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


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Abstract: Facile successive insertion of carbon monoxide and strained alkenes has been observed for both neutral Pd(R)(NC)(Ar-BIAN) and cationic [Pd(R)(MeCN)(Ar-BIAN)]SO3CF3 complexes, i.e., complexes containing the rigid bidentate nitrogen ligands bis(arylimino)acenaphthene (Ar-BIAN); Ar = p-MeOC6H4 (p-Ar), p-MeC6H5 (p-Tol), o,o'-Me2C6H4, leading to the formation of new multiple insertion products of the type Pd(CH(R')(CH(R')(C=O)R)X(Ar-BIAN). It appears that the rigidly chelating Ar-BIAN ligands have an activating effect on the insertion of CO and alkenes in palladium–carbon bonds as compared to other (bidentate) phosphorus and nitrogen ligands and a stabilizing effect on the Pd–acyl and Pd–alkyl complexes formed. Insertion of carbon monoxide was completed within 1 min (R = Me, X = Cl, I; R = PhCH2, X = Br; R = p-MeC6H4, X = I), except in the case of RX = p-N2C6H4CH2Br, 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)]SO3CF3 occurred instantaneously. Reaction of norbornadiene with the neutral acyl complexes Pd(C(O)MeCl(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 alkenes insertion have a similar structure, arising from cis addition of Pd(CO)R to the exo face of the alkene, with the acyl oxygen atom coordinating to the palladium and the chloride or trifluoromethanesulfonate present as anion. After insertion of norbornadiene in the neutral acyl palladium complex, the resulting alkylpalladium compound [Pd(C(H2)(C(O)Me)(p-An-BIAN)]Cl reacted further with carbon monoxide to give the isolable complex Pd(C(O)C7H8C(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(H2)(C(O)C7H8C(O)Me)(p-An-BIAN)]Cl (14a), which reacted with AgSO3CF3 to give [Pd(C(H2)(C(O)C7H8C(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.1 One special class of carbonylation reactions concerns the copolymerization of alkenes and carbon monoxide,2−5 leading to the formation of polyketones, a reaction which is very efficiently catalyzed by complexes of the type PdX2(L−L) (L−L is a chelating phosphorus or nitrogen ligand, X is a weakly or noncoordinating anion). The reaction is proposed to proceed via a perfectly alternating sequence of carbon monoxide and alkene insertions in palladium–carbon bonds (Scheme 1),6,3 An alternative mechanism involving palladium carbene intermediates, explaining the formation of spiroketal products,6,3 has recently been proposed.5,6

A lot of experimental1 and theoretical6 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...
preferentially from a four-coordinate complex, formed by substitution of a phosphine ligand by CO. However, the coordination 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 alkenes inserted in platinum–hydroxy bonds, it appeared that insertion from a four-coordinate intermediate is the preferred reaction pathway. Intramolecular insertions of alkenes and alkynes in palladium–carbalkoxy bonds were shown to proceed via a four-coordinate intermediate, but intramolecular alkenes inserted in platinum–hydroxy bonds were proposed to occur via a five-coordinate intermediate. Five-coordinate intermediates might play a role in the intramolecular insertion of alkenes in palladium–acyl bonds, as can be derived from the complex kinetics of the insertion reactions and the facile containing rigidly chelating bidentate and tridentate ligands.

We investigated the insertion of carbon monoxide and alkynes in palladium–carbon bonds of complexes bearing the rigid bidentate nitrogen donor ligands bis(arylimino)acenaphthenes (Ar-BIAN) because of the observation that carbon monoxide and alkynes can be incorporated in the organic products of the Pd(II)–(Ar-BIAN)-[CO] 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 decreases 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 successive 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(R)CH2C(O)Me)(CO)(CO)BaC6H5 – n = 1–3, formed by successive insertions of CO and 4-tert-butylstyrene in cationic acylpalladium complexes. As chloride may, by association and dissociation when required, both facilitate insertion and stabilize the products formed, we have focused on multiple insertion reactions of CO and alkynes by starting from neutral acylpalladium complexes, and we describe here the isolation and full characterization of both the acyl- and the alkylpalladium complexes formed after successive CO and alkyn 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. 1H NMR spectra were recorded on a Bruker AMX 300 (300.13 MHz) and a Bruker AC 100 (100.13 MHz) spectrometer and 13C 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. 19F NMR spectra were recorded on a Bruker AC 100 spectrometer (94.20 MHz) relative to CFCl3 as external standard. 31P NMR spectra were recorded on a Bruker AMX 300 spectrometer (121.50 MHz) relative to 85% H3PO4 as external standard. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Elemental analyses were carried out by Donis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. Pd(Me)(CO)(COD) = (Z,Z)-1,5-cyclooctadiene, 17 Ar-BIAN, 18 PdBr2(C6H5)4-p-p(R)(Ar-BIAN) (R = H, NO2) and Pt(p-Tol)(Ar-BIAN) were synthesized according to previously reported procedures. 19, 20 Under a solution of 0.30 mol L–1 of H3PO4 (COD) (1.13 mmol) in 20 mL of dichloromethane was added 0.48 g of p-An-BIAN (1.22 mmol; p-An = -p-MeOC6H4H2), and the mixture was stirred at 20°C. After 1 h, the solution was filtered through Celite filter aid and the residue washed with dichloromethane (2 × 5 mL). The combined filtrates were evaporated to dryness. The product was washed with diethyl ether (3 × 10 mL) and dried in vacuo, yielding 0.55 g of a red solid (89%). Analytically pure samples were obtained by recrystallization from dichloromethane/hexane or by slow evaporation of a solution of the complex in dichloromethane into hexane. Anal. Found for C34H23CI3N2O2Pd: 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 for 1 min, after which a IH NMR spectrum was recorded connected to a vacuum line. The flask was evacuated and subsequently washed with 5 mL of diethyl ether (3 X 5 mL) and dried in vacuo, yielding 0.17 g of red/brown solid was obtained (81%).

After 1 min, the reaction flask was closed and the mixture stirred for 5 min at 20 °C. After 1 h, the solution was filtered and the product identified by ¹H NMR without isolation.

[Pd(C(O)C₇H₈C(O)Me)(p-An-BIAN)]SO₃CF₃ (13a). Carbon monoxide was bubbled through a solution of 0.18 g of [Pd(C(H₂)₃C(O)Me)(p-An-BIAN)-Cl (0.097 mmol) in 10 mL of dichloromethane for 1 min and the mixture was stirred under CO during 5 min at 20 °C. After that time the solution was filtered through Celite filter aid, the residue was washed with dichloromethane (5 mL), and the filtrate was evaporated to dryness. The product was washed with diethyl ether (5 mL) and dried in vacuo, giving 0.15 g of a brown product (80%). Anal. Found (Calcd for C₄₃H₃₁BrN₂O₄Pd): C, 60.86 (61.33); H, 4.59 (4.48); N, 4.15 (4.02).

[Pd(C(H₂)₃C(O)Me)(p-An-BIAN)]SO₃CF₃ (9a). To a solution of 31.8 mg of Ag₂O₃ (0.047 mmol) with 10.3 mg of AgSO₃CF₃ (0.029 mmol) in 0.5 mL of CDC1₃. After being stirred for 30 min at 20 °C in the dark, the mixture was filtered and the product identified by ¹F NMR, without isolation.

Results

Synthesis of the Starting Organopalladium Complexes. Metallapalladium chloride complexes 1 were synthesized starting from [Pd(Me)₃Cl(COD)] (eq 1; COD = (Z,Z)-1,5-cyclooctadiene), similar to the reported metallapalladium complexes with bidentate P,P- P,N, and N,N and tridentate N,N,N ligands.¹⁴ The facile high-yield synthesis of [Pd(Me)₃Cl(COD)] makes this route preferable to the one via [Pd(Me)(μ-Cl)(SM₂₃)₂]²⁰

The corresponding metallapalladium iodide complexes were obtained from [Pd(Me)₃Cl(COD)] by carrying out the substitution reaction in the presence of an excess sodium iodide. [Pd(Me)₃I-(p-Tol-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.¹⁹ Cationic complexes of the type [Pd(Me)(Ar-BIAN)(S)SO₂CF₃ (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 tentatively upon reaction of the cationic complexes. The reactions were completed within 1 min under ambient acetylpalladium complexes reversible, as the neutral complexes conditions in chloroform or dichloromethane, i.e., 20 °C and 1 capillary into a solution of the palladium complex or by refluxed in dichloromethane, after 1.5 h 75% unreacted identified: T6th, I.; Elsevier, C. J. Similar species containing a chelating diphosphine have recently been published: Kraakman, M. J. A.; de Klerk-Engels, B.; de Lange, P. P. M.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. Organometallics 1992, 11, 3774. (b) Noack, K.; Calderazzo, F. J. Organomet. Chem. 1967, 10, 101. (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), ZnCl2, and H+ has been published: Kraakman, M. J. A.; de Klerk-Engels, B.; de Lange, P. P. M.; Vrieze, K.; Smears, W. J. J.; Spek, A. L. Organometallics 1992, 11, 3774. (b) Similar species containing a chelating diphosphine have recently been identified: Töth, I.; Elsevier, C. J. Am. Chem. Soc. 1993, 115, 10388-10389.

Insertion of Carbon Monoxide. All methylpalladium complexes 1 reacted rapidly with carbon monoxide to give the corresponding acetyl-palladium complexes 3 (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. The insertion of carbon monoxide is reversible, but decarbonylation occurs much more slowly. When a solution of Pd(C(O)Me)Cl(p-An-BIAN) (3a) (p-An = p-anisyl = p-MeOC6H4) was refluxed in dichloromethane, after 1.5 h 75% unreacted 3a and 25% of the decarbonylated Pd(Me)(Cl)(p-An-BIAN) (1a) were present. Reaction of the cationic complexes [Pd(Me)(MeCN)(p-An-BIAN)]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)(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)(CD3CN)(p-Tol-BIAN)]SO3CF3 (4c′) was obtained via dehalogenation of the acyl complex 3c with silver trifluoromethanesulfonate in CD3CN and studied in situ. As compared to their neutral counterparts 3, the cationic complexes 4 undergo decarbonylation in the solid state more readily, i.e., drying in vacuo for several hours or storage at 20 °C for several days resulted in formation of methylpalladium complexes together with decomposition products. In coordinating solvents (acetonitrile or acetone), complex 4c′ was rather stable toward decarbonylation (no trace of Pd–Me after 20 h at 20 °C). Reaction of a mixture of the cationic acyl complexes 4a and 4a′ with 1 equiv of triphenylphosphine gave [Pd(C(O)Me)(p-An-BIAN)(PPPh3)]SO3CF3 (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(Ph) complexes occurred within 15 min, yielding quantitatively the acyl complexes PdBr(C(O)CH2-Ph)(Ar-BIAN) (5a, Ar = p-An; 5c, Ar = p-Tol) and Pd(C(O)-p-Tol)(p-An-BIAN) (7a), respectively. On the contrary, PdBr(CH2CH2-p-NO2)(p-Tol-BIAN) reacted much more slowly, and conversion to the acyl complex PdBr(C(O)CH2CH2-p-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.22 Use of a metallic needle to bubble CO gas through a solution of PdBr(CH2C6H4-p-NO2)-(p-Tol-BIAN) gave complete conversion to 6c within 5 min. Reaction of PdBr(C(O)CH2Ph)(Ar-BIAN) (5a,c) with AgSO3CF3 in the presence or in the absence of acetonitrile gave no cationic acyl-acyl palladium complex, but instead [Pd(η5-CH3Ph)(Ar-BIAN)]SO3CF3 was formed, which was identical to the reaction product obtained from PdBr(CH2Ph)(Ar-BIAN) and AgSO3CF3.

Insertion of Strained Alkenes in Acyl-Palladium Bonds. Reaction of neutral and cationic acyl-palladium complexes Pd(C(O)Me)(p-An-BIAN) (3a) and Pd(C(O)Me)(p-An-BIAN) (5a,c) with strained alkenes led to the insertion of the 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(C6H4C(O)Me)(p-An-BIAN)]X (8a, X = Cl; 9a, 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(C6H5C(O)Me)(p-An-BIAN)]SO3CF3 (10a) and [Pd(C6H4C(O)Me)(p-An-BIAN)]SO3CF3 (11a), respectively. However, the reaction of the neutral acyl-palladium 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 compared to norbornadiene insertion reactions (about 1 h at 20 °C before no further alkene insertion occurred).23 The analogous o,o′-di-PrC6H4-BIAN complexes 3,4b reacted with norbornadiene to give the insertion complexes 8,9b, but the reaction of the neutral complex 3b was much slower 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(C6H4C(O)Et)(p-An-BIAN)]Cl (12a) within 5 min. Interestingly, reaction of Pd(C(O)Et)(Cl)(p-An-BIAN) with...
norbornene and dicyclopentadiene produced mixtures of the acyl- and the alkene-inserted complexes in the same ratio (63:37 and 45:55, respectively) as observed in the reaction of the acetyl complex Pd(C(O)Me)(Ar-BIAN) with these alkenes.


In contrast to the ready insertion of carbon monoxide in the cationic complex 8a with a chloride anion, the corresponding trifluoroacetatesulfonate complex 9a is completely inert toward insertion of a second CO molecule. Insertion of CO after alkene insertion has also been observed as a secondary reaction after the reaction of norbornene with Pd(C)(O)(Me)Cl(P)(Ph)(P)(C)(H)(2)-PPb2.118 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(C)(C)(H)(C)(O)(C)(H)(C)(O)(Me)(p-An-BIAN)]Cl(14a) readily occurred (eq 6), whereas partial conversion was observed when norbornene was used (38%), similar to the reactions of the neutral acyl complex 3a with norbornene.23 The analogous complex [Pd(C)(C)(H)(C)(O)(C)(H)(C)(O)(Me)(p-An-BIAN)]SO4CF3 (15a) has been obtained by the reaction of 14a with AgSO4CF3.

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(3Ar-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)(MeCN)(Ar-BIAN)]SO4CF3 2 give Pd–Me resonances at somewhat lower frequencies, in agreement with earlier observations.24 The methyl resonance of coordinated acetoni (2.28 (2a) and 2.08 ppm (2b)) is observed at higher frequency than that of free acetoni (2.00 ppm). Remarkably, for the complexes [Pd(Me)(MeCN)(Ar-BIAN)]SO4CF3, the CN stretching frequency is absent in IR. Unfortunately, no IR data were reported.
The coordination of the phosphine in [Pd(C(O)Me)(p-AnBian)(PPh3)]SO3CF3 (4a) is clear from the observed frequency at 27.4 ppm in 13P NMR. In IR, a PdC(0)Me signal is observed at 1705 cm⁻¹, and in 13C NMR the methyl resonance has shifted to 1.69 ppm, in agreement with literature values for complexes with C(O)Me and PPh3 ligands in cis positions. This shift to low frequency must be ascribed to the anisotropic shielding of the methyl group by one of the phenyl rings of the phosphine.

Spectroscopic Characterization of the Alkene-Inserted Products 8–12. The complexes formed after insertion of norbornadiene, norbornene, and dicyclopentadiene (8–11) were characterized by 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 3J(H1,H3) and 3J(H2,H3), which are in the range 5.6–6.7 Hz, cis disposition of PdC(O)Me to the exo face of the alkene can be concluded.¹¹

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)]BF4,¹² and of dicyclopentadiene with [Pd(C(O)Me)(MeCN)(bpy)]SO3CF3,¹³ which were determined by X-ray crystallography. There is no evidence for the formation of a nortricycleylen complex 8, 9, as was observed for the reaction of norbornadiene with Pd(C(O)Me)(Cl)(P2Ph2)2.¹⁰ The acyl oxygen atom is coordinated to the palladium, forming a five-membered palladacycle, in agreement with previous observations,¹⁰,¹¹ as can be derived from the CO stretching frequency at 1600 cm⁻¹ in IR,²⁹ the carbon monoxide at approximately 240 ppm in 13C NMR, and the methyl resonance at about 2.4 ppm in 13C NMR. The presence of trifluoroacetic acid in the reaction mixture does not influence the organo-palladium bond.

For the cationic cis-Pd(II)(MeCN) complexes containing biphosphines,²⁷ by²⁴ and tmėda.²⁵

The formation of the acyl complexes Pd(C(O)Me)(Ar-Bian) 3 after reaction of the methyl complexes 1 with carbon monoxide is evident from the high-frequency shift of the methyl resonance from 0.8–0.9 to 2.2–2.5 ppm in 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-palladium complexes.²⁷a,b,9a and for those of Pd(C(O)Me)Cl(p-Tol-Bian) obtained via oxidative addition of acetyl chloride to Pd(p-Tol-Bian)(dimethyl fumarate).¹⁹

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

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*Recorded at 75.48 MHz in CDCl3 at 20 °C, unless noted otherwise (n.o. = not observed). For the cationic cis-Pd(II)(MeCN) complexes containing biphosphines,²⁷ by²⁴ and tmėda.²⁵

References:
Insertion of CO and Alkenes on the Way to Polyketones

The complex [Pd(C(=C(O)(C6H5)3C(O)Me)]SO3CF3 (13a), formed after reaction of 13a with norbornadiene, was characterized by IR, 1H, and 13C NMR spectroscopy. The observed coupling constant $\nu(H_{13}-H_{19})$ of 5.8 Hz in 1H NMR reveals that the insertion occurs via cis addition of Pd(CO)R to the exo face of norbornadiene, similar to the monoisomer complexes 8–12. 1H and 13C NMR revealed the presence of two distinct inserted norbornadiene moieties. One is part of a five-membered palladacycle formed by coordination of the carbonyl oxygen to palladium, as is clear from 1H NMR (H15/16 at 5.95 and 5.40 ppm), 13C NMR (CO at 241.2 ppm), and IR ($\nu(CO) = 1598$ cm$^{-1}$). The other norbornadiene is not part of a palladacycle and resembles the pendant norbornadiene moiety of complex 13a methyl (H31) at 2.09 ppm, H15/16 at 6.28 and 6.03 ppm in 1H NMR; CO at 208.7 ppm in 13C NMR; v(CO) at 1703 cm$^{-1}$ in IR). These results clearly rule out formation of an eight-membered palladacycle via coordination of the carbonyl oxygen of the C(O)Me group to palladium, in agreement with the expectation that eight-membered metallocycles are thermodynamically less favorable than five-membered rings. The presence of two different carbonyl carbon groups in 14a was unequivocally derived from the 13C NMR data [Pd(C6H5)(C=O)(C6H5)3C(O)Me](p-An-BIAN)]Cl, formed when 13C-labeled carbon monoxide was used. Furthermore, in IR the CO stretching frequencies of the 13C-labeled complex are observed at 1660 and 1550 cm$^{-1}$, and the found ratios v(12CO)/v(13CO) 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 AgSO3CF3 resulted in conversion to the analogous complex [Pd(C6H5)(CO)(C6H5)3C(O)Me](p-An-BIAN)]SO3CF3 (15a), which was stable enough to allow us to obtain analytical data.

Discussion

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

Spectroscopic Characterization of the Multiple Insertion Products 13–15. Formation of Pd(C(=C(O)(C6H5)3C(O)Me)Cl(p-An-BIAN) (13a) from the insertion of CO in the alkyl-palladium bond of 8a is clear from the observed high-frequency shift of H13 from 2.00 to 3.9–4.0 ppm. From 1H NMR (methyl resonance of H21 at 2.10 ppm and the alkenic protons H15/16 at 6.13 and 6.05 ppm) and 13C NMR (two carbononyl resonances at 222.0 and 210.1 ppm, comparable to the observed resonances for [Pd(C(O)CH2CH2C(O)Me)(bpy)(CO)]Br,49) formation of a neutral complex can be derived, i.e., coordination of chloride to palladium and no formation of a six-membered palladacycle via coordination of the acyl oxygen atom (eq 8). In agreement with this structure, the complex has a low equivalent conductance of 5.8 S2− cm−2 mol−1 and shows in IR a broad resonance at 1699 cm$^{-1}$, due to two overlapping CO stretching frequencies.

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(30) This large difference is chemical shift between H15 and H16 after norbornadiene insertion is possibly due to the rigidity of the moiety imposed by the chelating C,O coordination, leading to different chemical environments, whereas in the case of more flexible monodentate C(O)CH2C(O)Me moieties, as in 13a, the chemical environments of H15 and H16 are more alike (on average). The reason for the large differences in chemical shift of C13, C14 between complexes 8a and 9a is unclear: probably in the cationic complex 9a there is some interaction of the double bond with palladium or there is a slight distortion (possibly on the way to a nortricyclocyclopentyl) in the acetylarnoeborne moiety.
routes include insertion from a five-coordinate intermediate or from a four-coordinate intermediate formed via loss of the halide, which is aided by the approach or the precoordination of carbon monoxide. It must be noted here that the chloride might remain in the neighborhood of the palladium in the cationic complex, which can be expected in solvents like chloroform and dichloromethane, making the difference between a five-coordinate and a catonic four-coordinate complex very small. Similar mechanisms can be assumed for the insertion of alkenes in acyl-palladium bonds, as evidence for insertion of alkenes in metal–carbon and metal–hydrogen bonds from both four-coordinate and five-coordinate intermediates has been presented.

The rate of insertion of carbon monoxide in methyl-palladium bonds and of alkenes in acyl-palladium bonds is higher for palladium complexes containing Ar-BIAN ligands than for complexes containing (di)phosphine ligands. For complexes with the bidentate phosphine ligands PhP(CH2)3PPh2 (n = 2–4), the rate of CO and alkene insertion decreased in the order n = 4 ≫ 3 ≫ 2, i.e., with increasing ligand rigidity. However, the high reactivity toward insertion reactions of complexes containing rigid Ar-BIAN ligands suggests that the flexibility of the ligands, which was reported to be important for the creation of open coordination sites and facilitation of the insertion reaction by modification of the L–Pd–L angle, is not an important prerequisite for the Pd(Ar-BIAN) complexes. The activating effect of the Ar-BIAN ligand can be ascribed to its rigidity, which disables dissociation of one ligating N-atom, which would in turn lead to the formation of products in a “thermodynamic sink” or to decomposition: in the case of flexible bidentate ligands, preferential dissociation of the coordinating atom trans to the organic ligand is expected, leading to the formation of a complex which cannot undergo the insertion reaction (Scheme 2). In the case of rigid bidentate ligands, dissociation of the ligand trans to the organic group is prohibited and the only alternative is dissociation of the halide, generating a cis complex which can undergo insertion (Scheme 2). Although halide dissociation is expected to be a slow process due to the small trans influence of the Ar-BIAN ligand, it represents the only viable route (apart from a mechanism through five-coordinate species) to account for our results. Furthermore, the σ-donor capacities of the Ar-BIAN ligand, leading to a more positive polarization of the carbonyl C-atom, and the greater accessibility of the palladium center, as compared to Pd–bidentate-phosphine complexes, are expected to be favorable for the insertion process.

The facile insertion of CO and alkenes in the cationic methyl- and acetyl-palladium complexes 2 and 4, respectively, can be ascribed to the increased accessibility of the palladium center combined with less back-bonding to CO or alkene and concomitant lower activation energy for their transfer as compared to the neutral analogues 1 and 3. The weak coordination of acetonitrile to palladium is reflected in the formation of [Pd(C(O)Me)(Ar-BIAN)(CO)SO2CF3] in solution upon reaction of 2 with carbon monoxide and was also observed in the reaction of catonic [PtMe3(p-Tol-BIAN)]SO2CF3 complexes with acetonitrile.

Neutral acetyl-palladium complexes 3 containing rigid Ar-BIAN ligands are rather stable and decarbonylation is slow, in contrast to analogous complexes containing more flexible bidentate phosphine and nitrogen ligands. The slow rate of decarbonylation might be due to the greater thermodynamic stability of the acyl complexes 3 as compared to the alkyl complexes 1. Alternatively, the absence of low-energy pathways for decarbonylation via N or Cl dissociation to create empty coordination sites, due to the rigidity and the low trans influence of the Ar-BIAN ligands, is expected to play an important role. In this case, the equilibration of halide dissociation lies completely to the side of the neutral starting acyl complex 3, whereas in the case of the reverse CO insertion reaction, excess CO is present thereby shifting the equilibrium toward the complex [Pd(R)(Ar-BIAN)-CO]+ Cl−. The kinetic stabilization of acetyl-palladium 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-(Me2NC6H4)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 acetyl-palladium complexes formed but also activate the acetyl complexes to undergo alkene insertion reactions, as can be derived from the observed reactivity toward insertion of strained alkenes of both neutral Pd(C(O)Me)Cl(Ar-BIAN) (3) and catonic [Pd(C(O)Me)(MeCN)(Ar-BIAN)]SO2CF3 (4) palladium complexes. As opposed to the reactivity of the neutral acetyl-palladium(IV) complexes 3, no insertion was observed for the neutral complexes Pd(C(O)(Me)I(bpy) or Pd(C(O)(OMe)I(tmeda) (tmeda = N,N,N'-tetramethylethlenediamine), whereas catonic [Pd(C(O)Me)(MeCN)(bpy)]SO2CF3 underwent insertion of strained alkenes.

Another aspect of the use of rigid chelating ligands is that insertion of strained alkenes in both neutral and cationic complexes yields the same type of products 8 and 9, which only differ in the counteranion, as was also observed in the insertion of alkenes in acetyl-palladium bonds of complexes containing the chelating diphosphine Ph3P(CH2)3PPh2. On the contrary, reaction of norbornene with cationic palladium complexes containing monodentate phosphine ligands resulted in the formation of [Pd(C2H5C(O)Me)(MeCN)(bpy)]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(C2H5C(O)Me)Cl(PPh3).11c

Successful 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
**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-diporphosphate complexes decreased with increasing ligand rigidity9,11h and the observed unreactivity of analogous Pd(C(O)Me)(bpy) and Pd(C(O)Me)(tmdea) complexes toward alkenes.11a 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 ø-donor capacity of Ar-BIAN and the accessibility of the palladium center in the presented complexes, as compared to those bearing sterically crowding phosphine or nitrogen ligands, will facilitate the insertion reactions.

The activating effect of the rigid Ar-BIAN ligands on insertion of CO and alkenes in palladium–carbon bonds and the availability of pure complexes [Pd(C=CH2C(O)Me)(p-An-BIAN)]Cl(8a) allowed us to investigate stepwise the successive CO and alkene insertion reactions by starting from neutral acylpalladium complexes. After each separate insertion step, both acyl- and alkyl-palladium complexes of the type PdC(O)CH(R')CH(R')-Cl and palladium complexes of the type PdC=CH(R')CH(R')-C(O)Me and Pd(CH=CH(R')CH(R')C(O)Me)Cl, 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. Furthermore, the isolation of a living oligomer and its ability to undergo further insertions of CO and norbornadiene demonstrates the utility and aptness of rigid bidentate nitrogen ligands in both stabilizing and activating organopalladium systems.

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**Supplementary Material Available:** Listing of 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.