# Kinetic Study of the Insertion of Norbornadiene into Palladium−Carbon Bonds of Complexes Containing the Rigid Bidentate Nitrogen Ligand Bis(arylimino)acenaphthene

Johannes H. Groen, Johannes G. P. Delis, Piet W. N. M. van Leeuwen, and Kees Vrieze*

*Anorganisch Chemisch Laboratorium, J. H. van 't Hoff Research Instituut, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*

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The ionic [Pd($C_7H_8C$(O)R)(Ar-BIAN)]X (R = Me, Et, *i*Pr, Ph; X = Cl, Br, I; Ar = *p*-An, *p*-$FC_6H_4$, *p*-$BrC_6H_4$, *p*-Tol, Ph, *o*,*o*′-$Me_2C_6H_3$, *o*,*o*′-*i*$Pr_2C_6H_3$) complexes (**1b**−**12b**), bearing the bidentate nitrogen ligand bis(arylimino)acenaphthene (Ar-BIAN), have been synthesized via reaction of the corresponding neutral acylpalladium complexes Pd(C(O)R)X(Ar-BIAN) (**1a**−**12a**) with norbornadiene (nbd). For the first time, an extensive kinetic study of this migratory alkene insertion into acyl−palladium bonds of neutral complexes containing α-diimine ligands has been carried out. It has been found that under pseudo-first-order circumstances these reactions follow the rate law $k_{obsd} = k_1 + k_2$[nbd], which shows that these reactions proceed via a pathway independent of alkene concentration ($k_1$ pathway) and a pathway dependent on alkene concentration ($k_2$ pathway). The dramatic decrease of the rate constants $k_1$ and $k_2$ upon increasing the steric bulk of the BIAN ligand and the large negative entropy of activation and low enthalpy of activation for both pathways indicate that the $k_1$ and $k_2$ pathways are closely related and involve associative processes. From the influence of solvent, X and C(O)R ligand, steric and electronic properties of the BIAN ligand, the presence of free halide and free BIAN, and the parameters of activation, mechanisms have been proposed for both pathways. The $k_1$ pathway may proceed via a rate-determining solvent-assisted halide or nitrogen dissociation, followed by alkene association and migratory insertion, while the $k_2$ pathway may occur via a rate-determining migratory alkene insertion in a contact ion pair intermediate. This species may be formed via alkene association followed by either halide or nitrogen dissociation.



## Introduction

The insertion reaction of alkenes into palladium−carbon bonds is a crucial process in many palladium-catalyzed organic reactions.[1−3] A recent example is the copolymerization of CO and alkenes, resulting in the formation of polyketones. This process is proposed to proceed via alternating migratory insertion reactions of CO and alkenes into alkyl− and acyl−palladium bonds, respectively.[4−13] Many experimental[14−16] and theoretical[17−22] investigations have been carried out on insertion reactions of CO into alkyl−metal bonds, but studies of insertion reactions of alkenes into acyl−metal bonds are less abundant.[8,23−30] Sen *et al.* succeeded in isolating complexes obtained after alkene insertion into

* To whom correspondence should be addressed.

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acyl−palladium bonds by using *trans*-[Pd(C(O)R)(NCMe)-$(PPh_3)_2$]$BF_4$ and *trans*-Pd(C(O)R)Cl$(PPh_3)_2$ (R = Me, Ph) as starting compounds.[23] Later, also other groups isolated and characterized complexes obtained after alkene insertion by using acylpalladium complexes with bidentate phosphorus[24,25,29] and nitrogen[8,26−28,30,31] ligands. In these cases intramolecular chelation through the carbonyl group stabilizes the products by preventing decomposition via $\beta$-hydrogen elimination.

Although several complexes obtained after alkene insertion into acyl−metal bonds have been isolated, mechanistic and kinetic studies are very scarce. In a classic paper, Thorn and Hoffmann analyzed the energy requirements for insertion of ethylene into a hydride−platinum bond from three-, four-, and five-coordinate intermediates.[32] According to their calculations, insertion from a four-coordinate intermediate is preferred. More recent calculations support these results.[33,34] In accord with this finding, intramolecular alkene insertions into carbalkoxy−palladium bonds have been shown to proceed from four-coordinate intermediates.[35] Very recently, Brookhart *et al.* reported the formation of [Pd($C_2H_4$C(O)Me)(phen)]$BAr_4$ (Ar = 3,5-$(CF_3)_2C_6H_3$) upon warming a solution of [Pd(C(O)Me)($\eta^2$-$C_2H_4$)-(phen)]$BAr_4$ from −78 to −46 °C, which also shows that insertion occurs from a four-coordinate species.[31] However, both intra-[36] and intermolecular[37] alkene insertions into hydride−platinum bonds have been proposed to occur from five-coordinate intermediates. Furthermore, the stability of five-coordinate organoplatinum and -palladium complexes containing an alkene[38] and the reactivity of acylpalladium complexes containing both rigid bi- and terdentate nitrogen ligands toward alkenes suggest that insertion from five-coordinate species may also be a low-energy pathway.[27,39] The only kinetic study of alkene insertion reactions into acyl−metal bonds has been carried out by Sen *et al.*[23] However, the use of acylpalladium complexes bearing rather easily dissociating monophosphines resulted in complex kinetics. To gain more insight into the mechanism of alkene insertion reactions, we carried out a kinetic study of the alkene insertion into acyl−palladium bonds and used complexes of the type Pd(C(O)R)X(Ar-BIAN), bearing the bidentate nitrogen ligand bis(arylimino)acenaphthene. It has been shown that these complexes react readily and cleanly with unsaturated molecules such as strained alkenes[27] and allenes.[30]

## Experimental Section

**General Comments.** All manipulations were carried out under an atmosphere of purified dry nitrogen by using standard Schlenk techniques. Solvents were dried and stored under nitrogen. $Pd(DBA)_2$ (DBA = dibenzylideneacetone),[40] Ar-BIAN,[41] Pd(Me)X(Ar-BIAN),[27] Pd(C(O)Me)Cl(*p*-An-BIAN) (**1a**),[27] Pd(C(O)Me)Cl(*p*-Tol-BIAN) (**9a**),[27] Pd(C(O)Me)Cl(*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN) (**12a**),[27] [Pd($C_7H_8$C(O)Me)(*p*-An-BIAN)]Cl (**1b**),[27] [Pd($C_7H_8$C(O)Et)(*p*-An-BIAN)]Cl (**4b**),[27] and [Pd($C_7H_8$C(O)Me)-(*o*,*o*′-*i*$Pr_2C_6H_3$-BIAN)]Cl (**12b**)[27] were prepared according to the literature. All other starting chemicals were used as commercially obtained. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AMX 300 spectrometer (300.13 and 75.48 MHz, respectively) at 20 °C, unless noted otherwise. Chemical shifts are in ppm relative to TMS as external standard (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, pst = pseudotriplet, q = quartet, sep = septet, m = multiplet, br = broad). IR spectra were obtained on a Bio-Rad FTS-7 spectrophotometer and mass spectra on a JEOL JMS SX/SX102A four-sector mass spectrometer fitted with a 10 $\mu$m tungsten FD emitter or equipped with a fast atom bombardment source.

**Preparation of Complexes 2a−8a, 10a, and 11a.** The complexes Pd(C(O)R)Cl(*p*-An-BIAN) (R = Et (**4a**), *i*Pr (**5a**), Ph (**6a**)) were prepared by using the following procedure. To a solution of $Pd(DBA)_2$ (0.50 mmol) and *p*-An-BIAN (0.55 mmol) in 25 mL of acetone was added the corresponding carboxylic acid chloride (0.55 mmol). After being stirred for 2 h at 20 °C, the solution was evaporated and the residue was washed with diethyl ether (2 × 20 mL). Column chromatography over silica 60 with dichloromethane/diethyl ether (4/1) as eluent resulted in the product (45−71% yield). The acylpalladium complexes Pd(C(O)Me)X(*p*-An-BIAN) (X = Br (**2a**), I (**3a**)), Pd(C(O)Me)Cl(*p*-$XC_6H_4$-BIAN) (X= F (**7a**), Br (**8a**)), Pd(C(O)Me)-Cl(Ph-BIAN) (**10a**), and Pd(C(O)Me)Cl(*o*,*o*′-$Me_2C_6H_3$-BIAN) (**11a**) were synthesized by using essentially the following procedure. A solution of the corresponding methylpalladium complex (0.5 mmol) in 25 mL of dichloromethane was stirred under a CO atmosphere at 20 °C. After 30 min 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 products were washed with diethyl ether (2 × 20 mL) and dried in vacuo (72−96% yield). No correct microanalyses were obtained due to the presence of irreproducible amounts (1−2 equiv) of dichloromethane.

**Pd(C(O)Me)Br(*p*-An-BIAN) (2a).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.05 d (8.2 Hz), $H_5$; 7.46 pst, $H_4$; 7.27 m (4 H), $H_{10}$; 7.04 d (8.8 Hz), $H_9$; 6.7 br, $H_3$; 3.91 s, OMe; 2.25 s, C(O)Me. $^{13}$C NMR (75.48 MHz, $CDCl_3$, $\delta$): 223.2, $C_{12}$; 159.7, $C_{11}$; 144.7, $C_8$; 131.9, $C_6$; 131.7, $C_5$; 129.1, $C_4$; 127.1, $C_2$; 125.6, $C_3$; 123.4, $C_{10}$; 115.2, $C_9$; 56.2, OMe; 36.0, C(O)*Me*; not observed $C_1$, $C_7$. IR (KBr): 1709 $cm^{-1}$, $\nu$(CO). MS: found, *m*/*z* 542 (calcd for $C_{28}H_{23}N_2O_3Pd$, 542).

**Pd(C(O)Me)I(*p*-An-BIAN) (3a).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.05 d (8.3 Hz), $H_5$; 7.48 pst, $H_4$; 7.24 d (8.9 Hz), $H_{10}$; 7.05 d (8.9 Hz), $H_9$; 7.0 br, $H_3$; 3.91 s, OMe; 2.25 s, C(O)Me. $^{13}$C NMR (75.48 MHz, $CDCl_3$, $\delta$): 222.6, $C_{12}$; 159.6, $C_{11}$; 144.9, $C_8$; 132.0, $C_6$; 131.6, $C_5$; 129.2, $C_4$; 127.2, $C_2$; 125.7, $C_3$; 123.5, $C_{10}$; 115.3, $C_9$; 56.3, OMe; 40.2, C(O)*Me*; not observed $C_1$, $C_7$. IR (KBr): 1705 $cm^{-1}$, $\nu$(CO). MS: found *m*/*z* 542 (calcd for $C_{28}H_{23}N_2O_3Pd$, 542).

**Pd(C(O)Et)Cl(*p*-An-BIAN) (4a).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.04 d (8.4 Hz), $H_5$; 7.48 pst, $H_4$; 7.27 m (4 H), $H_{10}$; 7.03 d (8.9 Hz), $H_9$; 6.8 br, $H_3$; 3.89 s, OMe; 2.80 q (7.3 Hz), C$H_2$Me; 0.69 t (7.3 Hz), $CH_2$*Me*. $^{13}$C NMR (75.48 MHz, $CDCl_3$, −20 °C, $\delta$): 228.1, $C_{12}$; 170.7, 165.0, $C_1$; 159.4, 159.0, $C_{11}$; 144.6, $C_7$; 141.2, 138.6, $C_8$; 132.0, 131.4, $C_5$; 131.7, $C_6$; 129.1, $C_4$; 127.0, 126.6, $C_2$; 125.8, 125.2, $C_3$; 124.0, 122.8, $C_{10}$; 115.6, 114.7, $C_9$; 56.2, 56.1, OMe; 42.6, *C*$H_2$Me; 9.9, $CH_2$*Me*. IR (KBr): 1703 $cm^{-1}$, $\nu$(CO). MS: found, *m*/*z* 556 (calcd for $C_{29}H_{25}N_2O_3Pd$, 556).

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**Pd(C(O)*i*Pr)Cl(*p*-An-BIAN) (5a).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.03 d (7.9 Hz), $H_5$; 7.47 pst, $H_4$; 7.28 m (4 H), $H_{10}$; 7.04 d (8.7 Hz), $H_9$; 6.7 br, $H_3$; 3.90 s, OMe; 2.98 sep (7.0 Hz), C*H*Me$_2$; 0.98 d (7.0 Hz), CH*Me*$_2$. $^{13}$C NMR (75.48 MHz, $CDCl_3$, −20 °C, $\delta$): 230.8, $C_{12}$; 170.2, 164.3, $C_1$; 158.6, 158.5, $C_{11}$; 143.7, $C_7$; 140.7, 137.9, $C_8$; 131.1, 130.5, $C_5$; 130.9, $C_6$; 128.2, $C_4$; 126.5, 126.0, $C_2$; 125.1, 124.5, $C_3$; 123.3, 122.5, $C_{10}$; 114.7, 114.0, $C_9$; 55.5, 55.4, OMe; 47.3, *C*HMe$_2$; 18.5, CH*Me*$_2$. IR (KBr): 1702 cm$^{-1}$, $\nu$(CO). MS: found, *m*/*z* 570 (calcd for $C_{30}H_{27}N_2O_3Pd$, 570).

**Pd(C(O)Ph)Cl(*p*-An-BIAN) (6a).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.04 m (2 H), $H_5$; 7.98 d (7.9 Hz), $H_o$; 7.5 m (4 H), $H_{4,10}$; 7.37 t (7.2 Hz), $H_p$; 7.24 pst, $H_m$; 7.06 d (8.1 Hz), $H_{10}$; 6.8 m (6 H), $H_{3,9}$; 3.90 s, 3.82 s, OMe. $^{13}$C NMR (75.48 MHz, $CDCl_3$, $\delta$): 219.6, $C_{12}$; 171.2, 165.5, $C_1$; 160.0, 159.3, $C_{11}$; 144.8, $C_7$; 140.9, 138.9, $C_8$; 136.3, $C_{ips}$; 132.2 $C_p$; 131.9, $C_6$; 131.9, 131.4, $C_5$; 130.6, $C_o$; 129.1, $C_4$; 128.2, $C_m$; 127.3, 127.0, $C_2$; 125.8, 125.3, $C_3$; 124.5, 122.9, $C_{10}$; 115.3, 115.0, $C_9$; 56.3, OMe. IR (KBr): 1680 cm$^{-1}$, $\nu$(CO). MS: found, *m*/*z* 604 (calcd for $C_{33}H_{25}N_2O_3Pd$, 604).

**Pd(C(O)Me)Cl(*p*-FC$_6$H$_4$-BIAN) (7a).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.10 d (8.3 Hz), $H_5$; 7.52 pst, $H_4$; 7.30 dd (13.2 Hz, 8.7 Hz), $H_{10}$; 7.23 d (8.7 Hz), $H_9$; 6.8 br, $H_3$; 2.27 s, C(O)Me. $^{13}$C NMR (75.48 MHz, $CDCl_3$, $\delta$): 222.4, $C_{12}$; 164.1, $C_1$; 160.8, $C_{11}$; 145.1, $C_8$; 132.2, $C_5$; 132.0, $C_6$; 129.3, $C_4$; 126.7, $C_2$; 125.9, $C_3$; 123.7 d (6.0 Hz), $C_{10}$; 117.5 br, $C_9$; 34.0, C(O)*Me*; not observed $C_7$. IR (KBr): 1711 cm$^{-1}$, $\nu$(CO). MS: found, *m*/*z* 518 (calcd for $C_{26}H_{17}N_2OF_2Pd$, 518).

**Pd(C(O)Me)Cl(*p*-BrC$_6$H$_4$-BIAN) (8a).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.11 d (8.3 Hz), $H_5$; 7.67 d (8.3 Hz), $H_{10}$; 7.54 pst, $H_4$; 7.21 d (8.3 Hz), $H_9$; 6.9 br, $H_3$; 2.27 s, C(O)Me. $^{13}$C NMR (75.48 MHz, $CDCl_3$, $\delta$): 221.6, $C_{12}$; 145.1, $C_8$; 133.6, $C_5$; 132.3, $C_4$; 132.1, $C_6$; 129.5, $C_{10}$; 126.7, $C_2$; 126.1, $C_3$; 123.6, $C_9$; 122.2, $C_{11}$; 34.0, C(O)*Me*; not observed $C_1$, $C_7$. IR (KBr): 1707 cm$^{-1}$, $\nu$(CO). MS: found, *m*/*z* 640 (calcd for $C_{26}H_{17}N_2OBr_2$-Pd, 640).

**Pd(C(O)Me)Cl(Ph-BIAN) (10a).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.06 d (8.3 Hz), $H_5$; 7.54 pst, $H_4$; 7.44 m (6 H), $H_{10,11}$; 7.31 d (7.8 Hz), $H_9$; 6.7 br, $H_3$; 2.24 s, C(O)Me. $^{13}$C NMR (75.48 MHz, $CDCl_3$, −20 °C, $\delta$): 224.5, $C_{12}$; 170.5, 166.0, $C_1$; 148.0, $C_7$; 145.7, 145.0, $C_8$; 132.3, 131.7, $C_5$; 131.7, $C_6$; 130.8, 129.9, $C_{10}$; 129.2, 129.1, $C_4$; 128.5, 128.3, $C_3$; 126.7, 126.3, $C_2$; 126.0, 125.8, $C_{11}$; 121.6, 121.1, $C_9$; 34.0, C(O)*Me*. IR (KBr): 1708 cm$^{-1}$, $\nu$(CO). MS: found, *m*/*z* 482 (calcd for $C_{26}H_{19}N_2OPd$, 482).

**Pd(C(O)Me)Cl(*o*,*o*′-Me$_2$C$_6$H$_3$-BIAN) (11a).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.09 d (8.2 Hz), 8.05 d (8.2 Hz), $H_5$; 7.50 m (2 H), $H_4$; 7.22 m (6 H), $H_{10,11}$; 6.78 d (6.7 Hz), 6.62 d (6.8 Hz), $H_3$; 2.42 s, 2.34 s, Me; 2.20 s, C(O)Me. $^{13}$C NMR (75.48 MHz, $CDCl_3$, $\delta$): 221.4, $C_{12}$; 169.9, 166.9, $C_1$; 145.6, 144.9, $C_8$; 144.5, $C_7$; 132.3, 131.7, $C_5$; 131.9, $C_6$; 129.9, $C_{10}$; 129.8, 129.3, $C_4$; 129.0, $C_9$ (signal of other $C_9$ is overlapping with signals of $C_4$); 128.1, 127.3, $C_3$; 127.8, 127.2, $C_2$; 124.9, $C_{11}$; 33.4, C(O)*Me*; 19.1, 18.6, Me. IR (KBr): 1704 cm$^{-1}$, $\nu$(CO). MS: found, *m*/*z* 538 (calcd for $C_{30}H_{27}N_2OPd$, 538).

**Preparation of Complexes 2b, 3b, and 5b−11b.** To solutions of **2a**, **3a**, and **5a−11a** (0.10 mmol) in dichloromethane (20 mL) was added norbornadiene (0.11 mmol). After being stirred at 20 °C for 2 h, each solution was evaporated to dryness and the residue was washed with diethyl ether (2 × 20 mL) and dried in vacuo, resulting in **2b**, **3b**, and **5b−11b** (74−87% yield), which were too unstable to allow microanalysis and $^{13}$C NMR.

**[Pd(C$_7$H$_8$C(O)Me)(*p*-An-BIAN)]Br (2b).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.15 d (8.3 Hz), $H_5$; 7.54 pst, $H_4$; 7.42 d (8.7 Hz), $H_{10}$; 7.21 d (7.3 Hz), $H_3$; 7.14 d (8.7 Hz), $H_9$; 5.98 dd (5.2, 2.8 Hz), 5.44 dd (5.2, 3.1 Hz), $H_{14,15}$; 3.94 s, OMe; 3.02 br, 2.31 br, $H_{13,16}$; 2.58 d (5.9 Hz), $H_{18}$; 2.51 s, C(O)Me; 2.01 d (5.9 Hz), $H_{12}$; 1.59 d (9.0 Hz), 1.27 d (9.0 Hz), $H_{17}$. IR (KBr): 1599 cm$^{-1}$, $\nu$(CO). MS: found, *m*/*z* 634 (calcd for $C_{35}H_{31}N_2O_3Pd$, 634).

**[Pd(C$_7$H$_8$C(O)Me)(*p*-An-BIAN)]I (3b).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.12 d (8.3 Hz), $H_5$; 7.52 d (8.6 Hz), $H_{10}$; 7.51 pst, $H_4$; 7.19 d (7.3 Hz), $H_3$; 7.12 d (8.6 Hz), $H_9$; 5.96 dd (4.8, 2.7 Hz), 5.45 dd (4.8, 3.0 Hz), $H_{14,15}$; 3.94 s, OMe; 2.98 br, 2.33 br, $H_{13,16}$; 2.53 d (5.9 Hz), $H_{18}$; 2.44 s, C(O)Me; 2.11 d (5.9 Hz), $H_{12}$; 1.60 d (9.0 Hz), 1.24 d (9.0 Hz), $H_{17}$. IR (KBr): 1600 cm$^{-1}$, $\nu$(CO). MS: found, *m*/*z* 634 (calcd for $C_{35}H_{31}N_2O_3Pd$, 634).

**[Pd(C$_7$H$_8$C(O)*i*Pr)(*p*-An-BIAN)]Cl (5b).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.16 d (8.3 Hz), $H_5$; 7.55 pst, $H_4$; 7.38 d (8.7 Hz), $H_{10}$; 7.12 d (8.7 Hz), $H_9$; 7.00 d (7.0 Hz), $H_3$; 5.96 dd (4.8, 2.5 Hz), 5.46 dd (4.8, 2.9 Hz), $H_{14,15}$; 3.92 s, OMe; 3.06 sep (6.8 Hz), CH (*i*Pr); 3.01 br, 2.30 br, $H_{13,16}$; 2.51 d (5.7 Hz), $H_{18}$; 1.95 d (5.7 Hz), $H_{12}$; 1.53 d (8.7 Hz), $H_{17}$ (signals of Me (*i*Pr) are overlapping with signal of the other $H_{17}$); 1.25 d (6.8 Hz), 1.02 d (6.8 Hz), Me (*i*Pr). IR (KBr): 1599 cm$^{-1}$, $\nu$(CO). MS: found, *m*/*z* 662 (calcd for $C_{37}H_{35}N_2O_3Pd$, 662).

**[Pd(C$_7$H$_8$C(O)Ph)(*p*-An-BIAN)]Cl (6b).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.18 d (8.3 Hz), $H_5$; 7.90 d (8.0 Hz), $H_o$; 7.71 t (7.4 Hz), $H_p$; 7.56 pst, $H_m$; 7.51 pst, $H_4$; 7.43 d (8.7 Hz), $H_{10}$; 7.29 br, $H_3$; 7.17 d (8.7 Hz), $H_9$; 6.12 dd (5.2, 2.7 Hz), 5.52 dd (5.2, 3.1 Hz), $H_{14,15}$; 3.96 s, OMe; 3.06 d (5.4 Hz), $H_{18}$; 3.05 br, 2.39 br, $H_{13,16}$; 2.07 dd (5.4, 1.5 Hz), $H_{12}$; 1.70 d (9.1 Hz), 1.26 d (9.1 Hz), $H_{17}$. IR (KBr): 1598 cm$^{-1}$, $\nu$(CO). MS: found, *m*/*z* 696 (calcd for $C_{40}H_{33}N_2O_3Pd$, 696).

**[Pd(C$_7$H$_8$C(O)Me)(*p*-FC$_6$H$_4$-BIAN)]Cl (7b).** $^1$H NMR (300.13 MHz, $CDCl_3$, 0 °C, $\delta$): 8.16 d (8.3 Hz), $H_5$; 7.54 pst, $H_4$; 7.53 pst, $H_{10}$; 7.32 pst, $H_9$; 7.03 d (7.3 Hz), $H_3$; 5.96 dd (5.3, 2.9 Hz), 5.50 dd (5.3, 3.1 Hz), $H_{14,15}$; 2.96 br, 2.39 br, $H_{13,16}$; 2.51 s, C(O)Me; 2.47 d (6.2 Hz), $H_{18}$; 2.10 dd (6.2, 1.7 Hz), $H_{12}$; 1.71 d (8.9 Hz), 1.27 d (8.9 Hz), $H_{17}$. IR (KBr): 1596 cm$^{-1}$, $\nu$(CO). MS: found, *m*/*z* 610 (calcd for $C_{33}H_{25}N_2OF_2Pd$, 610).

**[Pd(C$_7$H$_8$C(O)Me)(*p*-BrC$_6$H$_4$-BIAN)]Cl (8b).** $^1$H NMR (300.13 MHz, $CDCl_3$, −20 °C, $\delta$): 7.98 d (8.3 Hz), $H_5$; 7.61 d (8.5 Hz), $H_{10}$; 7.47 pst, $H_4$; 7.03 d (8.5 Hz), $H_9$; 6.94 d (7.0 Hz), $H_3$; 6.13 dd (5.4, 2.8 Hz), 5.94 dd (5.4, 3.1 Hz), $H_{14,15}$; 2.96 br, 1.78 br, $H_{13,16}$; 2.75 d (6.5 Hz), $H_{18}$; 2.36 s, C(O)Me; 2.03 d (6.5 Hz), $H_{12}$; 1.45 d (9.3 Hz), 1.32 d (9.3 Hz), $H_{17}$. IR (KBr): 1601 cm$^{-1}$, $\nu$(CO). MS: found, *m*/*z* 732 (calcd for $C_{33}H_{25}N_2OBr_2$-Pd, 732).

**[Pd(C$_7$H$_8$(C(O)Me)(*p*-Tol-BIAN)]Cl (9b).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.15 d (8.3 Hz), $H_5$; 7.53 pst, $H_4$; 7.41 d (8.0 Hz), $H_{10}$; 7.30 d (8.0 Hz), $H_9$; 7.08 d (7.3 Hz), $H_3$; 5.96 dd (5.1, 2.7 Hz), 5.43 dd (5.1, 3.1 Hz), $H_{14,15}$; 2.99 br, 2.40 br, $H_{13,16}$; 2.53 s, C(O)Me; 2.50 s, Me, 2.45 d (7.2 Hz), $H_{18}$; 1.99 d (7.2 Hz), $H_{12}$; 1.68 d (8.9 Hz), 1.28 d (8.9 Hz), $H_{17}$. IR (KBr): 1594 cm$^{-1}$, $\nu$(CO). MS: found, *m*/*z* 602 (calcd for $C_{35}H_{31}N_2OPd$, 602).

**[Pd(C$_7$H$_8$C(O)Me)(Ph-BIAN)]Cl (10b).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.14 d (8.3 Hz), $H_5$; 7.65 pst, $H_{10}$; 7.50 pst, $H_4$; 7.43 d (7.6 Hz), $H_9$; 6.96 d (7.3 Hz), $H_3$; 5.94 dd (5.0, 2.7 Hz), 5.45 dd (5.0, 3.0 Hz), $H_{14,15}$; 2.97 br, 2.43 br, $H_{13,16}$; 2.51 s, C(O)Me; 2.41 d (6.4 Hz), $H_{18}$; 2.02 d (6.4 Hz), $H_{12}$; 1.72 d (9.0 Hz), 1.28 d (9.0 Hz), $H_{17}$; signal of $H_{11}$ is overlapping with signal of $H_4$. IR (KBr): 1591 cm$^{-1}$, $\nu$(CO). MS: found, *m*/*z* 574 (calcd for $C_{33}H_{27}N_2OPd$, 574).

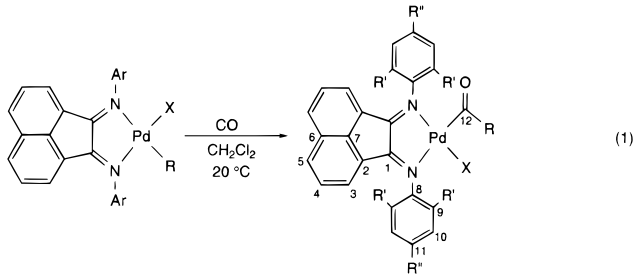
**[Pd(C$_7$H$_8$C(O)Me)(*o*,*o*′-Me$_2$C$_6$H$_3$-BIAN)]Cl (11b).** $^1$H NMR (300.13 MHz, $CDCl_3$, $\delta$): 8.22 d (8.3 Hz), $H_5$; 7.53 pst, $H_4$; 7.28 m (6H), $H_{10,11}$; 6.69 d (7.3 Hz), $H_3$; 5.92 dd (5.3, 2.9 Hz), 5.37 dd (5.3, 3.1 Hz), $H_{14,15}$; 3.55 br, 2.99 br, $H_{13,16}$; 2.52 s, C(O)Me; 2.34 s, 2.31 s, Me; 1.73 d (8.9 Hz), 1.24 d (8.9 Hz), $H_{17}$; 1.69 dd (6.7, 2.0 Hz), $H_{12}$; signal of $H_{18}$ is overlapping with signals of Me. IR (KBr): 1700 cm$^{-1}$, $\nu$(CO). MS: found, *m*/*z* 630 (calcd for $C_{37}H_{33}N_2O_3Pd$, 630).

**Kinetics.** The rates of the reactions of norbornadiene with complexes **1a−12a**, resulting in complexes **1b−12b**, were followed spectrophotometrically by repetitive scanning of the spectrum at suitable times at a fixed wavelength, where the difference between the absorbances of educt and product was largest. The reactions were started by addition of norbornadiene to a 4.3 × 10$^{-4}$ M solution of palladium complex in a quartz cell, in the thermostated cell compartment of a Perkin-Elmer Lambda 5 spectrophotometer, with a temperature accuracy of ±0.5 °C. The use of at least a 10-fold excess of norbornadiene over complex ensured pseudo-first-order kinet-

ics in all runs. All reactions obeyed a first-order rate law for at least 4 half-lives of the reaction. The rate constants $k_{obsd}$ were calculated from the slopes of plots of $\ln\{(A_t - A_\infty)/(A_0 - A_\infty)\}$ vs time ($A_0$ = absorbance after mixing of the reagents, $A_\infty$ = absorbance at completion of the reaction).

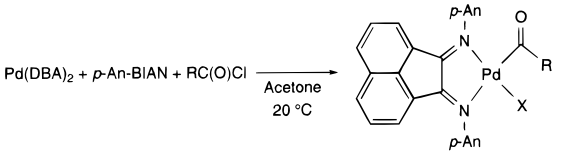
## Results

**Synthesis and Characterization of Complexes 1−12.** Carbon monoxide inserts readily into the methylpalladium bond of complexes of the type Pd(Me)X(Ar-BIAN) to give acylpalladium compounds **1a**−**3a** and **7a**−**12a** in high yields (eq 1). The complexes Pd(C(O)R)Cl(*p*-An-BIAN) (R = Et (**4a**), *i*Pr (**5a**), Ph (**6a**)) were synthesized via the oxidative addition of the corresponding carboxylic acid chloride to $Pd(DBA)_2$ in the presence of *p*-An-BIAN in acetone (eq 2).




(1)

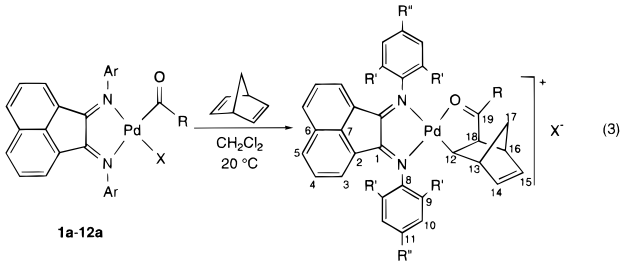
R = Me; R' = H; R" = OMe; X = Cl(**1a**), Br(**2a**), I(**3a**)
R = Me; R' = H; X = Cl; R" = F(**7a**), Br(**8a**), Me(**9a**), H(**10a**)
R = Me; R" = H; X = Cl; R' = Me(**11a**), *i*Pr(**12a**)




(2)

R = Et(**4a**), *i*Pr(**5a**), Ph(**6a**)

The acylpalladium compounds **1a**−**3a** and **7a**−**12a** are stable toward decarbonylation in the solid state as well in solution at 20 °C (no trace of decarbonylated methylpalladium complexes after 16 h in dichloromethane at 20 °C). However, at higher temperature slow decarbonylation occurred. When a solution of **1a**−**3a** and **7a**−**12a** was refluxed in dichloromethane for 2.5 h, 10−20% of the corresponding decarbonylated methylpalladium complex and 80−90% unreacted acylpalladium complex were present. The novel acylpalladium complexes **2a**−**8a**, **10a**, and **11a** were characterized by $^1$H and $^{13}$C NMR, mass, and IR spectroscopy. Unfortunately, no correct microanalyses were obtained due to the presence of irreproducible amounts of dichloromethane, varying from 1 to 2 equiv. Formation of these complexes is clear from the resonance of the carbonyl group in the $^{13}$C NMR (at about 220 ppm) and the observation of a CO stretching frequency (in the region of 1680−1720 cm$^{-1}$) in the IR. These data agree well with those reported for other acylpalladium complexes bearing bidentate nitrogen ligands.[27,28,30,39,42−44] The reaction of the neutral acylpalladium complexes **1a**−**12a** with norbornadiene led to insertion of the alkene into the acyl−palladium bond, resulting in the formation of complexes **1b**−**12b** (eq 3). This reaction




(3)

R = Me; R' = H; R" = OMe; X = Cl(**1b**), Br(**2b**), I(**3b**)
R' = H; R" = OMe; X = Cl; R = Et(**4b**), *i*Pr(**5b**), Ph(**6b**)
R = Me; R' = H; X = Cl; R" = F(**7b**), Br(**8b**), Me(**9b**), H(**10b**)
R = Me; R" = H; X = Cl; R' = Me(**11b**), *i*Pr(**12b**)

occurred within 2 h, and the products were formed in high yields (74−87%). The novel alkylpalladium complexes **2b**, **3b**, and **5b**−**11b** were characterized by $^1$H NMR, IR, and mass spectroscopy. Unfortunately, these complexes are too unstable to allow microanalysis or $^{13}$C NMR. Formation of **2b**, **3b**, and **5b**−**11b** is clear from the well-defined pattern of the inserted norbornadiene in the $^1$H NMR. In all cases a coupling constant $^3J(H_{12},H_{18})$ of about 6 Hz is observed, indicating a syn addition of Pd−C(O)R to the exo face of the alkene. This syn-exo addition of the alkene is in agreement with previous observations.[23,27,28,30,39,45] The low CO stretching frequency of about 1600 cm$^{-1}$ indicates that the carbonyl oxygen atom is coordinated to the metal center, forming a five-membered palladacycle, which is a common feature for complexes (bearing uni- and bidentate ligands) formed via insertion of alkenes into a palladium−acyl bond.[8,23,27,28,30,39,45] The observed high equivalent conductances of 15−26 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ in dichloromethane at 20 °C for complexes **2b**, **3b**, and **5b**−**11b** are in agreement with an ionic structure, whereas those for the neutral precursors **2a**, **3a**, and **5a**−**11a** are 0.02−0.08 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

As reported for similar acyl− and alkylpalladium complexes,[27,44] all novel acyl− and alkylpalladium compounds, except for **11a**, show fluxional behavior on the $^1$H NMR time scale: the complexes are in fast exchange at 20 °C and give one averaged signal for the protons on both halves of the BIAN ligand. In the case of the acylpalladium complexes mechanisms via halide dissociation,[28,44] nitrogen dissociation,[43] and CO deinsertion[44] have been proposed to explain the isomerization, whereas isomerization of the alkylpalladium complexes has been proposed to proceed via site exchange of the acetylnorbornene moiety, aided by coordination of the halide.[27]

**Kinetics.** Similar to the conditions used for the synthesis of complexes **1b**−**12b**, the reaction of norbornadiene (nbd) with the neutral acylpalladium complexes **1a**−**12a** in dichloromethane occurred cleanly and quantitatively under pseudo-first-order conditions, *i.e.* when a large excess of norbornadiene, [nbd] ≫ [Pd], was employed. Under these conditions, the reaction could be followed spectrophotometrically, and in all cases isosbestic points were obtained. The reaction could also be followed by $^1$H NMR, which did not show the

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**Table 1. Rate Constants $k_1$ and $k_2$ and the Enthalpy and Entropy of Activation of the Reaction of Complexes Pd(C(O)R)X(Ar-BIAN) (1a−12b) with Norbornadiene (Standard Deviations in Parentheses)[a]**

| entry no. | compd | R | X | Ar | $10^2k_1$, $s^{-1}$ | $10^2k_2$, $s^{-1}$ $M^{-1}$ | $\Delta H^{\ddagger}$,[d] kJ $mol^{-1}$ | $\Delta S^{\ddagger}$,[d] J $mol^{-1}$ $K^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | **1a** | Me | Cl | *p*-An | 0.39(2) | 4.62(10) | $k_1$: 37.9(22)<br>$k_2$: 48.4(18) | $k_1$: −140(6)<br>$k_2$: −126(6) |
| 2[b] | **1a** | Me | Cl | *p*-An | 0.33(5) | 5.01(22) | | |
| 3[c] | **1a** | Me | Cl | *p*-An | 0.17(3) | 6.15(15) | | |
| 4 | **2a** | Me | Br | *p*-An | 0.47(6) | 7.23(29) | $k_1$: 43.2(21)<br>$k_2$: 40.5(43) | $k_1$: −142(7)<br>$k_2$: −127(15) |
| 5 | **3a** | Me | I | *p*-An | 0.55(8) | 8.10(36) | $k_1$: 43.7(40)<br>$k_2$: 45.0(17) | $k_1$: −137(14)<br>$k_2$: −111(6) |
| 6 | **4a** | Et | Cl | *p*-An | 0.25(3) | 2.64(13) | $k_1$: 50.9(38)<br>$k_2$: 43.9(28) | $k_1$: −121(13)<br>$k_2$: −124(10) |
| 7 | **5a** | *i*Pr | Cl | *p*-An | 0.17(2) | 1.77(7) | $k_1$: 50.5(37)<br>$k_2$: 38.6(15) | $k_1$: −124(13)<br>$k_2$: −146(5) |
| 8 | **6a** | Ph | Cl | *p*-An | 0.22(4) | 6.12(20) | $k_1$: 31.5(76)<br>$k_2$: 25.6(28) | $k_1$: −187(26)<br>$k_2$: −180(10) |
| 9 | **7a** | Me | Cl | *p*-$FC_6H_4$ | 0.75(4) | 11.63(19) | | |
| 10 | **8a** | Me | Cl | *p*-$BrC_6H_4$ | 0.64(9) | 22.72(42) | | |
| 11 | **9a** | Me | Cl | *p*-Tol | 0.56(5) | 5.26(26) | | |
| 12 | **10a** | Me | Cl | Ph | 0.83(7) | 8.70(32) | | |
| 13 | **11a** | Me | Cl | *o,o′*-$Me_2C_6H_3$ | 0.33(3) | 1.58(6) | | |
| 14 | **12a** | Me | Cl | *o,o′*-$iPr_2C_6H_3$ | 0.05(1) | 0.40(1) | | |

[a] Conditions: dichloromethane solvent; 19.5 °C; [Pd] = $3.8 \times 10^{-4}$ M, unless noted otherwise. [b] THF solvent. [c] 2-Me-THF solvent. [d] $k_1$ and $k_2$ in these columns refer to the data for the respective kinetic pathways.



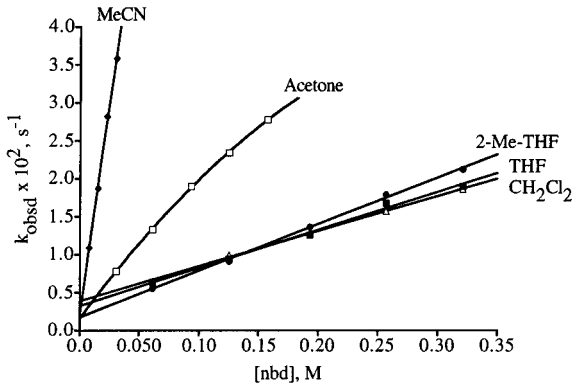



**Figure 1.** Pseudo-first-order rate constants ($k_{obsd}$) of the reaction of **1a** with nbd in different solvents as a function of the concentration of nbd. Conditions: 19.5 °C; [Pd] = $4.3 \times 10^{-4}$ M.

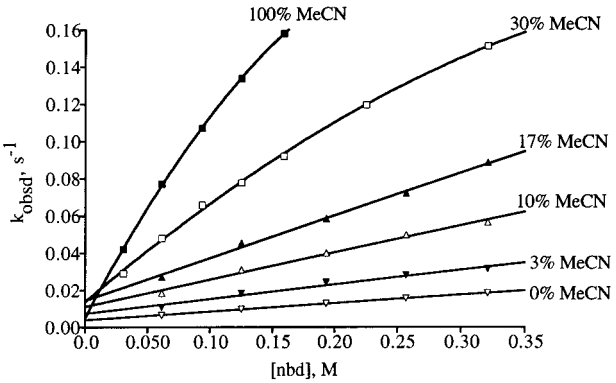



**Figure 2.** Pseudo-first-order rate constants ($k_{obsd}$) of the reaction of **1a** with nbd in dichloromethane/acetonitrile mixtures as a function of the concentration of nbd. Conditions: 19.5 °C; [Pd] = $4.3 \times 10^{-4}$ M.

presence of any intermediate in the temperature range of −80 to +20 °C. A plot of the observed rate constants $k_{obsd}$ (which were calculated from the slope of plots of $\ln\{(A_t - A_\infty)/(A_0 - A_\infty)\}$ vs time) vs the concentration of nbd resulted in straight lines with an intercept with the *y* axis, indicating that the kinetics obey the typical rate law $k_{obsd} = k_1 + k_2$[nbd]. The values of the observed rate constant $k_{obsd}$ of the reactions of **1a**−**12a** with nbd have been collected in Table S1 (Supporting Information). The values of the first-order rate constant $k_1$ and the second-order rate constant $k_2$ at 19.5 °C, obtained from linear regression analysis of the experimental data, along with the values of the parameters of activation $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, determined from the values of $k_1$ and $k_2$ measured at different temperatures (for these values, see Table S2 in the Supporting Information), have been collected in Table 1.

**Influence of the Solvent.** To study the influence of the solvent on the kinetics, the insertion reaction of nbd into the carbon−palladium bond of **1a** was carried out in different solvents at 19.5 °C (Figure 1). The use of solvents with comparable polarity, *i.e.* dichloromethane, THF, and 2-Me-THF, resulted in small differences in both $k_1$ and $k_2$ (Table 1, entries 1−3). Interestingly, carrying out the reaction in acetone and acetonitrile led to curved-line plots. The same observation was made when using mixtures of dichloromethane and acetonitrile as solvent (Figure 2). Increasing the percentage of acetonitrile in a dichloromethane solution from 0% v/v to 17% v/v led to an increase of both $k_1$ and $k_2$. Further increase of the acetonitrile/dichloromethane ratio resulted in curved-line plots.

**Influence of the C(O)R and X Ligands.** From Figures 3 and 4 it is clear that the pseudo-first-order rate constant $k_{obsd}$ of the reaction of nbd with Pd(C(O)R)X(*p*-An-BIAN) in dichloromethane at 19.5 °C depends on both the nature of the halide X and the nature of the C(O)R ligand. The second-order rate constant $k_2$ increases in the order X = Cl < Br < I and in the order R = *i*Pr < Et < Me < Ph. The first-order rate constant $k_1$ is less sensitive to variation of X or C(O)R. The values of $k_1$ are within experimental error equal for R = Et, *i*Pr, and Ph and somewhat larger for R = Me. Also, variations in the value of $k_1$ upon varying the X ligand are small and are within experimental error.

**Influence of the Ar Group.** To examine the influence of the BIAN ligand on the observed rate constant of the reaction of nbd with Pd(C(O)Me)Cl(Ar-BIAN) in dichloromethane at 19.5 °C, both steric and electronic properties of the aryl groups of the Ar-BIAN ligand were

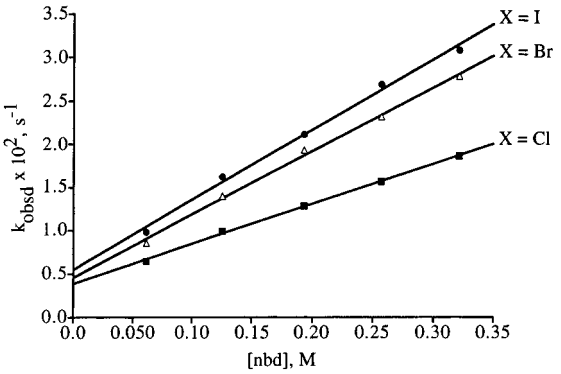



**Figure 3.** Pseudo-first-order rate constants ($k_{obsd}$) of the reaction of Pd(C(O)Me)X(*p*-An-BIAN) (X = Cl (**1a**), Br (**2a**), I (**3a**)) with nbd as a function of the concentration of nbd. Conditions: dichloromethane solvent; 19.5 °C; [Pd] = 4.3 × $10^{-4}$ M.

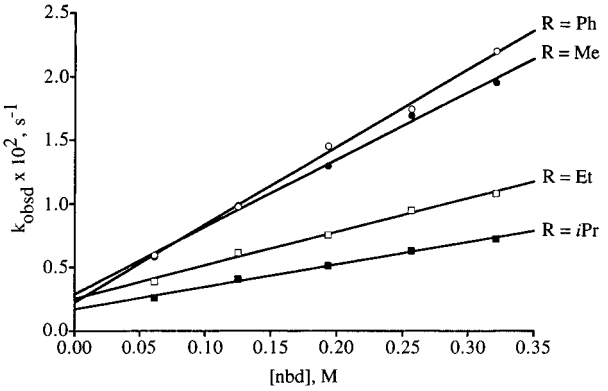



**Figure 4.** Pseudo-first-order rate constants ($k_{obsd}$) of the reaction of Pd(C(O)R)Cl(*p*-An-BIAN) (R = Me (**1a**), Et (**4a**), *i*Pr (**5a**), Ph (**6a**) with nbd as a function of the concentration of nbd. Conditions: dichloromethane solvent; 19.5 °C; [Pd] = 4.3 × $10^{-4}$ M.

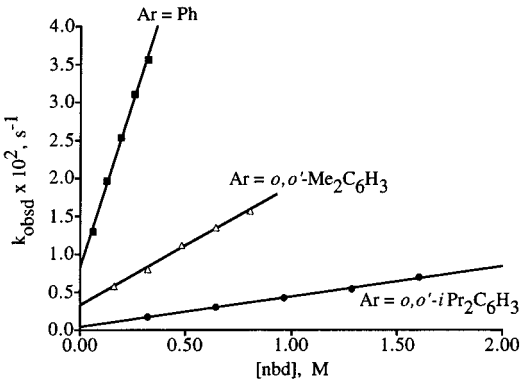



**Figure 5.** Pseudo-first-order rate constants ($k_{obsd}$) of the reaction of Pd(C(O)Me)Cl(Ar-BIAN) (Ar = Ph (**10a**), *o,o'*-$Me_2C_6H_3$ (**11a**), *o,o'*-*i*$Pr_2C_6H_3$ (**12a**)) with nbd as a function of the concentration of nbd. Conditions: dichloromethane solvent; 19.5 °C; [Pd] = 4.3 × $10^{-4}$ M.

varied (Table 1, entries 1, 9−14). Figure 5 clearly shows a dramatic influence of the steric bulk of the aryl groups on the values of $k_1$ and $k_2$, which both increase in the order Ar = *o,o'*-*i*$Pr_2C_6H_3$ ≪ *o,o'*-$Me_2C_6H_3$ ≪ Ph. The influence of the electronic properties of the BIAN ligand was determined by varying the para substituent on the aryl groups of the ligand (Figure 6). While the small variations in $k_1$ are within experimental error, the value of $k_2$ increases in the order Ar = *p*-An < *p*-Tol < Ph < *p*-$FC_6H_4$ < *p*-$BrC_6H_4$. A plot of the value of log $k_2$ vs

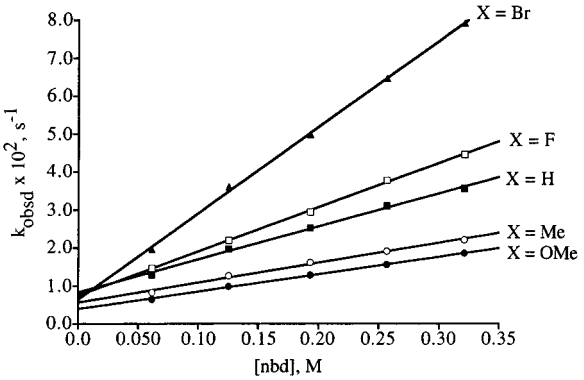



**Figure 6.** Pseudo-first-order rate constants ($k_{obsd}$) of the reaction of Pd(C(O)Me)Cl(*p*-$XC_6H_4$-BIAN) (X = OMe (**1a**), F (**7a**), Br (**8a**), Me (**9a**), H (**10a**)) with nbd as a function of the concentration of nbd. Conditions: dichloromethane solvent; 19.5 °C; [Pd] = 4.3 × $10^{-4}$ M.

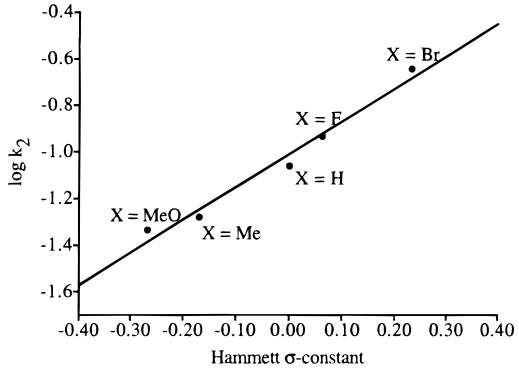



**Figure 7.** Hammett plot for the second-order rate constants $k_2$ of the reaction of Pd(C(O)Me)Cl(*p*-$XC_6H_4$-BIAN) (X = OMe (**1a**), F (**7a**), Br (**8a**), Me (**9a**), H (**10a**)) with nbd as a function of the $\sigma$ value of the para substituents X on the aryl groups of the BIAN ligand. Conditions: dichloromethane solvent; 19.5 °C; [Pd] = 4.3 × $10^{-4}$ M.

the Hammett $\sigma$ values[46] of the substituents at the para position of the aryl groups of the ligand resulted in a straight line with a slope ($\rho$) of 1.4 ± 0.1 (Figure 7). A similar plot for $k_1$ did not show a clear-cut dependence, because of the small variations and the relatively large experimental errors in the values of $k_1$.

**Influence of Excess Free *p*-An-BIAN and Free Chloride.** In Figures 8 and 9 the influence of addition of excess free *p*-An-BIAN on the values of $k_1$ and $k_2$, respectively, is shown. Interestingly, the $k_1$ pathway is strongly retarded by addition of small amounts of free ligand (in the absence of free *p*-An-BIAN $k_1$ = (0.39 ± 0.02) × $10^{-2}$ $s^{-1}$; with 1 equiv or more of *p*-An-BIAN $k_1$ ≈ 0.09 × $10^{-2}$ $s^{-1}$). However, the $k_2$ pathway is only slightly retarded by addition of free ligand. Increasing the free chloride concentration from 0.0 M to 4.3 × $10^{-3}$ M (0 to 10 equiv with respect to the palladium concentration), while maintaining a constant ionic strength, influenced neither $k_1$ nor $k_2$.

## Discussion

Insertions of unsaturated molecules (=un) in square-planar organoplatinum and -palladium complexes of the type M(R)X(L)$_2$ may occur via an associative pathway (Scheme 1, pathway II) and a dissociative pathway.

(46) Hammett, L. P. *Physical Organic Chemistry: Reaction Rates, Equilibria, and Mechanisms*, 2nd ed.; McGraw-Hill: New York, 1970.

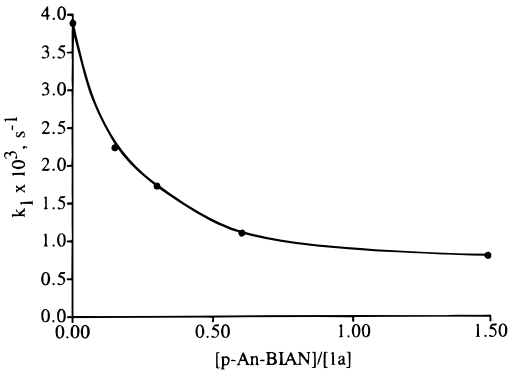



**Figure 8.** First-order rate constants $k_1$ of the reaction of **1a** with nbd as a function of the ratio [*p*-An-BIAN]/[**1a**]. Conditions: dichloromethane solvent; 19.5 °C; [Pd] = 4.3 × $10^{-4}$ M.

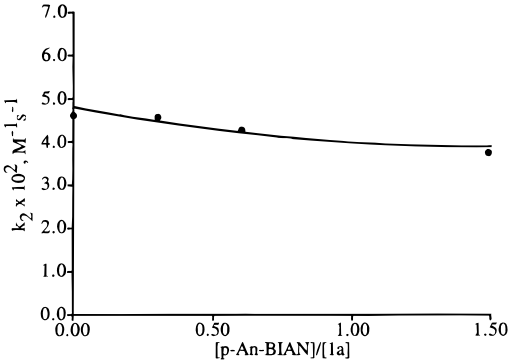
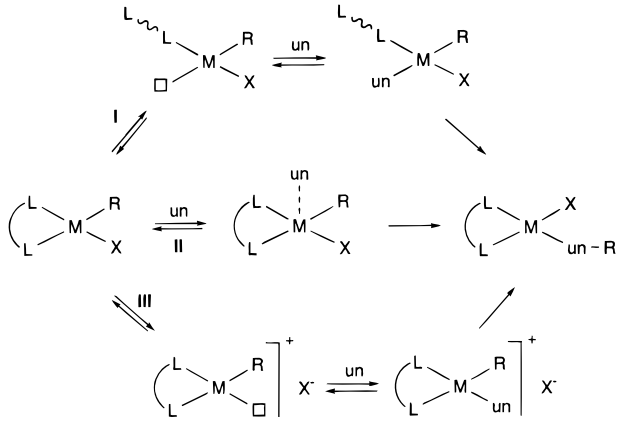



**Figure 9.** Second-order rate constants $k_2$ of the reaction of **1a** with nbd as a function of the ratio [*p*-An-BIAN]/[**1a**]. Conditions: dichloromethane solvent; 19.5 °C; [Pd] = 4.3 × $10^{-4}$ M.

In the latter case association of the substrate may be preceded by dissociation of either the neutral ligand L or the anionic ligand X (Scheme 1, pathways I and III, respectively). Studies on insertion reactions of both carbon monoxide[47−49] and alkenes[23] in neutral complexes bearing phosphine ligands have revealed that insertion predominantly occurs via dissociation of one of the phosphine ligands. For complexes containing the rigid bidentate nitrogen ligand BIAN, dissociation of one of the nitrogen atoms might seem to be more difficult.[27] However, complexes of the type Pd(R)X(Ar-BIAN) exhibit a high reactivity toward CO,[27] norbornadiene,[27] and allenes,[30,50] which indicates the presence of low-energy pathways for insertion reactions in these complexes.

From the results it is clear that insertion of norbornadiene into the acyl−palladium bond of complexes Pd(C(O)R)X(Ar-BIAN) (**1a**−**12a**) proceeds via (at least) two pathways, which are both first order with respect to the concentration of palladium: a pathway independent of the alkene concentration with a rate constant $k_1$ (the so-called $k_1$ pathway) and a pathway with a rate constant $k_2$, which is first order with respect to the concentration of alkene (the so-called $k_2$ pathway). The contributions of both pathways are about the same in the case of the lowest used concentration of nbd (0.061 M). For example, the contribution of $k_1$ to the observed rate constant of the reaction of **1a** with nbd in dichloromethane at 19.5 °C is 0.39 × $10^{-2}$ $s^{-1}$, while the contribution of $k_2$ to $k_{obs}$ is (4.62 × $10^{-2}$) × 0.061 = 0.28 × $10^{-2}$ $s^{-1}$.

**Scheme 1. Possible Mechanisms for Insertion of an Unsaturated Molecule (un) in Complexes of the Type M(R)X(L)$_2$**




**The Alkene-Independent $k_1$ Pathway.** Similar to substitution reactions in square-planar complexes, the $k_1$ pathway can be assigned either to a dissociative pathway, *i.e.* pathways I and III in Scheme 1, or to an associative solvento pathway.[51−56] Strong evidence supports the view, however, that in the present system the $k_1$ pathway may be an associative process rather than a dissociative process. (i) The value of $k_1$ decreases significantly with the increasing steric demand of the BIAN ligand, *i.e.* in the range Ph-BIAN ≫ *o,o′*-$Me_2C_6H_3$-BIAN ≫ *o,o′*-*i*$Pr_2C_6H_3$-BIAN, while the opposite is expected in the case of a dissociative pathway. (ii) The low value of the enthalpy of activation (31.5−50.9 kJ $mol^{-1}$) and the large negative value of the entropy of activation (−121 to −187 J $mol^{-1}$ $K^{-1}$) are consistent with an associative process. These parameters of activation are comparable with those reported for associative substitution reactions in palladium(II) complexes, *e.g.* $\Delta H^{\ddagger} = 51 \pm 1$ kJ $mol^{-1}$ and $\Delta S^{\ddagger} = -114 \pm 4$ J $mol^{-1}$ $K^{-1}$ for the nucleophilic substitution reaction of *trans*-Pd$(C_6F_5)_2$(tht)$_2$ (tht = tetrahydrothiophene) with 2-methylpyridine[57] and $\Delta H^{\ddagger} = 41 \pm 4$ kJ $mol^{-1}$ and $\Delta S^{\ddagger} = -172 \pm 8$ J $mol^{-1}$ $K^{-1}$ for the solvent-assisted dissociation of the acetate ligand in Pd(Et)OOCMe-$(PMe_3)_2$.[58]

The first possible solvento pathway (Scheme 2, pathway A) involves a rate-determining associative substitution of the halide X by solvent, *i.e.*, the making of the solvent−palladium bond is more important than the breaking of the halide−palladium bond.[53,54] Since most reactions were performed in dichloromethane, which is



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(54) Romeo, R. *Comments Inorg. Chem.* **1990**, *11*, 21 and references therein.
(55) Romeo, R.; Arena, G.; Monsù Scolaro, L.; Plutino, M. R.; Bruno, G.; Nicolò, F. *Inorg. Chem.* **1994**, *33*, 4029.
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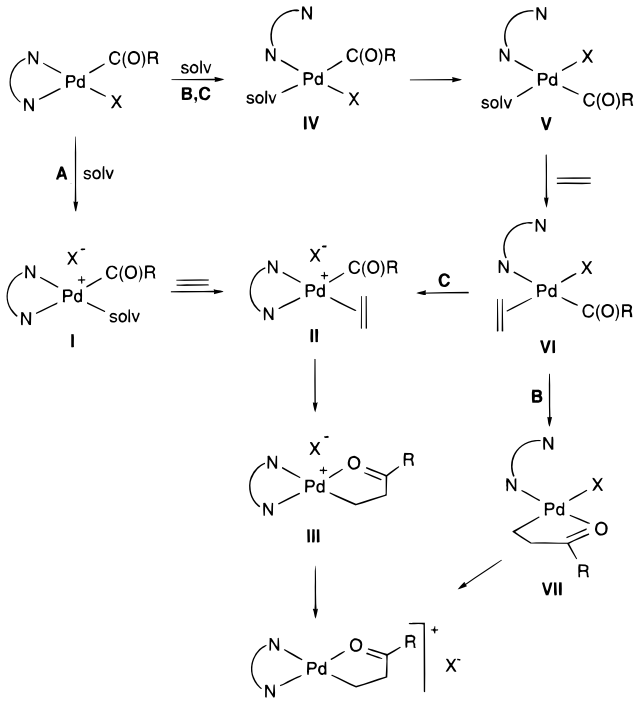
**Scheme 2. Three Possible Pathways for the $k_1$ Pathway of the Alkene Insertion in Acylpalladium Complexes Bearing Ar-BIAN**



a moderately polar solvent, it is likely that the dissociated halide remains in the neighborhood of the complex, forming contact ion pair intermediate I.[27,39,59] Substitution of the weakly coordinated solvent molecule by the alkene results in species II, from which a migration of the acyl ligand to the precoordinated alkene may occur. Migratory insertion reactions from this kind of ionic complex are known to proceed very easily.[23−25,27,28,31,60] Complete halide dissociation in species III results in the product. Two alternative pathways (Scheme 2, pathways B and C) proceed via a rate-determining associative substitution of a nitrogen atom by solvent. This involves dissociation of the nitrogen atom positioned *trans* to the acyl ligand, which has a larger *trans* influence than the halide ligand.[61] Since the BIAN ligand is a rigid ligand, the dissociated nitrogen atom will remain in the vicinity of the palladium center, which will result in intermediate IV. Coordination of a bidentate ligand in such an asymmetric fashion has been reported very recently for the BIAN ligand[30] and has been observed also for other rigid nitrogen ligands.[62,63] Species IV may be considered to be a T-shaped intermediate in which the fourth coordination site is occupied by a weakly coordinating solvent molecule. A *cis*−*trans* isomerization, which is known to proceed rather quickly in this kind of T-shaped intermediate,[54] followed by an alkene association leads to species VI. In this species the nitrogen atom, which has a larger *trans* influence than the halide ligand, is positioned *trans* to the acyl ligand,[61] which is favorable in view of a subsequent migratory insertion (pathway B). Migratory insertion and rearrangements result in formation of the product. Alternatively, substitution of the halide X by the apically coordinated nitrogen atom in species VI may occur (pathway C). This reaction, which can be expected to occur rather easily due to the relatively large *trans* influence of the precoordinated alkene positioned *trans* to the halide ligand, results via formation of species II in the product as proposed in pathway A.

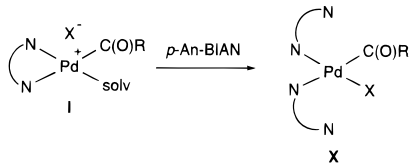
Pathways A−C are in agreement with the following observations.

(i) Increasing of the coordinating ability of the solvent, *i.e.* increasing the acetonitrile percentage in a dichloromethane solution, leads to an increase of $k_1$.

(ii) The nature of neither the halide X nor the C(O)R ligand in the complexes Pd(C(O)R)X(Ar-BIAN) influences the first-order rate constant $k_1$ significantly.

(iii) The value of $k_1$ is independent of the presence of free halide.

Considering the pathway via partial halide dissociation (pathway A), the remarkable retardation of the $k_1$ pathway upon addition of free ligand may be explained by substitution of the weakly coordinated solvent in species I by BIAN (eq 4). This may result in species X,



(4)

in which both nitrogen ligands are coordinated in a unidentate fashion.[64−66] Since substitution of one of the ligands in species X by nbd can be expected to be more difficult than in the case of species I, a decrease of the value of $k_1$ might be observed. Also, in the case of the alternative pathways B and C free BIAN may substitute the coordinated solvent in species IV or V, resulting in the formation of less reactive complexes. It must be noted, however, that upon addition of free *p*-An-BIAN to a solution of **1a** in $CDCl_3$, in the presence or in the absence of nbd, species of the type X have not been observed in the $^1$H NMR in the temperature range of −80 to +20 °C. This is to say that if the supposed intermediates in Scheme 2 were in fast preequilibrium, we could not explain the retarding influence of free BIAN.

**The Alkene-Dependent $k_2$ Pathway.** Analogous to the alkene-independent $k_1$ pathway, the large negative value of the entropy of activation (−180 to −111 J mol$^{-1}$ K$^{-1}$) and the observed decrease of the value of $k_2$

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(64) Very recently, an X-ray structure of [Pd(Me)(*p*-An-BIAN)$_2$]SO$_3$CF$_3$ has been determined. The X-ray structure shows one BIAN ligand coordinated in a bidentate fashion, while the other BIAN ligand is coordinated in a unidentate fashion.[65] The observed equivalence of both ligands in the $^1$H NMR in the temperature range −80 to +20 °C indicates also the presence of a species containing two unidentate coordinated BIAN ligands, *i.e.* a species similar to species X. Furthermore, coordination of two bidentate nitrogen ligands in a unidentate fashion has been observed recently for [Rh($\eta^2$:$\eta^2$-nbd)(*i*Pr-6-Me-PyCa)$_2$]SO$_3$CF$_3$ (*i*Pr-6-Me-PyCa = 2-(N-2-propanecarbaldimino)-6-methylpyridine).[66]
(65) Groen, J. H.; de Jong, B. J.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. To be submitted for publication.
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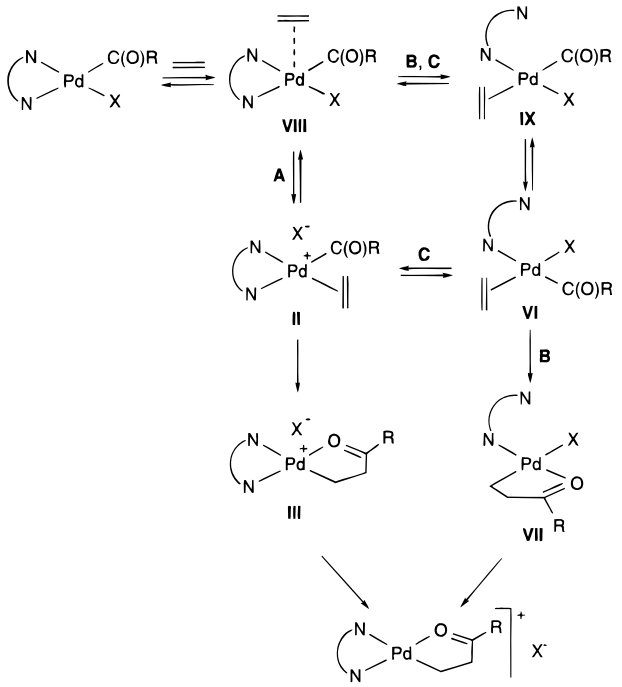
**Scheme 3. Three Possible Pathways for the $k_2$ Pathway of the Alkene Insertion in Acylpalladium Complexes Bearing Ar-BIAN**




upon increasing the steric demand of the BIAN ligand indicate an associative process. Taking also into account the first order with respect to the nbd concentration, the $k_2$ pathway may proceed via the square-pyramidal intermediate VIII (Scheme 3), resulting in the formation of the contact ion pair intermediate II (pathway A). A rate-determining migratory insertion followed by halide dissociation leads to the product. This pathway is an attractive one for the $k_2$ pathway, since it explains the following observations.

(i) Increase of the polarity of the solvent leads to a rate enhancement of the $k_2$ pathway. Polar solvents will stabilize the highly polarized contact ion pair II by efficient solvation.

(ii) The $k_2$ rate constant increases in the range X = Cl < Br < I, *i.e.* with decreasing Pd−X bond strength.[67] Weakening of the halide−palladium bond will result in a more facile formation of intermediate II.

(iii) No mass-law retardation upon addition of free halide is observed, which is in line with a pathway in which no (complete) halide dissociation is involved before or during the rate-determining step.

(iv) A Hammett plot for the $k_2$ rate constant as a function of the $\sigma$ values of the para substituents on the aryl groups of the BIAN ligand results in a straight line, with a positive slope ($\rho$) of 1.4 ± 0.1, indicating that the rate of the $k_2$ pathway increases with the electron-withdrawing character of the para substituent on the aryl groups of the BIAN ligand. It is known that the resulting decrease of electron density on the metal center leads to an increase of the stability of five-coordinate species, such as intermediate VIII, in the case of complexes bearing sterically demanding rigid bidentate nitrogen ligands.[38,63]

Two alternative pathways (Scheme 3, pathways B and C) also involve the formation of species VIII, followed, however, by dissociation of the nitrogen atom positioned *trans* to the acyl ligand. This results in species IX, which subsequently may isomerize to species VI. It should be noted that VI also may be formed directly from VIII. However, this must involve dissociation of the nitrogen atom positioned *trans* to the halide ligand, which can be considered to be more difficult. Formation of VI may be followed by either a rate-determining migratory insertion followed by rearrangements (pathway B) or substitution of the halide X by the apically coordinated nitrogen atom (pathway C). The latter reaction results via formation of species II in the product as proposed in pathway A. Also, pathways B and C are at first sight attractive ones for the $k_2$ pathway, since they both explain the unobserved mass-law retardation upon addition of free halide and free ligand and the increase of $k_2$ upon increasing the electron-withdrawing character of the Ar-BIAN ligand in a way similar to that mentioned for pathway A. Furthermore, increase of the electron-withdrawing properties of the BIAN ligand may weaken the nitrogen−palladium bonds, leading to a more facile formation of species IX. However, pathway B does not explain the observed rate enhancement upon increasing the polarity of the solvent and is not in line with the dependence of the value of $k_2$ of the halide ligand. Therefore, we prefer a pathway proceeding via formation of contact ion pair intermediate II, *i.e.* pathway A and/or C.

Interestingly, a retardation of the $k_2$ pathway is observed upon increasing the electron-releasing property of the migrating C(O)R group, while maintaining a constant steric demand, *i.e.* in the range R = Ph > *i*Pr; the opposite is a more common feature in migratory insertion reactions.[21,22,49,68−73] Comparison of the parameters of activation indicates that the relatively high reactivity of Pd(C(O)Ph)Cl(*p*-An-BIAN) (**6a**) is attributable to a more favorable enthalpy of activation rather than entropy of activation. This is not unexpected, since all complexes can be assumed to react via a mechanism with similar intermediates. The relatively low enthalpy of activation for **6a** may be explained by considering the five-coordinate species VIII. This species may be more stabilized than those derived from **1a**, **4a**, and **5a**, which contain the more electron-releasing C(O)Me, C(O)Et, and C(O)*i*Pr ligands, respectively. Higher CO insertion rates into phenyl-metal bonds compared to insertion rates into alkyl−metal bonds have been observed earlier for rhodium(III)[74] and palladium(II)[75] complexes, but a higher reactivity of M−C(O)Ph bonds compared to M−C(O)R bonds (R = Me, Et, *i*Pr) toward alkene insertion reactions has never been reported before.

When the norbornadiene insertion in **1a** is performed in acetone, acetonitrile, and mixtures of dichloromethane with large amounts of acetonitrile, the reactions are no longer first-order with respect to the nbd concentration

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but start to exhibit saturation kinetics. This will result in more complex kinetics, and insertion reactions in these solvents were not studied any further.

## Conclusion

The stability and reactivity of palladium complexes containing the bidentate nitrogen ligand Ar-BIAN have made it possible to carry out for the first time an extensive kinetic study of the migratory insertion of norbornadiene into carbon−palladium bonds of neutral acylpalladium complexes. The reaction proceeds via an alkene-independent pathway and an alkene-dependent pathway. Both pathways are closely related and involve associative processes. In both cases the mechanism may involve halide or nitrogen dissociation, which may be solvent-assisted in the case of the alkene-independent pathway. In the case of the alkene-dependent pathway alkene association may precede the dissociation step.

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**Supporting Information Available:** Tables giving primary kinetic data for the reactions of **1a**−**12a** with nbd (8 pages). Ordering information is given on any current masthead page.

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