7a	163.6	128.3	124.8	128.4	130.8	131.6	143.1	142.6	115.1	122.1	158.7	56.4	111.4, 83.5, 54.8	200.8, *C*(O)Me; 28.6, C(O)*Me;* 26.4/24.8, Me$_{syn,anti}$
7b	172.3	126.2	126.1	129.0	132.4	131.8	146.7	141.3	115.8	122.4	159.8	56.2	125.8, 87.3, 61.2	200.6, *C*(O)Me; 29.9, C(O)*Me;* 23.6/22.9, Me$_{syn,anti}$
8a	165.7	127.2	124.6	128.0	130.4	130.9	143.2	141.5	114.5	121.1	159.9	55.4	119.2, 79.6	205.6, *C*(O)Me; 33.0, C(O)*Me*; 25.7/25.5, Me$_{syn,anti}$
8b	171.7	125.3	125.7	128.5	131.9	130.9	145.7	139.6	115.1	121.0	158.6	55.5	123.4, 83.8	203.6, *C*(O)Me; 30.4, C(O)*Me*; 24.1, Me$_{syn,anti}$
9[c]	170.7	126.1	125.3	128.5	131.6	129.8	144.1	140.0	114.6	123.3	158.6	55.7		*d*
	165.1	125.6	124.7	128.4	131.0			139.9	114.0	122.4	158.3	55.6		
10[c]	171.3	126.1	125.3	128.5	131.6	130.7	144.2	139.5	115.0	123.3	158.7	55.6		*e*
	165.1	125.6	124.7	128.4	130.9			137.7	113.9	122.1	158.5	55.5		
11	163.8	128.1	124.7	128.6	130.9	131.7	143.5	142.4	115.3	122.4	158.9	56.2	110.1, 56.4	*f*
12	163.8	128.3	124.9	128.6	130.9	131.6	143.1	142.6	115.2	122.0	158.7	56.2	111.5, 83.7, 54.7	*g*
13a	n.o.	126.3	125.9	129.4	132.7	131.9	145.7	138.9	115.4	124.1	160.1	56.5		*h*
13b	174.8, 165.3	125.6, 125.0	125.6, 124.7	128.5	132.3, 131.6	131.1	145.0	138.2, 137.9	115.1, 114.7, 114.4	123.6, 122.9, 122.7	159.7, 159.2	55.7		*i*

[a] Recorded at 75.48 MHz in $CDCl_3$ at 0 °C, unless noted otherwise. See Table 3 for the adopted numbering scheme (n.o. = not observed). [b] Resonances of allyl carbon atoms are listed in the order central, most substituted, and less substituted carbon atom. [c] Recorded at −40 °C. [d] 222.4, Pd*C*(O)R; 198.5, R*C*(O)Me; 137.7, *C*═CH_2; 130.8, ═CH_2; 48.2, CH_2; 25.8, C(O)*Me*. [e] 222.3, Pd*C*(O)R; 204.5, R*C*(O)Me; 144.1, ═*C*Me_2; 129.6, *C*═CMe_2; 49.9, CH_2; 29.8, C(O)*Me*; 22.8/22.1, C*Me*$_2$. [f] 199.4, C_3H_4*C*(O)R; 195.1, R*C*(O)Me; 143.1, *C*═CH_2; 129.4, ═CH_2; 39.8, CH_2; 26.0, C(O)*Me*. [g] 203.9, C_5H_8*C*(O)R; 200.2, R*C*(O)Me; 144.7, ═*C*Me_2; 130.7, *C*═CMe_2; 42.5, CH_2; 31.1, C(O)*Me*; 26.6/24.8, Me$_{syn,anti}$; 23.8/23.6, C*Me*$_2$. [h] 229.2, C_7H_8*C*(O)R; 202.8, R*C*(O)Me; 147.9, ═*C*Me_2; 130.9, *C*═CMe_2; 42.4, CH_2; 31.9, C(O)*Me*; 25.0/24.4, C*Me*$_2$. Signals of C_7H_8 moiety: 136.0/134.5, ═CH; 61.8, *C*HC(O)R; 49.9, Pd*C*H; 49.1/47.3, *C*HC═; 46.4, CH_2. [i] 236.6, C_7H_8*C*(O)R; 201.7, R*C*(O)Me; 148.0, ═*C*Me_2; 129.8, *C*═CMe_2; 41.1, CH_2; 31.1, C(O)*Me*; 24.1/23.6, C*Me*$_2$. Signals of C_7H_8 moiety: 134.5/133.0, ═CH; 61.7, *C*HC(O)R; 49.8, Pd*C*H; 48.7/46.0, *C*HC═; 45.1, CH_2.

in $CDCl_3$ indicates an intermolecular transfer of the chloride ion from **7a** to **7b**, which is fast on the NMR time scale. Also the observed equivalent conductivities for **3a**−**8a** in dichloromethane at 20 °C (2.1−4.5 Ω^{-1} cm^2 mol^{-1}), which are in between that of the neutral complex **2a** (0.1 Ω^{-1} cm^2 mol^{-1}) and those of the ionic complexes **3b**−**8b** (25−45 Ω^{-1} cm^2 mol^{-1}), point to the presence of an equilibrium between the neutral and ionic structure for complexes **3a**−**8a**.

Spectroscopic Characterization of Complexes 9 and 10. The acylpalladium complexes Pd(C(O)C_3H_4C(O)Me)Cl(*p*-An-BIAN) (**9**) and Pd(C(O)C_5H_8C(O)Me)Cl(*p*-An-BIAN) (**10**), obtained via the reaction of CO with **6a** and **7a**, respectively, were isolated and fully characterized (Tables 3 and 4). Complex **9** shows two characteristic alkene proton resonances in the region of 5−7 ppm in the ^{1}H NMR spectrum and two alkene carbon resonances of 130.8 and 137.7 ppm in the ^{13}C NMR spectrum. In contrast to the reaction of CO with **6a**, insertion of CO into the allyl−palladium bond of **7a** may lead to two different products, **I** and **II** (Figure 2). The absence of signals in the 5−7 ppm region in the ^{1}H NMR region of **10** indicates that structure **I** is the correct structure for **10**.

Complexes **9** and **10** both show two ^{13}CO resonances (at about 222 and 200 ppm) in the ^{13}C NMR spectra and two CO stretching frequencies in the IR in the region of 1670−1710 cm^{-1}. These data are comparable to those reported for Pd(C(O)C_7H_8C(O)Me)Cl(*p*-An-BIAN),[19] Pd(C(O)C_7H_{10}C(O)Me)X(bpy) (X = Cl, I),[17] and [Pd(C(O)CH(Ar)CH_2C(O)Me)CO(bpy)]BAr_4[11] and suggest the formation of a neutral complex, *i.e.* coordination of the chloride to the palladium center and no formation of a six-membered palladacycle or coordination of the carbon−carbon double bond to palladium. Also the low equivalent conductivities of 0.39 Ω^{-1} cm^2 mol^{-1} for **9** and 0.25 Ω^{-1} cm^2 mol^{-1} for **10** in dichloromethane at 20 °C are in agreement with this structure.



I **II**

Figure 2. Possible products **I** and **II** from the insertion of CO in complex **7a**.

Spectroscopic Characterization of Complexes 11−13. Complexes **11** and **12**, formed after the reaction of propadiene and DMA with **9** and **10**, respectively, were isolated and characterized by ^{1}H NMR, ^{13}C NMR (Tables 3 and 4, respectively), and IR spectroscopy and elemental analysis. The formation of **11** and **12** is apparent from the presence of a broad allyl proton signal at 3.3−3.4 ppm in the ^{1}H NMR spectra, similar to **6a**

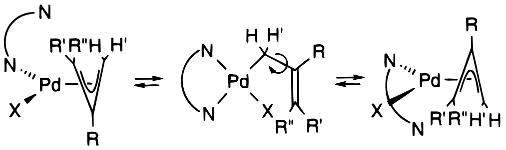
and **7a**, and a frequency shift of one ^{13}CO resonance from about 222 ppm to 199.4 ppm for **11** and to 203.9 ppm for **12** in the ^{13}C NMR.

Complex $[Pd(C_7H_8C(O)C_5H_8C(O)Me)(p\text{-An-BIAN})]Cl$ (**13a**), formed after the insertion of norbornadiene into the acyl−palladium bond of **10**, was characterized by ^1H NMR, ^{13}C NMR (Tables 3 and 4, respectively), and IR spectroscopy. Unfortunately **13a** is too unstable in the solid state to allow outside microanalysis. *Cis* addition of Pd−C(O)R to the exo face of the alkene may be inferred from the coupling constant $^3J(CHC(O)R, Pd-CH)$ of 6.6 Hz.[44] The observed chemical shift difference of about 0.4 ppm for the two remaining alkene protons in the $C_7H_8C(O)R$ fragment in the ^1H NMR, together with the high chemical shift of 229.2 ppm in the ^{13}C NMR and the low CO stretching frequency of 1601 cm^{-1} in the IR for the CO in the $C_7H_8C(O)R$ fragment indicate that the oxygen atom of this CO is coordinated to the palladium resulting in a five-membered palladacycle.[17,19,44,45] The observed high equivalent conductivity of 19.0 Ω^{-1} cm^2 mol^{-1} in dichloromethane at 20 °C is also in agreement with a structure, in which the chloride is dissociated. $[Pd(C_7H_8C(O)C_5H_8C(O)Me)(p\text{-An-BIAN})]SO_3CF_3$ (**13b**), obtained by reacting **13a** with 1 equiv of $AgSO_3CF_3$, is in contrast to **13a** stable enough to obtain correct analytical data.

Fluxional Behavior of Complexes 3−8. The ionic complexes **3b**, **5b**, **6b**, and **8b**, containing a bidentate bonded BIAN ligand and a symmetrically substituted allyl moiety, show in the ^1H NMR at 300.13 MHz in the temperature range of −70 to −30 °C one averaged signal for each pair of acenaphthene protons on either side of the BIAN ligand, as expected. However, in the case of **4b** and **7b**, which both contain an asymmetrically substituted allyl moiety, we also discern that both sides of the BIAN ligand are magnetically equivalent in the ^1H NMR time scale in the same temperature range. Since this process occurs intramolecularly, as addition of free ligand gave sharp signals for both free and coordinated BIAN at 20 °C, we have to assume for **4b** and **7b** a process involving a mechanism via nitrogen dissociation and a *cis*−*trans* isomerization of the formed T-shaped intermediate (which might be stabilized by coordination of a solvent molecule or the trifluoromethanesulfonate ion), followed by nitrogen association. A similar mechanism has been proposed by Pregosin *et al.*[43] and has been confirmed later by Bäckvall *et al.* for ionic palladium complexes containing an asymmetrically substituted allyl moiety and the bidentate bonded 2,2′-bipyrimidyl ligand.[46]

As observed for the analogous trifluoromethanesulfonate complexes, the chloride complexes **3a**−**8a** also show one averaged signal for the pairs of acenaphthene protons on both sides of the BIAN ligand in the ^1H NMR in the temperature range −70 to −30 °C. Analogous to **3b**−**8b**, complete dissociation of the BIAN ligand can be excluded as the source of the observed exchange for **3a**−**8a**.[47] In the case of these chloride complexes an equilibrium between the five-coordinate neutral complex and a four-coordinate ionic species might be responsible for the observed exchange process (eq 4). It should be noted that for none of these complexes any exchange of *syn* and *anti* positioned groups occurred in the temperature range of −70 to −30 °C, showing that during this fluxional process the allyl moieties remain coordinated in an η^3-fashion.

Scheme 3



Interestingly, in the case of the chloride complexes **3a**, **4a**, **6a**, and **7a** at higher temperatures (−30 to 20 °C) now also the *syn* and *anti* protons of the CH_2 moiety for **4a**, **7a** and CH_2 moieties for **3a**, **6a** interchange, showing that an $\eta^3-\eta^1-\eta^3$ isomerization process[48,49] occurs, whereby the palladium atom has to move from one face of the allyl group to the other and vice versa, thereby rendering the coordination plane a mirror plane on the ^1H NMR time scale (Scheme 3). In contrast, the analogous trifluoromethanesulfonate complexes **3b**, **4b**, **6b**, and **7b** do not show *syn*-*anti* proton exchange in the same temperature range (−30 to 20 °C). However, in the presence of 5 bar of CO (at 20 °C) the *syn* and *anti* proton signals are broadening. It might well be that CO takes up the role of the chloride ion causing the BIAN ligand to become unidentate bonded.

Discussion

Insertion of Allenes into Alkyl− and Acyl−Palladium Bonds. Analogous to insertion reactions of CO[50−52] and alkenes[53] in square planar organo−palladium(II) and −platinum(II) complexes, the insertion of allenes may occur via a four-coordinate intermediate (Scheme 4, pathway 1 and 2) or via a five-coordinate intermediate (Scheme 4, pathway 3).

The results of extensive kinetic studies on the insertion of allenes into the Pd−C(O)Me bond of $Pd(C(O)Me)Cl(p\text{-An-BIAN})$ (**2a**) carried out very recently in our laboratory,[54] indicate that the insertion may take place via dissociation of one of the nitrogen atoms of the *p*-An-BIAN ligand (insertion via a neutral four-coordinate intermediate; pathway 2) or via an associative pathway (pathway 3) rather than via dissociation of the halide (insertion via an ionic four-coordinate intermediate; pathway 1). Although *p*-An-BIAN is a rigid bidentate ligand and insertion via dissociation of one of the coordinating nitrogen atoms appeared unlikely,[19] we

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[44] Brumbaugh, J. S.; Whittle, R. R.; Parvez, M.; Sen, A. *Organometallics* **1990**, *9*, 1735.

[45] Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Roobeek, C. F. *J. Organomet. Chem.* **1992**, *430*, 357.

[46] Gogoll, A.; Örnebro, J.; Grennberg, H.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1994**, *116*, 3631.

[47] Addition of free BIAN to a solution of **3a**−**8a** in $CDCl_3$ gave sharp signals for both free and coordinated BIAN at 20 °C, indicating that ligand exchange is slower than the observed fluxional process.

[48] Vrieze, K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; pp 441−487.

[49] Vrieze, K.; Volger, H. C.; van Leeuwen, P. W. N. M. *Inorg. Chim. Acta Rev.* **1969**, *3*, 109.

[50] Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115.

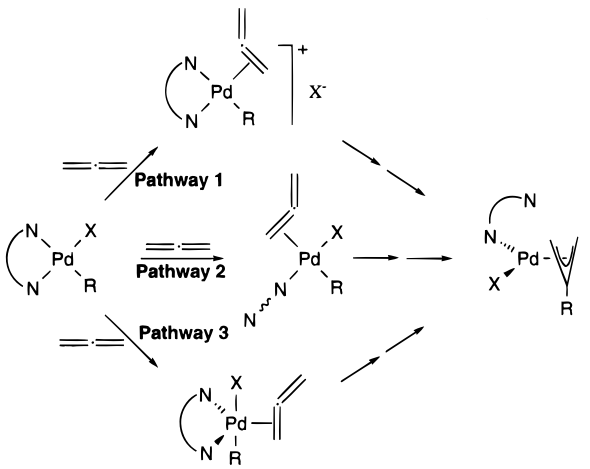
[51] Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1246.

[52] Anderson, G. K.; Cross, R. J. *Acc. Chem. Res.* **1984**, *17*, 67.

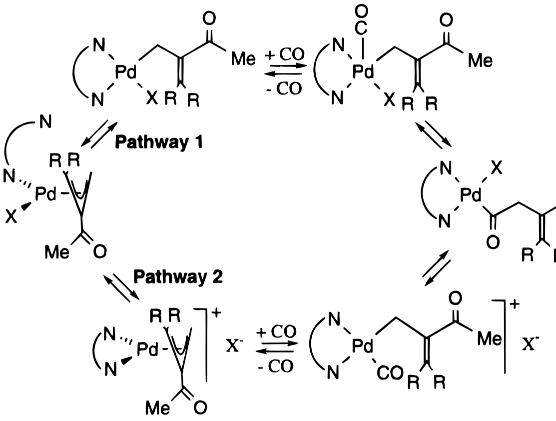
[53] Torn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.

[54] Delis, J. G. P.; Groen, J. H.; Vrieze, K.; van Leeuwen, P. W. N. M.; Veldman, N.; Spek, A. L. To be published.

Scheme 4



Scheme 5



cannot rule out insertion via this mechanism. The molecular structure of complex **7a** for example clearly shows a more or less unidentate coordinated *p*-An-BIAN ligand, while the starting compound **2a** contains a bidentate coordinated BIAN ligand, indicating that dissociation of a nitrogen atom of the BIAN ligand has occurred during the insertion reaction. Also Natile *et al.*[42] have demonstrated that rigid bidentate nitrogen ligands like dmphen and phen can be bonded to a palladium(II) or platinum(II) center in various modes ranging from bidentate to unidentate, depending on the donor and acceptor properties of the trans ligands.[55] It certainly should be noted that in our case the differences between the intermediates of the three pathways are really rather small. Because of the rigidity of the *p*-An-BIAN ligand the formation of an unidentate bonded ligand cannot be accompanied by a turning away of the dissociated nitrogen atom from the palladium center. Also the difference between ionic four-coordinate complexes and five-coordinate complexes will be small, because in chloroform and dichloromethane the chloride might remain in the neighborhood of the palladium to form an ion pair.[19,56]

The rate of the insertion reaction of allenes into the Pd−R bond of complexes of the type Pd(R)X(*p*-An-BIAN) is highly dependent on the nature of the X and R ligand and the allene used. The relative high reactivity of the ionic methyl- and acylpalladium complexes **1b** and **2b** can be related to the formation of a more easily accessible coordination site. Stevens and Shier also observed that abstraction of the halide in *trans*-Pd(PPh$_3$)$_2$(R)Br (R = Me, Ph) facilitated propadiene insertion into the Pd−R bond.[32] Rate enhancement by abstraction of the halide has been observed in general for insertion reactions in square planar organo−palladium and −platinum complexes.[17,19,45,57]

The influence of the R group in Pd(R)Cl(*p*-An-BIAN) on the allene insertion rate is clear from the much higher reactivity of **2a** (R = C(O)Me) compared to **1a** (R = Me) toward allene insertion reactions. The same trend has been observed for allene insertion reactions into Pd−R bonds of complexes of the type Pd(R)Cl(bpy), and has been explained by a more efficient overlap of the π-orbitals of the C(O)Me group (homo) with accessible π-orbitals of the precoordinated allene (lumo) in the transition state, while a Me group bonded to palladium does not have suitable orbitals for this type of overlap.[23]

As observed earlier, the insertion rate decreases with increasing substitution at the allenic termini: propadiene $\approx$ DMA $\gg$ TMA.[23,58] This order may be explained by considering both the initial state, in which the allene is precoordinated perpendicular to the coordination plane, and the transition state, in which the allene is coordinated in an in-plane position. In the case of TMA, coordinated at a carbon−carbon double bond containing two sterically demanding methyl groups, the later will be much more destabilized than in the case of propadiene or DMA, both coordinated at a nonsubstituted carbon−carbon double bond.

Successive Insertion of CO and Allenes. The propensity of the BIAN ligand to form reactive yet stable isolable complexes, such in contrast to *e.g.* bpy, has allowed us to study a novel example of the stepwise copolymerization via successive insertion of CO and allenes into palladium−carbon bonds by starting from a neutral acylpalladium complex. There are two possible mechanisms for the CO insertion reaction into the allyl−palladium bond (Scheme 5; pathway 1 and 2).[59]

Both possible mechanisms are proposed to proceed via the formation of an η^1-allyl type of intermediate prior to the insertion reaction. Several studies on insertion reactions of CO, CO$_2$, SO$_2$, and allenes into palladium−allyl bonds indicate that insertion takes place via this type of intermediate.[58,60−62] Both mechanisms explain why the ionic allylpalladium complexes **3b**−**8b** do not undergo CO insertion. The weakly coordinating trifluoromethanesulfonate anion is in pathway 1 unable to stabilize the η^1-allyl type of intermediates. In pathway 2 the trifluoromethanesulfonate anion will not be able to stabilize the CO insertion product by coordination, but one might think of stabilization of the product via coordination of the distal carbonyl group resulting in a six-membered palladacycle. However, the observed

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[55] Also zerovalent palladium complexes containing monodentate coordinated rigid bidentate nitrogen ligands have been observed: (a) Klein, R. A.; Witte, P.; van Belzen, R.; Elsevier, C. J.; Fraanje, J.; Goubitz, K.; Numan, M. To be published. (b) Klein, R. A.; van Belzen, R.; Elsevier, C. J.; Fraanje, J.; Goubitz, K. To be published.

[56] Oslinger, M.; Powell, J. *Can. J. Chem.* **1973**, *51*, 274.

[57] Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M. *Organometallics* **1992**, *11*, 1598.

[58] Hughes, R. P.; Powell, J. *J. Organomet. Chem.* **1973**, *60*, 409.

[59] Ozawa, F.; Son, T.-i.; Osakada, K.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1989**, 1067.

[60] Hung, T.; Jolly, P. W.; Wilke, G. *J. Organomet. Chem.* **1980**, *190*, C5.

[61] Santi, R.; Marchi, M. *J. Organomet. Chem.* **1979**, *182*, 117.

[62] Behr, A.; Juszak, K.-D. *J. Organomet. Chem.* **1983**, *255*, 263.

immediate formation of the decarbonylation products **6b** and **7b** upon abstracting the chloride ion from **9** and **10**, respectively, by addition of $AgSO_3CF_3$ indicates that ionic CO insertion products cannot be stabilized by formation of a six-membered palladacycle. Stabilization of the CO insertion products by coordination of CO is also unlikely since it is known that these kinds of species are generally unstable and readily decarbonylate.[19] The inertness of both **5a** and **8a** toward CO is probably due to the fact that it is highly unlikely that the necessary η^1-allyl type of intermediate, in which the palladium center is bonded to a carbon atom bearing two sterically demanding methyl substituents, will be formed. This kind of intermediate, as far as we are aware, has never been observed. The observation of *syn*−*anti* proton exchange in the ionic complexes **6b** and **7b** in the presence of CO (*vide supra*) points to the likelihood of the formation of an η^1-allyl type of intermediate by coordination of CO, which therefore favors pathway 2.

The acylpalladium complexes **9** and **10** reacted almost quantitatively with 1,2-propadiene and DMA to give the allylpalladium complex **11** and **12**, respectively, both containing alternating inserted CO and allene fragments. Also the strained alkene norbornadiene reacted with complex **10** to give the alkyl complex **13a**. Complexes **11** and **12** are the first isolated allyl complexes, containing alternating inserted CO and allene fragments, while complex **13a** is the first isolated alkylpalladium complex, containing a metal-bonded ter-oligomer of carbon monoxide, an allene, and norbornadiene.

Conclusion

The reactivity of organo−palladium complexes, containing the bidentate nitrogen *p*-An-BIAN ligand, has made it possible to carry out for the first time a stoichiometric co-oligomerization of CO and allenes, and also a ter-oligomerization of CO, allenes, and norbornadiene, leading to metal-bonded polyketone fragments. Furthermore, the stability of these complexes has allowed us to isolate and characterize the acyl- and allylpalladium intermediates, formed after each CO and allene insertion, respectively. Hereby we again have demonstrated the ability of the rigid bidentate nitrogen BIAN ligand in stabilizing and activating organo−palladium complexes.

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Supporting Information Available: Listings of final atomic coordinates, bond distances and angles, torsion angles, and equivalent isotropic and anisotropic thermal parameters for **7a** (8 pages). Ordering information is given on any current masthead page.

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