Insertion of Unsaturated Hydrocarbons into the Palladium−Carbon Bond of Complexes (N⌒N)Pd(C(=N-2,6-Me_2Ph)Me)X (N⌒N = bpy, phen; X = Cl, Br, I, BF_4): A Structural and Mechanistic Study

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Received March 10, 1997⊗

The reactivity of Pd−carboimine complexes toward unsaturated hydrocarbon bonds has been studied. Insertion of norbornadiene and norbornene into the Pd−C bond of the neutral complexes (N⌒N)Pd(C(=N-2,6-$Me_2C_6H_3$)Me)X (X = Cl (**1**), Br (**2**), I (**3**); N⌒N = 2,2′-bipyridine (bpy, **a**), 1,10-phenanthroline (phen, **b**)) afforded quantitatively the novel and stable complexes [(N⌒N)Pd(C_7H_8C(=NR)Me)]X and [(N⌒N)Pd(C_7H_{10}C(=NR)Me)]X (R = 2,6-$Me_2C_6H_3$). Insertion reactions of the unstrained unsaturated hydrocarbons ethylene, propylene, 3-methyl-1,2-butadiene, and acetylene with the cationic complexes [(N⌒N)Pd-(C(=NR)Me)]X (N⌒N = bpy, phen; R = 2,6-$Me_2C_6H_3$; X = BF_4) provided the complexes [(N⌒N)-Pd(C_2H_4C(=NR)Me)]X, [(N⌒N)Pd(C_3H_6C(=NR)Me)]X, [(N⌒N)Pd(C_5H_8C(=NR)Me)]X, and [(bpy)Pd(C_2H_2C(=NR)Me)]X. The remarkable stability of these products is caused by the strong coordination of the carboimine nitrogen to the palladium center. Reaction of **1a** and **1b** with HC≡CCOOMe gave, instead of an insertion product, the Michael addition product (N⌒N)Pd[C(=CH_2)N(2,6-$Me_2C_6H_3$)(CH=CHCOOMe)]Cl. Kinetic measurements carried out on the norbornadiene insertion reactions with **1a**,**b**, **2a**, and **3a** revealed that the reactions are first order in the palladium concentration and occur via a norbornadiene concentration-independent and dependent pathway.

Introduction

The insertion of unsaturated hydrocarbons like olefins and acetylenes into metal−carbon bonds is a very important reaction in many homogeneously catalyzed processes.[1−4] An example of such a process is the palladium-catalyzed copolymerization of CO and alkenes leading to the formation of polyketones,[2,3,5−10] which involves successive insertions of CO and alkene.[4,11−13]

The insertion of an alkene into L_2M(R)X complexes (M = Pd, Pt) can follow two possible routes: one that involves X or L displacement by the alkene, affording a four-coordinate intermediate, followed by migratory insertion, and one in which the alkene adds to the complex to give a five-coordinate alkene adduct followed by migratory insertion. *Ab initio* calculations carried out by Thorn and Hoffmann on ethylene insertion into the Pt−H bond demonstrated that insertion from a four-coordinate intermediate is preferred.[14] Experimental studies on these reactions supported the calculations and showed that, particularly when X is a weakly bound ligand, the insertion occurs via a four-coordinate intermediate.[15−18] Insertion of alkenes into Pd−C bonds has also been demonstrated to occur via four-coordinate intermediates, such as the intramolecular alkene insertion reaction of $(PPh_3)_2$Pd($CO_2(CH_2)_2$CH=CH_2)Cl[19] and

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⊗ Abstract published in *Advance ACS Abstracts,* August 15, 1997.

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S0276-7333(97)00194-5 CCC: $14.00

alkene insertion into [(phen)Pd(R)L]BAr_4 (R = H, CH_3, $C(O)CH_3$; L = OEt_2).[13] On the other hand, it has been proposed that five-coordinate intermediates are involved in the insertion of ethylene into the Pt−H bond of the $L_2PtH(SnCl_3)$ complex[20] and in the intramolecular insertion reaction of the $(Ph_2POHOPPh_2)PtH(Ph_2P(CH_2)_n$-$CH{=}CH_2)$ complex.[21]

Examples of insertion of unsaturated hydrocarbons into Pd−acyl bonds are relatively scarce. Some studies are known for complexes containing phosphine ligands,[19,22−24] bidentate[11−13,25,26] and terdentate nitrogen ligands,[27] and N⌒O ligands,[28] of which a few deal with kinetic measurements. Sen *et al.* carried out a kinetic study on insertion of the strained alkene norbornadiene into the Pd−acyl bond of the complexes $[(PPh_3)_2Pd(CH_3$-$CN)(C(O)R)]BF_4$.[23] However, dissociation of the phosphine ligands resulted in complex kinetics.

Recently, we performed a detailed kinetic study on insertion reactions of norbornadiene and allenes with the neutral complexes (Ar-BIAN)Pd(C(O)R)X and (N⌒N)-Pd(C(O)R)X, respectively (N⌒N = 8-(2-pyridyl)quinoline, Ar-BIAN, R-DAB),[25,29] which indicated that Pd−N bond breaking rather than Pd−X bond breaking is involved in the insertion reaction. Lately, we reported the first isocyanide insertion reaction in (N⌒N)Pd(Me)Cl complexes (N⌒N = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 2,2′-bipyrimidine (bpm)) leading to the carboimine products (N⌒N)Pd(C(=NR)Me)Cl (R = 2,6-$Me_2C_6H_3$, *t*-Bu, CH_2tosyl).[29,30] We were interested in whether the carboimine products would allow insertion of unsaturated hydrocarbons and if so whether the reactivity would be similar to the analogous (N⌒N)Pd-(C(O)Me)Cl complexes. Moreover, the direct synthesis of the polyimine analogue of polyketone via subsequent alternating insertion of isocyanides and alkenes would be of great interest.

Experimental Section

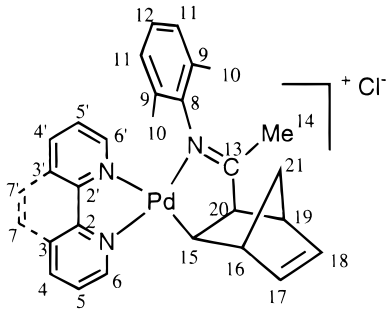
Material and Apparatus. All manipulations have been carried out in an atmosphere of purified, dry nitrogen using standard Schlenk techniques. Solvents were dried and stored under nitrogen. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX 300 and DRX 300 (300.13 and 75.48 MHz respectively). Elemental analyses were carried out in our institute. Mass spectrometry was carried out on a JEOL JMS SX/SX102A four-sector mass spectrometer coupled to a JEOL MS-MP 7000 data system. IR spectra were recorded on a Bio-Rad FTS-7. Synthesis of the complexes (bpy)Pd(C(=N-2,6-$Me_2C_6H_3$)Me)Cl and (phen)Pd(C(=N-2,6-$Me_2C_6H_3$)Me)Cl has been described before.[29]

Synthesis of (bpy)Pd(C(=N-2,6-$Me_2C_6H_3$)Me)Br (2a). The complex (bpy)Pd(C(=N-2,6-$Me_2C_6H_3$)Me)Cl (100 mg; 0.23 mmol) and KBr (164 mg; 1.4 mmol) were dissolved in a mixture of dichloromethane (60 mL) and acetone (40 mL) and stirred for 2 h. The solvent was evaporated, and the residue was washed twice with dichloromethane. The volume of the solvent was concentrated and hexane (30 mL) was added, providing a yellow crystalline material, which was collected by centrifugation. Yield: 101 mg; 0.21 mmol; 90%. ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 9.31 (d, ^3J = 4.4 Hz, 1H, H6), 9.05 (d, ^3J = 4.4 Hz, 1H, H6′), 8.11 (br, 2H, H3, H3′), 8.02 (t, 8.1 Hz, 1H, H4), 7.97 (t, 8.0 Hz, 1H, H4′), 7.60 (m, 1H, H5), 7.51 (t, ^3J = 6.5 Hz, 1H, H5′), 6.97 (d, ^3J = 7.2 Hz, 2H, H_{meta}), 6.84 (t, ^3J = 7.2 Hz, 1H, H_{para}), 2.34 (s, 3H, C(=NR)CH_3), 2.26 (s, 6H, $(CH_3)_2$Ph). IR ν(C=N) (KBr): 1623 cm^{-1}. A ^{13}C NMR spectrum could not be obtained because of the low solubility. FAB MS found (calcd for $C_{20}H_{20}N_3PdBr$): 488 (488).

Synthesis of (bpy)Pd(C(=N-2,6-$Me_2C_6H_3$)Me)I (3a). The synthesis was carried out according to the procedure followed above for **2a**, yielding a dark yellow crystalline material (112 mg; 0.19 mmol; 85%). ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 9.47 (d, ^3J = 4.9 Hz, 1H, H6), 8.94 (d, ^3J = 4.9 Hz, 1H, H6′), 8.12 (d, ^3J = 4.1 Hz, 2H, H3, H3′), 8.04 (t, 7.9 Hz, 1H, H4), 7.70 (t, 7.7 Hz, 1H, H4′), 7.63 (m, 1H, H5), 7.48 (m, 1H, H5′), 6.96 (d, ^3J = 7.1 Hz, 2H, H_{meta}), 6.85 (t, ^3J = 6.9 Hz, 1H, H_{para}), 2.43 (s, 3H, C(=NR)CH_3), 2.26 (s, 6H, $(CH_3)_2$Ph). IR ν(C=N) (KBr): 1635 cm^{-1}. A ^{13}C NMR spectrum could not be obtained because of the low solubility. FAB MS found (calcd for $C_{20}H_{20}N_3PdI$): 535 (535).

General Procedure for Insertion of Norbornadiene and Norbornene in Complexes (N⌒N)Pd(C(=N-2,6-$Me_2C_6H_3$)Me)X (N⌒N = bpy (a), phen (b)) providing complexes 4a,b (X = Cl), 5a (X = Br), 6a (X = I) (Insertion of Norbornadiene), and 7a,b (Insertion of Norbornene). The complex (N⌒N)Pd(C(=N-2,6-$Me_2C_6H_3$)Me)Cl (40 mg; 0.090 mmol) and the appropriate alkene (5.0 equiv; 0.45 mmol; 41 mg) were dissolved in dichloromethane (20 mL) and stirred for 2 h for reaction with norbornadiene and 24 h for reaction with norbornene. The volume of the solution was concentrated to 5 mL, and diethyl ether (30 mL) was added. The crystalline material was collected by centrifugation.

Atom labeling schemes for the complexes **4a**,**b, 5a, 6a**, and **7a**,**b** are as follows.



[(bpy)Pd(C_7H_8C(=N-2,6-$Me_2C_6H_3$)Me)]Cl (4a). Yield: 43 mg; 0.086 mmol; 95%. ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 9.13 (d, ^3J = 8.0 Hz, 1H, H3), 9.00 (d, ^3J = 8.1 Hz, 1H, H3′), 8.56 (d, ^3J = 5.0 Hz, 1H, H6), 8.37 (t, ^3J = 7.8 Hz, 1H, H4), 8.08 (t, ^3J = 7.8 Hz, 1H, H4′), 7.73 (t, ^3J = 6.1 Hz, 1H, H5), 7.28 (m, 3H, H11, H12), 6.97 (t, ^3J = 6.1 Hz, 1H, H5′), 6.35 (dd, ^3J = 5.5 Hz, ^3J = 2.8 Hz, 1H, H17), 6.24 (dd, ^3J = 5.5 Hz, ^3J = 2.8 Hz, 1H, H18), 5.69 (d, ^3J = 4.4 Hz, 1H, H6′), 3.11 (s, 1H, H16),

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3.06 (s, 1H, H19), 2.65 (dd, ^3J = 6.3 Hz, ^3J = 3.3 Hz, 1H, H15), 2.59 (d, ^3J = 6.2 Hz, 1H, H20), 2.30 (s, 3H, H10), 2.21 (s, 3H, H10), 2.10 (d, ^3J = 8.7 Hz, 1H, H21), 1.94 (s, 3H, H14), 1.58 (d, ^3J = 8.7 Hz, 1H, H21). ^{13}C NMR data (75.48 MHz, $CDCl_3$) δ: 197.4 (C13), 156.7 (C2), 153.7 (C2′), 148.9 (C6), 147.1 (C6′), 141.5 (C4), 140.7 (C4′), 136.5 (C3), 134.4 (C3′), 144.2, 130.6, 130.5, 130.1, 129.7, 128.2, 125.7, 124.8 (C_{Ph}, C═C_{nbd}), 127.4 (C5), 126.5 (C5′), 58.6, 51.4, 48.6, 47.3, 45.6 (C_{nbd}), 19.0, 18.7, 19.2 (C_{Me}). Elemental analysis found (calcd for $C_{27}H_{28}N_3PdCl\cdot CH_2Cl_2$): C, 53.88 (54.13); H, 5.15 (4.87); N, 6.72 (6.76). FAB MS found (calcd for $C_{27}H_{28}N_3PdCl$ − Cl): 500 (500).

[(bpy)Pd(C_7H_8C(═N-2,6-$Me_2C_6H_3$)Me)]Br (5a): Yield: 47 mg; 0.086 mmol; 95%. ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 9.03 (d, ^3J = 8.1 Hz, 1H, H3), 8.92 (d, ^3J = 8.1 Hz, 1H, H3′), 8.59 (d, ^3J = 5.4 Hz, 1H, H6), 8.35 (t, ^3J = 7.8 Hz, 1H, H4), 8.08 (t, ^3J = 7.8 Hz, 1H, H4′), 7.76 (t, ^3J = 6.7 Hz, 1H, H5), 7.28 (m, 3H, H11, H12), 7.00 (t, ^3J = 6.7 Hz, 1H, H5), 6.38 (dd, ^3J = 5.4 Hz, ^3J = 3.0 Hz, 1H, H17), 6.24 (dd, ^3J = 5.4 Hz, ^3J = 2.9 Hz, 1H, H18), 5.70 (d, ^3J = 5.2 Hz, 1H, H6′), 3.11 (s, 1H, H16), 3.06 (s, 1H, H19), 2.67 (dd, ^3J = 6.3 Hz, ^3J = 2.1 Hz, 1H, H15), 2.60 (d, ^3J = 6.2 Hz, 1H, H20), 2.30 (s, 3H, H10), 2.21 (s, 3H, H10), 2.10 (d, ^3J = 8.8 Hz, 1H, H21), 1.94 (s, 3H, H14), 1.58 (d, ^3J = 8.7 Hz, 1H, H21). ^{13}C NMR data (75.48 MHz, $CDCl_3$) δ: 197.0 (C13), 156.2 (C2), 153.2 (C2′), 148.6 (C6), 146.7 (C6′), 140.9 (C4), 140.2 (C4′), 143.8, 136.0, 133.8, 130.2, 130.1, 129.6, 129.2, 124.3 (C_{Ph}, C═C_{nbd}), 127.7 (C3), 127.0 (C3′), 125.9 (C5), 125.2 (C5′), 58.2, 50.9, 48.1, 46.9, 45.1 (C_{nbd}), 18.7, 18.5, 18.1 (C_{Me}). FAB MS found (calcd for $C_{27}H_{28}N_3PdBr$ − Br): 500 (500).

[(bpy)Pd(C_7H_8C(═N-2,6-$Me_2C_6H_3$)Me)]I (6a): Yield: 51 mg; 0.081 mmol; 90%. ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 8.94 (d, ^3J = 8.2 Hz, 1H, H3), 8.84 (d, ^3J = 8.0 Hz, 1H, H3′), 8.61 (d, ^3J = 5.3 Hz, 1H, H6), 8.36 (t, ^3J = 7.5 Hz, 1H, H4), 8.08 (t, ^3J = 7.3 Hz, 1H, H4′), 7.77 (t, ^3J = 6.4 Hz, 1H, H5), 7.28 (m, 3H, H11, H12), 7.02 (t, ^3J = 6.6 Hz, 1H, H5′), 6.40 (dd, ^3J = 5.5 Hz, ^3J = 2.9 Hz, 1H, H17), 6.26 (dd, ^3J = 5.5 Hz, ^3J = 2.8 Hz, 1H, H18), 5.71 (d, ^3J = 4.6 Hz, 1H, H6′), 3.12 (s, 1H, H16), 3.08 (s, 1H, H19), 2.70 (dd, ^3J = 6.3 Hz, ^3J = 2.3 Hz, 1H, H15), 2.61 (d, ^3J = 6.3 Hz, 1H, H20), 2.32 (s, 3H, H10), 2.23 (s, 3H, H10), 2.13 (d, ^3J = 8.9 Hz, 1H, H21), 1.95 (s, 3H, H14), 1.60 (d, ^3J = 8.7 Hz, 1H, H21). ^{13}C NMR data (75.48 MHz, $CDCl_3$) δ: 197.7 (C13), 156.6 (C2), 153.4 (C2′), 149.4 (C6), 147.4 (C6′), 141.4 (C4), 140.7 (C4′), 144.4, 136.7, 134.5, 130.8, 130.7, 130.2, 129.8, 124.6 (C_{Ph}, C═C_{nbd}), 128.3 (C3), 127.8 (C3′), 126.6 (C5), 125.5 (C5′), 58.8, 51.7, 48.8, 47.5, 45.7 (C_{nbd}), 19.4, 19.1, 18.8 (C_{Me}). FAB MS found (calcd for $C_{27}H_{28}N_3PdI$ − I): 500 (500).

[(phen)Pd(C_7H_8C(═N-2,6-$Me_2C_6H_3$)Me)]Cl (4b): Yield: 46 mg; 0.088 mmol; 98%. ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 9.06 (m, 1H, H6), 9.04 (d, ^3J = 4.6 Hz, 1H, H4), 8.70 (dd, ^3J = 8.0 Hz, ^{4}J = 2.2 Hz, 1H, H4′), 8.29 (dd, ^3J = 8.2 Hz, ^3J = 5.3 Hz, 1H, H5), 8.26 (d, ^3J = 8.2 Hz, 1H, H7), 8.19 (d, ^3J = 8.2 Hz, 1H, H7′), 7.44 (dd, ^3J = 8.0 Hz, ^3J = 5.3 Hz, 1H, H5′), 7.35 (m, 2H, H11), 7.30 (dd, ^3J = 2.1 Hz, 1H, H12), 6.50 (dd, ^3J = 5.6 Hz, ^3J = 3.0 Hz, 1H, H17), 6.29 (dd, ^3J = 5.5 Hz, ^3J = 3.0 Hz, 1H, H18), 6.00 (dd, ^3J = 5.0 Hz, ^{4}J = 1.0 Hz, 1H, H6′), 3.17 (d, ^3J = 1.9 Hz, 2H, H16, H19), 2.96 (dd, ^3J = 6.2 Hz, ^3J = 2.2 Hz, 2H, H15, H20), 2.34, (s, 3H, H10), 2.29 (s, 3H, H10), 2.17 (d, ^3J = 8.8 Hz, 1H, H21), 2.01 (s, 3H, H14), 1.62 (d, ^3J = 8.8 Hz, 1H, H21). ^{13}C NMR data (75.48 MHz, $CDCl_3$) δ: 197.7 (C13), 149.8 (C6), 148.0 (C6′), 146.8 (C2), 144.6 (C2′), 140.6 (C4), 139.6 (C4′), 136.6 (C7), 134.3 (C7′), 144.6 (C3), 144.4 (C3′), 128.2 (C5), 127.8 (C5′), 130.8, 130.6, 130.1, 129.7, 128.4, 126.5, 125.5 (C_{Ph}, C═C_{nbd}), 58.8, 51.1, 48.8, 47.3, 45.5 (C_{nbd}) 19.1, 18.6, 19.0 (C_{Me}). Elemental analysis found (calcd for $C_{29}H_{28}N_3PdCl\cdot CH_2Cl_2$): C, 55.53 (55.83); H, 5.04 (4.96); N, 6.38 (6.51). FAB MS found (calcd for $C_{29}H_{28}N_3PdCl$ − Cl): 524 (524).

[(bpy)Pd($C_7H_{10}C$(═N-2,6-$Me_2C_6H_3$)Me)]Cl (7a): Yield: 42 mg; 0.084 mmol; 93%. ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 9.00 (d, ^3J = 8.1 Hz, 1H, H3), 8.88 (d, ^3J = 8.2 Hz, 1H, H3′), 8.52 (d, ^3J = 5.6 Hz, 1H, H6), 8.32 (t, ^3J = 7.8 Hz, 1H, H4), 8.05 (dt, ^3J = 7.7 Hz, ^{4}J = 1.2 Hz, 1H, H4′), 7.67 (t, ^3J = 6.3 Hz, 1H, H5), 7.23 (m, 3H, H11, H12), 6.96 (t, ^3J = 6.3 Hz, 1H, H5′), 5.64 (d, ^3J = 4.7 Hz, 1H, H6′), 3.06 (dd, ^3J = 6.5 Hz, ^3J = 1.8 Hz, 1H, H16), 2.78 (d, ^3J = 6.5 Hz, 1H, H19), 2.48 (d, ^3J = 3.8 Hz, 1H, H15), 2.41 (d, ^3J = 3.8 Hz, 1H, H20), 2.26 (s, 3H, H10), 2.24 (s, 3H, H10), 2.13 (d, ^3J = 13 Hz, 1H, H21), 1.83 (s, 3H, H14), 1.50 (d, ^3J = 13 Hz, 1H, H21), 1.62−1.50 (m, 4H, H_{nbn}). ^{13}C NMR data (75.48 MHz, $CDCl_3$) δ: 199.1 (C13), 156.6 (C2), 153.7 (C2′), 149.3 (C6), 147.0 (C6′), 141.4 (C4), 140.6 (C4′), 127.2 (C3), 126.3 (C3′), 125.7 (C5), 124.8 (C5′), 144.4, 130.6, 130.3, 129.6, 128.0 (C_{Ph}), 65.7, 57.1, 43.8, 42.2, 36.2, 30.5, 29.9 (C_{nbn}) 18.9, 18.4, 19.0 (C_{Me}). FAB MS found (calcd for $C_{27}H_{30}N_3PdCl$ − Cl): 502 (502).

[(phen)Pd($C_7H_{10}C$(═N-2,6-$Me_2C_6H_3$)Me)]Cl (7b): Yield: 45 mg; 0.085 mmol; 95%. ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 9.03 (d, ^3J = 7.3 Hz, 1H, H4), 8.99 (d, ^3J = 5.2 Hz, 1H, H6), 8.68 (dd, ^3J = 8.2 Hz, ^{4}J = 1.3 Hz, 1H, H4′), 2.27 (d, ^3J = 8.8 Hz, 1H, H7), 8.22 (dd, ^3J = 8.2 Hz, ^3J = 5.0 Hz, 1H, H5), 8.20 (d, ^3J = 8.8 Hz, 1H, H7′), 7.43 (d, ^3J = 8.2 Hz, 5.0 Hz, 1H, H5′), 7.34 (m, 3H, H11, H12), 5.97 (dd, ^3J = 5.0 Hz, ^{4}J = 1.3 Hz, 1H, H6′), 3.38 (dd, ^3J = 6.5 hz, ^3J = 2.1 Hz, 1H, H16), 2.91 (d, ^3J = 6.5 Hz, 1H, H19), 2.55 (s, 2H, H15, H20), 2.34 (s, 3H, H10), 2.31 (s, 3H, H10), 2.21 (d, ^3J = 10 Hz, 1H, H21), 1.88−1.53 (m, 4H, H_{nbn}), 1.43 (d, ^3J = 10 Hz, 1H, H21). ^{13}C NMR data (75.48 MHz, $CDCl_3$) δ: 198.6 (C13), 149.6 (C6), 147.4 (C6′), 146.3 (C2), 144.1 (C2′), 140.1 (C4), 139.1 (C4′), 125.9 (C7), 125.0 (C7′), 130.4, 130.2, 129.9, 129.8, 129.6, 129.3, 127.9, 127.7, 127.4 (C_{Ph}, C_{phen}), 65.5, 56.5, 43.6, 41.8, 35.8, 30.1, 29.4 (C_{nbn}), 18.6, 18.5, 18.0 (C_{Me}). Elemental analysis found (calcd for $C_{29}H_{30}N_3PdCl\cdot CH_2Cl_2$): C, 55.66 (55.66); H, 5.09 (4.99); N, 6.44 (6.49). FAB MS found (calcd for $C_{29}H_{30}N_3PdCl$ − Cl): 526 (526).

General Procedure for Insertion of Ethylene, Propylene, 3-Methyl-1,2-butadiene, and Acetylene in Complexes (N⌒N)Pd(C(═N-2,6-$Me_2C_6H_3$)Me)Cl (N⌒N = bpy (1a), phen (1b)) Providing Complexes 9a,b (Insertion of Ethylene), 10a,b (Insertion of Propylene), 11a,b (Insertion of 3-Methyl-1,2-butadiene), and 12 (Insertion of Acetylene). The complex (N⌒N)Pd(C(═N-2,6-$Me_2C_6H_3$)Me)-Cl (40 mg, 0.090 mmol) and $AgBF_4$ (1.2 eq; 0.1 mmol; 21 mg) were dissolved in a mixture of dichloromethane and acetonitrile (5:1) and stirred for 5 min. The suspension was filtered, after which, the alkene, acetylene, or allene was added by a microsyringe in the case of a liquid reagent or by bubbling through the solution in the case of a gaseous reagent. The solution was stirred until it changed from yellow to almost colorless. The solvent was evaporated and the residue dissolved in dichloromethane. The solution was filtered, after which, ether was added to the solution to result in the formation of a crystalline material.

[(bpy)Pd(C_2H_4C(═N-2,6-$Me_2C_6H_3$)Me)]BF_4 (9a): Yield: 22 mg; 0.051 mmol; 57%. ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 8.43 (m, 2H, H3, H3′), 8.38 (d, ^3J = 4.8 Hz, 1H, H6), 8.20 (dd, ^3J = 7.8 Hz, ^{4}J = 1.4 Hz, 1H, H4), 8.01 (dd, ^3J = 7.8 Hz, ^{4}J = 1.4 Hz, 1H, H4′), 7.61 (dt, ^3J = 6.3 Hz, ^{4}J = 1.0 Hz, H, H5), 7.27 (m, 3H, H11, H12), 7.08 (t, ^3J = 6.3 Hz, 1H, H5′), 5.84 (d, ^3J = 4.8 Hz, 1H, H6′), 2.95 (t, ^3J = 6.3 Hz, 2H, CH_2), 2.81 (t, ^3J = 6.3 Hz, 2H, CH_2), 2.27 (s, 6H, H10), 1.88 (s, 3H, H14). ^{13}C NMR data (75.48 MHz, $CDCl_3$) δ: 198.8 (C13), 156.1 (C2), 153.2 (C2′), 149.2 (C6), 148.7 (C6′), 140.6 (C4), 140.0 (C4′), 124.0 (C3), 123.1 (C3′), 126.8 (C5), 126.1 (C5′), 45.1 (C15), 27.1 (C20), 143.7, 130.3, 129.2, 127.6 (C_{Ph}), 17.7, 18.6 (C_{Me}). Elemental analysis found (calcd for $C_{22}H_{24}N_3PdBF_4\cdot{}^1/_2C_4H_8O$): C, 50.61 (51.50); H, 5.15 (5.05); N, 7.44 (7.51). FAB MS found (calcd for $C_{22}H_{24}N_3PdBF_4$ − BF_4): 436 (436).

[(phen)Pd(C_2H_4C(═N-2,6-$Me_2C_6H_3$)Me)]BF_4 (9b): Yield: 25 mg; 0.054 mmol; 60%. ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 8.85 (d, ^3J = 5.1 Hz, 1H, H6), 8.69, (d, ^3J = 7.4 Hz, 1H, H7), 8.53 (d, ^3J = 8.1 Hz, 1H, H7′), 8.01 (d, ^3J = 5.3 Hz, 1H, H4), 7.98 (d, ^3J = 5.3 Hz, 1H, H4′), 7.46 (d, ^3J = 5.1 Hz, 1H, H5), 7.45 (d, ^3J = 5.1 Hz, 1H, H5′), 7.30 (m, 3H, H11, H12), 6.11 (d, ^3J = 4.8 Hz, 1H, H6′), 3.03 (m, 4H, CH_2), 1.93 (s, 3H, H14), 2.31 (s, 6H, H10). ^{13}C NMR data (75.48 MHz, $CDCl_3$) δ: 197.0

(C13), 144.3 (C2), 141.9 (C2′), 147.8 (C6), 145.3 (C6′), 137.5 (C4), 136.8 (C4′), 128.3 (C3), 127.8 (C3′), 125.6 (C5), 125.1 (C5′), 123.5 (C7), 123.0 (C7′), 142.2 128.3, 127.2, 125.6 (C_{Ph}), 43.3 (C15), 24.9 (C20), 15.8, 16.6 (C_{Me}). Elemental analysis found (calcd for $C_{24}H_{24}N_3PdBF_4$): C, 52.12 (52.63); H, 4.45 (4.42); N, 7.63 (7.67). FAB MS found (calcd for $C_{24}H_{24}N_3PdBF_4 - BF_4$): 460 (460).

[(bpy)Pd(C_3H_6C(=N-2,6-$Me_2C_6H_3$)Me)]BF_4 (10a): Yield: 28 mg; 0.061 mmol; 68%. ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 8.58 (d, ^3J = 5.7 Hz, 1H, H6), 8.50 (d, ^3J = 7.9 Hz, 1H, H3′), 8.41 (d, ^3J = 8.1 Hz, 1H, H3), 8.24 (dt, ^3J = 7.8 Hz, ^{4}J = 1.4 Hz, 1H, H4), 8.00 (dt, ^3J = 7.8 Hz, ^{4}J = 1.4 Hz, 1H, H4′), 7.70 (dt, ^3J = 7.2 Hz, ^{4}J = 1.4 Hz, 1H, H5), 7.26 (m, 3H, H11, H12), 7.02 (dd, ^3J = 7.8 Hz, ^{4}J = 1.0 Hz, 1H, H5′), 5.87 (d, ^3J = 5.3 Hz, 1H, H6′), 3.53 (dd, ^{2}J = 19.2 Hz, ^3J = 7.5 Hz, 1H, $H_{propenyl}$), 2.84 (t, ^3J = 7.2 Hz, 1H, $H_{propenyl}$), 2.44 (s, 3H, H10), 2.13 (s, 3H, H10), 1.95 (s, 3H, H14), 1.25 (d, ^3J = 7.2 Hz, 3H, $CH_{3propenyl}$). ^{13}C NMR data (75.48 MHz, $CDCl_3$) δ: 196.8 (C13), 155.9 (C2), 153.0 (C2′), 149.0 (C6), 146.9 (C6′), 140.5 (C4), 140.0 (C4′), 127.2 (C5), 126.3 (C5′), 124.0 (C3), 123.1 (C3′), 143.7, 130.3, 130.3, 129.5, 128.9, 127.6 (C_{Ph}), 42.1 (C15), 53.1 (C20), 24.1, 19.4, 18.3, 17.5 (C_{Me}). FAB MS found (calcd for $C_{23}H_{26}N_3PdBF_4 - BF_4$): 450 (450).

[(phen)Pd(C_3H_6C(=N-2,6-$Me_2C_6H_3$)Me)]BF_4 (10b): Yield: 29 mg; 0.062 mmol; 69%. ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 8.73 (d, ^3J = 8.3 Hz, 1H, H4), 9.00 (d, ^3J = 5.3 Hz, 1H, H6), 8.51 (d, ^3J = 8.1 Hz, 1H, H4′), 8.10 (dd, ^3J = 8.3 Hz, ^3J = 5.3 Hz, 1H, H5), 8.07 (d, ^3J = 8.8 Hz, 1H, H7), 8.02 (d, ^3J = 8.8 Hz, 1H, H7′), 7.42 (dd, ^3J = 8.2 Hz, ^3J = 5.3 Hz, 1H, H5′), 7.32 (m, 3H, H11, H12), 6.16 (d, ^3J = 5.0 Hz, 1H, H6′), 3.63 (dd, ^{2}J = 19.3 Hz, ^3J = 7.6 hz, 1H, $H_{propenyl}$) 3.11 (m, $H_{propenyl}$), 2.41 (s, 3H, H14), 2.24 (d, ^3J = 19.3 hz, 1H, $H_{propenyl}$), 2.00 (s, 3H, H14), 2.22 (s, 6H, H10), 1.43 (d, ^3J = 7.2 Hz, 3H, $CH_{3propenyl}$). ^{13}C NMR data (75.48 MHz, $CDCl_3$) δ: 195.0 (C13), 147.7 (C6), 145.6 (C6′), 144.2 (C2), 142.1 (C2′), 137.6 (C4), 136.8 (C4′), 128.3 (C3), 127.8 (C3′), 125.6 (C5), 125.2 (C5′), 123.9 (C7), 123.0 (C7′), 141.9, 128.4, 128.4, 127.5, 127.0, 125.7 (C_{Ph}), 51.3 (C15), 40.2 (C20), 22.4, 17.3, 16.3, 15.6 (C_{Me}). FAB MS found (calcd for $C_{25}H_{26}N_3PdBF_4 - BF_4$): 474 (474).

[(bpy)Pd(C_5H_8C(=N-2,6-$Me_2C_6H_3$)Me)]BF_4 (11a): Yield: 28 mg; 0.059 mmol; 65%. ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 8.58 (d, ^3J = 4.8 Hz, 1H, H6), 8.50 (d, ^3J = 8.0 Hz, 1H, H3′), 8.44 (d, ^3J = 8.2 Hz, 1H, H3), 8.24 (dt, ^3J = 7.9 Hz, ^{4}J = 1.3 Hz, 1H, H4), 8.03 (dt, ^3J = 7.8 Hz, ^{4}J = 1.3 Hz, 1H, H4′), 7.66 (dt, ^3J = 6.6 Hz, ^{4}J = 1.3 Hz, 1H, H5), 7.28 (m, 3H, H11, H12), 7.07 (dt, ^3J = 6.0 Hz, ^{4}J = 1.3 Hz, 1H, H5′), 6.00 (d, ^3J = 5.5 Hz, 1H, H6′), 3.39 (s, 2H, Pd−CH_2), 2.30 (s, 6H, H10), 2.15 (s, 6H, =$C(CH_3)_2$), 2.02 (s, 3H, H14). ^{13}C NMR data (75.48 MHz, $CDCl_3$) δ: 186.3 (C13), 155.9 (C2), 153.3 (C2′), 149.5 (C6), 147.0 (C6′), 140.6 (C4), 140.0 (C4′), 127.0 (C5), 126.5 (C5′), 124.0 (C3), 123.1 (C3′), 141.9, 130.1, 129.2, 127.6 (C_{Ph}), 34.6 (C15), 143.6 (=CMe_2), 18.1, 21.3 (C_{Me}). Elemental analysis found (calcd for $C_{25}H_{28}N_3PdBF_4$): C, 53.05 (53.26); H, 5.04 (5.01); N, 7.41 (7.45). FAB MS found (calcd for $C_{25}H_{28}N_3PdBF_4 - BF_4$): 476 (476).

[(phen)Pd(C_5H_8C(=N-2,6-$Me_2C_6H_3$)Me)]BF_4 (11b): Yield: 27 mg; 0.054 mmol; 60%. ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 9.03 (d, ^3J = 5.1 Hz, 1H, H6), 8.71 (d, ^3J = 8.1 Hz, 1H, H4), 8.53 (d, ^3J = 8.0 Hz, 1H, H4′), 8.08 (dd, ^3J = 8.2 Hz, ^3J = 5.1 Hz, 1H, H5), 8.03 (s, 2H, H7, H7′), 7.46 (dd, ^3J = 8.1 Hz, ^3J = 5.1 Hz, 1H, H5′), 7.33 (m, 3H, H11, H12), 6.24 (d, ^3J = 5.0 Hz, 1H, H6′), 3.62 (s, 2H, Pd−CH_2), 2.33 (s, 6H, H10), 2.11 (s, 3H, =$C(CH_3)_2$), 2.07 (s, 3H, =$C(CH_3)_2$), 2.04 (s, 3H, H14). ^{13}C NMR data (75.48 MHz, $CDCl_3$) δ: 150.5 (C6), 148.1 (C6′), 144.8 (C2), 144.2 (C2′), 140.0 (C4), 139.4 (C4′), 130.8 (C3), 130.3 (C3′), 128.1 (C5), 127.6 (C5′), 126.3 (C7), 125.4 (C7′), 142.1, 130.8, 129.8, 128.1 (C_{Ph}), 34.7 (C15). FAB MS found (calcd for $C_{27}H_{28}N_3PdBF_4 - BF_4$): 500 (500).

[(bpy)Pd(C_2H_2C(=N-2,6-$Me_2C_6H_3$)Me)]BF_4 (12): ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 8.99, (d, ^3J = 5.2 Hz, 1H, H6), 8.66 (d, ^3J = 8.0 Hz, 1H, H3), 8.57 (d, ^3J = 8.0 Hz, 1H, H3′), 8.33 (dt, ^3J = 7.9 Hz, ^{4}J = 1.1 Hz, 1H, H4), 8.10 (dt, ^3J = 7.9 Hz, ^{4}J = 1.3 Hz, 1H, H4′), 7.76 (t, ^3J = 6.4 Hz, 1H, H5), 7.66 (d, ^3J = 6.9 Hz, 1H, =CH), 7.32 (m, 3H, H11, H12), 7.08 (t, ^3J = 6.4 Hz, 1H, H5′), 6.30 (d, ^3J = 6.8 Hz, 1H, =CH), 5.91 (d, ^3J = 5.2 Hz, 1H, H6′), 2.26 (s, 6H, H10), 2.02 (s, 3H, H14). ^{13}C NMR data (75.48 MHz, $CDCl_3$) δ: C13 not observed, 155.8 (C2), 154.0 (C2′), 148.7 (C6), 147.2 (C6′), 141.6 (C4), 141.2 (C4′), 127.4 (C5), 126.2 (C5′), 124.7 (C3), 123.8 (C3′), 143.0, 131.5, 129.0, 128.0 (C_{Ph}), 108.6 (C15), 107.7 (C20), 17.8, 17.8, (C_{Me}).

Reaction of Methyl Propiolate with (N⌒N)Pd(C(=N-2,6-$Me_2C_6H_3$)Me)Cl (N⌒N = bpy (1a), phen (1b)) Providing Complexes 13a,b. The complex (N⌒N)Pd(C(=N-2,6-$Me_2C_6H_3$)-Me)Cl (40 mg, 0.090 mmol) and methylpropiolate (2 equiv; 0.18 mmol; 0.18 mg) were dissolved in dichloromethane and stirred for 2 h. The volume of the solution was concentrated to 5 mL, and diethyl ether (30 mL) was added. The crystalline material was collected by centrifugation.

(bpy)Pd[C(=CH_2)N(2,6-$Me_2C_6H_3$)(CH=CHCOOMe)]Cl (13a): Yield: 47 mg; 0.088 mmol; 98%. ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 9.57 (d, ^3J = 13.0 Hz, =CH), 9.30 (d, ^3J = 5.0 Hz, 1H, H6′), 9.20 (d, ^3J = 5.5 Hz, 1H, H6), 8.12 (m, 4H, H4, H4′, H3, H3′), 7.61 (t, ^3J = 5.5 Hz, 1H, H5), 7.52 (t, ^3J = 5.9 Hz, 1H, H5′), 7.15 (d, ^3J = 5.4 Hz, 2H, H11), 7.10 (t, ^3J = 4.6 Hz, 1H, H12), 4.24 (d, ^3J = 13.0 Hz, 1H, =CH), 4.16 (d, ^3J = 2.0 Hz, 1H, =CH_2), 3.81 (d, ^3J = 2.0 Hz, 1H, =CH_2), 3.50 (s, 3H, OMe), 2.18 (s, 6H, H10, 2.30 (s, 6H, H10). ^{13}C NMR data (75.48 MHz, $CDCl_3$) δ: 170.0 (C=O), 156.0 (C2′), 154.6 (C2), 151.9 (C6), 149.4 (C6′), 139.1 (C4), 139.3 (C4′), 127.9 (C5), 127.6 (C5′), 129.3 (C3), 122.5 (C3′), 153.2 (Pd−C=), 152.2 (=*C*H-(COOMe), 138.0, 136.8, 134.4, 126.4, 126.3 (C_{Ph}), 93.4 (H_2C=), 87.4 (CH=), 50.2 (*C*OOMe), 17.7, 17.5 (C_{Me}). FAB MS found (calcd for $C_{24}H_{24}N_3O_2PdCl$): 528 (528).

(phen)Pd[C(=CH_2)N(2,6-$Me_2C_6H_3$)(CH=CHCOOMe)]-Cl (13b): Yield: 47 mg; 0.085 mmol; 95%. ^{1}H NMR data (300 MHz, $CDCl_3$) δ: 9.67 (d, ^3J = 13.0 Hz, 1H, =CH), 9.56 (dd, ^3J = 4.9 Hz, ^{4}J = 1.5 Hz, 1H, H6), 9.46 (dd, ^3J = 5.2 Hz, ^{4}J = 1.2 Hz, 1H, H6′), 8.57 (m,, 2H, H4, H4′), 8.05 (d, ^3J = 8.8 Hz, 1H, H7), 8.00 (d, ^3J = 8.8 Hz, 1H, H7′), 7.94 (dd, ^3J = 8.2 Hz, ^3J = 4.8 Hz, 1H, H5), 7.86 (dd, ^3J = 8.2, ^3J = 4.8 Hz, 1H, H5′), 7.17 (d, ^3J = 5.4 Hz, 2H, H11), 7.12 (t, ^3J = 5.4 Hz, 1H, H12), 4.28 (d, ^3J = 13.0 Hz, 1H, =CH), 4.25 (d, ^3J = 2.0 Hz, 1H, =CH_2), 3.88 (d, ^3J = 2.0 Hz, 1H, =CH_2), 3.50 (s, 3H, OMe), 2.34 (s, 6H, H10), 2.24 (s, 6H, H10). A ^{13}C NMR spectrum could not be obtained because of solubility problems. Elemental analysis found (calcd for $C_{26}H_{24}N_3O_2PdCl\cdot{}^1/_2CH_2Cl_2$): C, 54.11 (53.51); H, 4.55 (4.24); N, 6.86 (7.06). FAB MS found (calcd for $C_{26}H_{24}N_3O_2PdCl$): 552 (552).

Crystal Structure Determination and Refinement of 10b and 13a. Crystals of **10b** and **13a** were mounted on a Lindemann glass capillary and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-Turbo diffractometer on a rotating anode. Accurate unit cell parameters and an orientation matrix were determined by least-squares fitting of the setting angles of 25 well-centered reflections (set 4)[31] in the range 11.52° < θ < 14.04° and 5.47° < θ < 15.47°, for 10b and **13a**, respectively. Reduced cell calculations did not indicate higher lattice symmetry.[32] Crystal data and details on data collection and refinement are given in Table 1. Data were corrected for *Lp* effects and the observed linear decay. Data were not corrected for absorption for **10b**. An empirical absorption/extinction correction was applied (DIFABS[33] as implemented in PLATON)[34] to **13a** (transmission range 0.145−1.000).

The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92).[35] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93);[36] no observance criterion was applied during refinement. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier

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(32) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.
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Table 1. Crystal and Refinement Data for [(phen)Pd(C_3H_6C(=N-2,6-$Me_2C_6H_3$)Me)]BF_4 (10b) and (bpy)Pd[C(=CH_2)N(2,6-$Me_2C_6H_3$)(CH=CHCOOMe)]Cl (13a)

	10a	13b
	Crystal Data	
formula	$C_{25}H_{26}N_3Pd\cdot BF_4\cdot CH_2Cl_2$	$C_{24}H_{24}ClN_3O_2Pd$
mol wt	646.66	528.35
crystal system	orthorhombic	triclinic
space group	P*bca* (No. 61)	$P\bar{1}$ (No. 2)
a, Å	11.6278(9)	8.659(4)
b, Å	20.978(2)	9.098(8)
c, Å	21.768(2)	15.137(14)
α, deg		92.74(8)
β, deg		102.33(5)
γ, deg		104.12(6)
V, Å^3	5309.9(7)	1123.5(15)
D_{calc}, g cm^{-3}	1.618	1.562
Z	8	2
F (000)	2608	536
μ, cm^{-1}	9.5	9.7
crystal size, mm	0.15 × 0.45 × 0.50	0.05 × 0.20 × 0.30
	Data Collection	
T, K	150	150
θ_{min}, θ_{max} deg	1.9, 27.5	1.4, 23.0
wavelength (Mo Kα) Å	0.710 73 graphite monochromator	0.710 73 graphite monochromator
scan type	*ω*	*ω*
Δ*ω*, deg	0.66 + 0.35 tan *θ*	0.90 + 0.35 tan *θ*
Hor, vert aperture, mm	2.18 + 1.09 tan *θ*, 4.00	3.00, 4.00
X-ray exposure time, h	17.9	17.9
linear decay, %	2	1
reference reflections	$\bar{1}\,\bar{2}\,\bar{6}$, $\bar{1}\,\bar{5}\,2$, $\bar{2}\,\bar{1}\,5$	$\bar{4}\,1\,1$
data set (*hkl*)	−15:0, −27:25, 0:28	−9:0, −9:9, −16:16
no. of total data	10627	3355
no. of total unique data	6072	3112
R_{int}	0.0470	0.1536
DIFABS transm. range		0.145−1.000
	Refinement	
No. of refined parameters	338	279
$wR2^a$	0.1391	0.2620
R^b	0.0558 [for 3845 $F_o > 4\sigma(Fo)$]	0.0945 [for 1783 $F_o > 4\sigma(Fo)$]
S	1.06	1.03
w^{-1c}	$\sigma^2(F^2) + (0.0608P)^2$	$\sigma^2(F^2) + (0.1000P)^2$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.000, 0.000	0.001, 0.000
min and max *ρ*, e Å^{-3}	−0.62, 1.15 (near Pd)	−1.22, 1.50 (near Pd)

[a] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$. [b] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [c] $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic displacement parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms by a factor of 1.5 for the methyl hydrogen atoms and 1.2 for the other hydrogen atoms, respectively. Weights were introduced in the final refinement cycles for **10b** but not **13a**. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 37. Geometrical calculations and illustrations were performed with PLATON.[34] All calculations were performed on a DECstation 5000/133.

Kinetic Measurements. The reaction rates were obtained spectrophotometrically by repetitive scanning of the spectrum at that wavelength, at which the difference in absorbance of product and educt was largest. Norbornadiene was added to a prethermostated solution of the palladium complex in the appropriate solvent in a 1 cm quartz cell. The UV spectra were recorded on a Perkin-Elmer Lambda 5 spectrometer, and the solution was thermostated by a MGW Lauda K4R electronic with a temperature accuracy of 0.5 °C.

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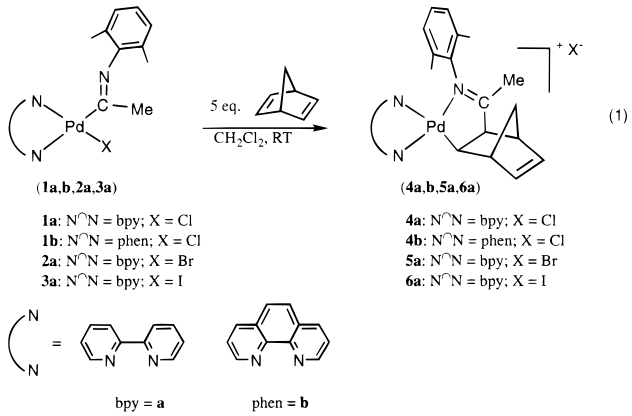
(36) Sheldrick, G. M. SHELXL-93 Program for crystal structure refinement. University of Göttingen, Germany 1993.

(37) Wilson, A. J. C. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.

Results and Discussion

Insertion of Alkenes into Pd−C(=NR)Me Bonds. Reaction of the neutral carboimine complexes (N⌒N)-Pd(C(=N-2,6-$Me_2C_6H_3$)Me)X (**1a**, N⌒N = 2,2′-bipyridine (bpy), X = Cl; **1b**, N⌒N = 1,10-phenanthroline (phen), X = Cl; **2a**, N⌒N = bpy, X = Br, **3a**: N⌒N = bpy; X = I) with excess norbornadiene afforded the insertion products [(N⌒N)Pd(C_7H_8C(=N-2,6-$Me_2C_6H_3$)Me)]X (**4a**, N⌒N = bpy, X = Cl; **4b**, N⌒N = phen, X = Cl; **5a**, N⌒N = bpy, X = Br; **6a**, N⌒N = bpy, X = I) (see eq 1).



(1)

The conversion of the complexes **1a**, **1b**, **2a**, and **3a** to the products **4a**, **4b**, **5a**, and **6a** was quantitative within 30 min for **1a**, **2a**, and **3a** and 16 h for **1b** at 293 K, when 5 equiv of the alkene was added to a solution of the starting complex in dichloromethane. The insertion goes to completion upon addition of 1 equiv of norbornadiene, but the reaction rate is much lower. Insertion of norbornadiene into the Pd−C bond of complex (N⌒N)Pd(C(=N-*t*-Bu)Me)Cl (N⌒N = bpy, phen) led to the formation of several uncharacterized side products beside the expected insertion product, while complex (N⌒N)Pd(C(=NCH$_2$tosyl)Me)Cl (N⌒N = bpy, phen) did not react with norbornadiene even after several days in dichloromethane.

In complexes **4a**, **4b**, **5a**, and **6a**, the nitrogen atom of the carboimine group is coordinated to the palladium forming a five-membered palladacycle, as could be inferred from the high equivalent conductance measured in acetonitrile for the mentioned complexes of about 140 Ω^{-1} cm^2 mol^{-1}, when compared to the conductance for (bpy)Pd(Me)Cl of 4 Ω^{-1} cm^2 mol^{-1} and for **1a** of 3 Ω^{-1} cm^2 mol^{-1}. The products **4ab**, **5a**, and **6a** are very stable when compared to the acetyl analogues [(bpy)Pd(C$_7$H$_8$C(O)Me)]Cl[12] and [(Ar-BIAN)Pd(C$_7$H$_8$(C(O)Me)]Cl,[11] which can be ascribed to the strong coordination of the imine nitrogen to the palladium center, preventing decomposition of the complex via β-H elimination.

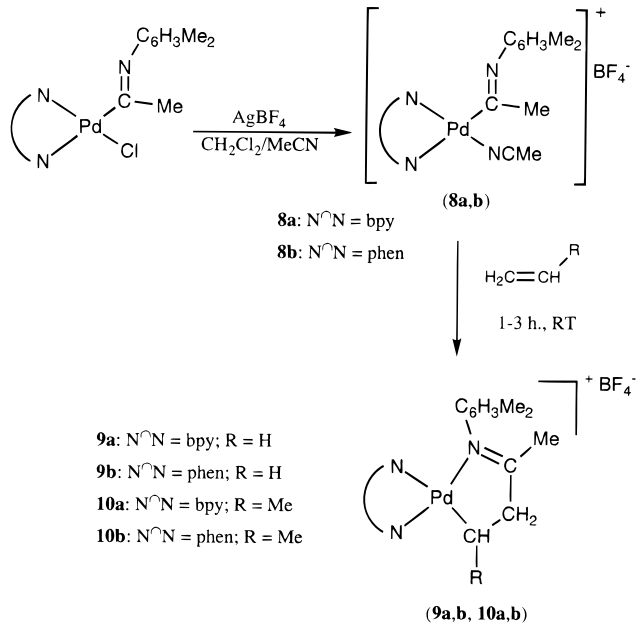
An interesting reaction is the insertion of norbornene into the Pd−C bond of the neutral complexes **1a** and **1b** in dichloromethane leading to a quantitative formation of the complexes [(N⌒N)Pd(C$_7$H$_{10}$C(=N-2,6-Me$_2$C$_6$H$_3$)Me)]Cl (N⌒N = bpy (**7a**), phen (**7b**)). Insertion of norbornene is much slower than insertion of norbornadiene and goes to completion within 16 h and several days for complexes **1a** and **1b**, respectively, while the reaction of (bpy)Pd(C(O)Me)Cl with norbornene resulted in only 16% conversion of the starting complex.[12] Probably, the coordination of the imine nitrogen to the palladium center of the products **7a** and **7b** causes the reaction to go to completion.

The complexes **1a** and **1b** did not react with ethylene and propylene in dichloromethane. However, the ionic complexes [(bpy)Pd(C(=N-2,6-Me$_2$C$_6$H$_3$)Me)(NCMe)]BF$_4$ (**8a**) and [(phen)Pd(C(=N-2,6-Me$_2$C$_6$H$_3$)Me)(NCMe)]BF$_4$ (**8b**), prepared *in situ* by reaction with AgBF$_4$ in the presence of acetonitrile, readily underwent insertion of ethylene and propylene to form the insertion products as shown in Scheme 1.

The insertion products [(N⌒N)Pd(C$_2$H$_4$C(=N-2,6-Me$_2$C$_6$H$_3$)Me)]BF$_4$ (N⌒N = bpy (**9a**), phen (**9b**)) and [(N⌒N)Pd(C$_3$H$_6$C(=N-2,6-Me$_2$C$_6$H$_3$)Me)]BF$_4$ (N⌒N = bpy (**10a**), phen (**10b**)) are formed within 1−3 h, when stirred under alkene atmosphere in 57−69% yield. The insertion of ethylene appeared to be about twice as fast as the insertion of propylene. Remarkable is that the products **9a**,**b** and **10**,**b** are stable for several days in solution at low temperature (273 K) and for several days in crystalline form at room temperature.

It is known that insertions of unactivated alkenes like ethylene and propylene do not occur in neutral complexes such as (L⌒L)Pd(R)X (X = halide), while in ionic complexes (X = solvent) where they do occur the products are susceptible to β-hydrogen elimination, as was shown for insertion reactions of unstrained alkenes

Scheme 1



with [(bpy)Pd(C(O)Me)(CH$_3$CN)]OTf.[12] Therefore, the products **9a**,**b** and **10a**,**b** can be considered as very rare examples of isolable products resulting from insertion of ethylene and propylene.[13,28]

Insertion of isocyanide into the Pd−C bond of the complexes **4a**,**b**, **5a**, and **6a** would be the next step in a co-oligomerization of isocyanides and alkenes. However, addition of the isocyanide DIC to these complexes in dichloromethane or in acetonitrile results in immediate substitution of the bidentate nitrogen ligand by the isocyanide. Insertion of an isocyanide needs initial precoordination to the palladium center, which is inhibited by the strongly coordinated imine nitrogen.

Characterization of the Products Obtained by Alkene Insertion. The products **4a**,**b**, **5a**, **6a**, **7a**,**b**, **9a**,**b**, and **10a**,**b** have been characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectroscopy, and/or elemental analyses, while an X-ray structure determination has been carried out for complex **10b**. The ^{1}H NMR spectra of the complexes **4a**,**b**, **5a**, **6a**, and **7a**,**b** showed the formation of only one isomer, *viz*. the *cis* addition of Pd−(C(=NR)Me) to the *exo* face of the alkene, as could be concluded from the coupling constants ^3J(H15−H20) which are around 6.2 Hz.[11,12,23,38] The ^{1}H NMR spectra of the complexes **4a**,**b**, **5a**, and **6a** showed a well-defined pattern for the inserted alkene with the remaining alkene protons H17 and H18 of the inserted norbornadiene at around 6.3 ppm.

A remarkable aspect of the ^{1}H NMR spectrum of the products **4a**,**b**, **5a**, **6a**, **7a**,**b**, **9a**,**b**, and **10a**,**b** is the high-field shift of the *ortho* proton H6′ adjacent to the nitrogen of the bpy and phen ligands, which can be observed at 5.8 ppm for bpy and at 6.0 ppm for phen, while normally these signals appear around 8.5 ppm. This high-field shift can be explained by the close proximity of the Me$_2$C$_6$H$_3$ group to the *ortho* proton H6′ caused by the coordination of the carboimine group to the palladium center, as is also clear from the molecular structure of [(phen)Pd(C$_3$H$_6$C(=N-2,6-Me$_2$C$_6$H$_3$)Me)]BF$_4$

(38) Groen, J. H.; Elsevier, C. J.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1996**, *15*, 3445−3455.

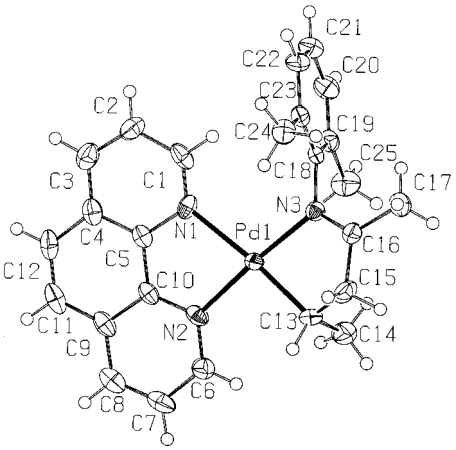


Figure 1. ORTEP plot[34] at 50% probability level of complex [(phen)Pd(C_3H_6C(=N-2,6-$Me_2C_6H_3$)Me)]BF_4 (**10b**).

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for [(phen)Pd(C_3H_6C(=N-2,6-$Me_2C_6H_3$)Me)]BF_4 (10b)[a]

bond distances (Å)		bond angles (deg)	
Pd−N(1)	2.177(4)	N(1)−Pd−N(2)	79.80(15)
Pd−N(2)	2.053(4)	N(1)−Pd−N(3)	103.66(15)
Pd−N(3)	2.049(4)	N(2)−Pd−C(13)	95.95(18)
Pd−C(13)	2.024(4)	N(3)−Pd−C(13)	80.75(19)
N(3)−C(16)	1.276(6)	Pd−N(3)−C(16)	115.5(3)
N(3)−C(18)	1.433(6)	Pd−C(13)−C(15)	106.1(3)
C(13)−C(14)	1.513(9)	N(3)−C(16)−C(15)	115.6(4)
C(13)−C(15)	1.515(7)	N(3)−C(16)−C(17)	125.1(5)
C(15)−C(16)	1.493(7)	C(16)−N(3)−C(18)	122.7(4)
C(16)−C(17)	1.493(8)	Pd−C(13)−C(14)	111.0(4)
		C(13)−C(15)−C(16)	110.2(4)
		C(15)−C(16)−C(17)	119.3(4)

[a] Esd's in parentheses.

(**10b**) (*vide infra*). Coordination of the carboimine group could not be inferred from IR spectrometry since the C=N stretch frequencies of the alkene insertion products were obscured by those of the bidentate nitrogen ligand. The C=N ^{13}C signal of the products **4a**,**b**, **5a**, **6a**, **7a**,**b**, **9a**,**b**, and **10a**,**b** can be observed at around 198 ppm, which is, as expected,[11,12,38] about 15 ppm higher than that of the starting complexes **1a** and **1b**.

The ^1H NMR spectrum of the propylene insertion products **10a** and **10b** exhibited the formation of only one isomer (see Scheme 1).

Molecular Structure of [(phen)Pd(C_3H_6C(=N-2,6-$Me_2C_6H_3$)Me)]BF_4 (10b). Crystals of complex **10b** suitable for an X-ray structure determination were obtained from slow diffusion of hexane in a solution of the complex in dichloromethane. The molecular structure is presented in Figure 1, and selected bond lengths and bond angles are collected in Table 2.

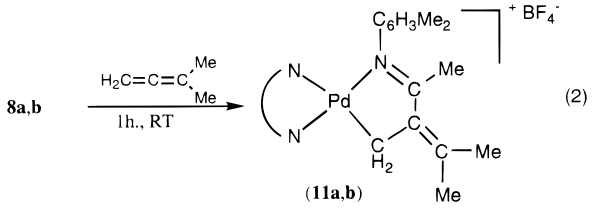
The structure of complex **10b** shows bidentate coordination of phenanthroline to the square planar palladium center with N(3) of the imine group and the chiral carbon atom C(13) of the secondary alkyl group completing the coordination plane. Due to coordination of N(3) (Pd−N(3) = 2.049(4) Å), the $Me_2C_6H_3$ group is in close proximity of C(1) of phenanthroline. The plane of the $Me_2C_6H_3$ group is orientated orthogonally to the coordination plane of palladium.

Both enantiomers are present in the crystal (lattice group P*bca*).

The Pd−N(1) bond distance of 2.177(4) Å is longer than the Pd−N(2) distance of 2.053(4) Å, showing that C(13) has a larger *trans* influence than N(3) of the imine group. The Pd−C(13) bond distance of 2.024(4) Å is comparable to other Pd−C(sp^3) bond distances *trans* to a Pd−N(sp^2) bond.[12,39−41] The bite angle N(1)−Pd−N(2) is 79.80(15)°, which is normal for (N⁀N)Pd(II) complexes containing bpy or phen ligands.[11,12,29,42]

It is clear from the molecular structure that propylene exclusively inserts via a 2,1-insertion. Hydrocarbonylation reactions of propylene[3] catalyzed by ($R_2P(CH_2)_3PR_2$)Pd(II) complexes and a study on enantioselective copolymerization of propylene and CO,[43] however, demonstrated that insertion of propylene into the Pd−acyl bond in these cases is preferentially 1,2 and larger R groups on the phosphine enhance this preference. The 2,1-insertion reaction of propylene with complexes **8a**,**b** might therefore be rationalized by the low steric bulk of the bpy and phen ligands and the large steric bulk of the C(=N-2,6-$Me_2C_6H_3$)Me group.

Insertion of Allenes into Pd−C(=NR)Me Bonds. Upon reaction of 3-methyl-1,2-butadiene with the neutral complexes **1a** and **1b** in dichloromethane, several uncharacterized products were obtained. Reaction of 3-methyl-1,2-butadiene with the ionic complexes **8a** and **8b**, however, resulted in the quantitative formation of [(bpy)Pd(C_5H_8C(=N-2,6-$Me_2C_6H_3$)Me)]BF_4 (**11a**), and [(phen)Pd(C_5H_8C(=N-2,6-$Me_2C_6H_3$)Me)]BF_4 (**11b**) respectively, as shown in eq 2.



(2)

These products are stable for several days in solution and can be stored under an atmosphere of nitrogen in crystalline form for several weeks without decomposition. They were characterized by ^1H and ^{13}C NMR and mass spectroscopy and/or by elemental analysis.

Analogous to the alkene-inserted products **4a**,**b**, **5a**, **6a**, **7a**,**b**, **9a**,**b**, and **10a**,**b**, the nitrogen of the carboimine group is coordinated to the metal center, which could be concluded from the high-field shift of the *ortho* proton H6′ of bpy and phen.

Reactions of Carboimine Complexes with Alkynes. Acetylene does not react with the neutral complexes **1a** and **1b**, but a very fast mono insertion into the Pd−C bond of the ionic complex **8a** occurs in dichloromethane leading to [(bpy)Pd(C_2H_2C(=N-2,6-$Me_2C_6H_3$)Me)]BF_4 (**12a**) (see eq 3). In several cases, double insertion of alkynes prevails over monoinsertion.[44−46] We may explain the monoinsertion by the strong coordination of the imine nitrogen atom to the

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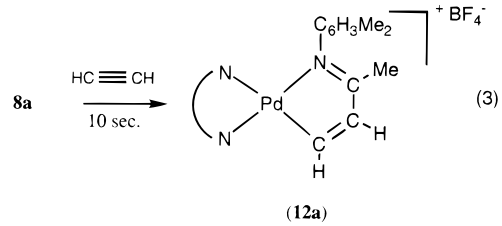
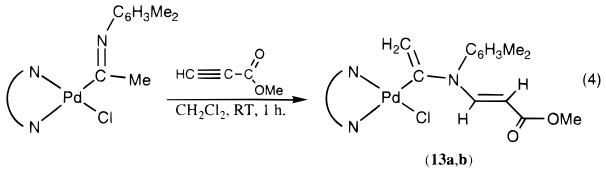


palladium center preventing precoordination of another equivalent of acetylene.

Unfortunately, the product **12a** is relatively unstable as compared to the alkene and allene insertion products mentioned above. Decomposition of the complex occurs within several hours in solution. Therefore, complex **12a** could be characterized by ^{1}H NMR spectroscopy only, showing two doublets for the alkenyl fragment at 7.66 and 6.30 ppm with a coupling constant of $^3J_{H-H}$ = 6.8 Hz between the two olefinic protons, characteristic of a *cis* configuration of the alkenyl fragment. It should be mentioned that reaction of acetylene with the cationic complex **8b** containing phenanthroline did not lead to formation of any stable or characterizable product.

Unexpectedly, the neutral complexes **1a** and **1b** reacted with methylpropiolate to give (bpy)Pd[C(=CH_2)N(2,6-$Me_2C_6H_3$)(CH=CHCOOMe)]Cl (**13a**) and (phen)Pd[C(=CH_2)N(2,6-$Me_2C_6H_3$)(CH=CHCOOMe)]Cl (**13b**) within 1 h, as shown in eq 4, instead of giving insertion



products.

These compounds are very stable and could be analyzed by ^{1}H and ^{13}C NMR, mass spectroscopy and/or elemental analysis, while an X-ray structure determination has been carried out for complex **13a**. The ^{1}H NMR spectrum showed the hydrogen atoms of the NCH=CHCOO fragment around 9.6 and 4.3 ppm with a coupling constant of $^3J_{H-H}$ = 13.1 Hz between the olefinic protons characteristic of a *trans* configuration of the olefin. The bpy and phen proton signals appear at values normally observed for (N⁀N)Pd(II) complexes.[29,41,42] Reaction of **1a**,**b** with MeO_2CCO_2Me (DMDCA) and **8a**,**b** with methylpropiolate and DMDCA resulted in formation of several uncharacterizable products.

The formation of complexes **13a** and **13b** can be explained by a mechanism involving initial imine−enamine tautomerism followed by a Michael addition of N−H to the α,*β*-unsaturated ester methylpropiolate (see Scheme 2).

Such an imine−enamine tautomerism also occurs in a reaction of *trans*-Pd(C(=N-C_6H_4-*p*-Me)Me)Cl(PEt_3)$_2$ with $MeO_2C{\equiv}CO_2Me$ (DMDCA).[47] Since we do not see any signal of the enamine complexes in the ^{1}H NMR spectrum of **1a** and **1b**, we may conclude that the equilibrium of the imine−enamine tautomerism lies

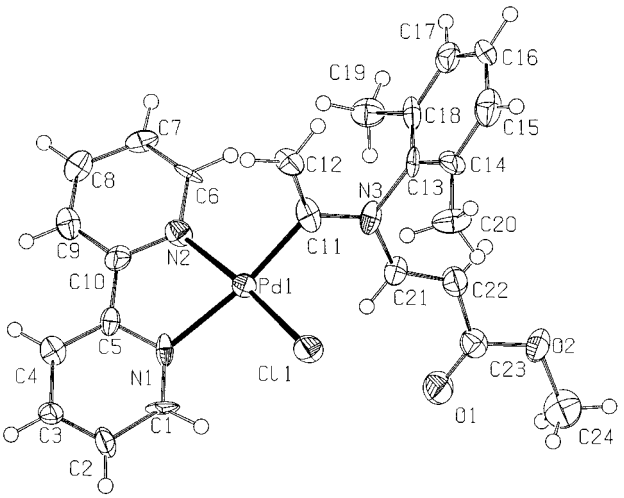
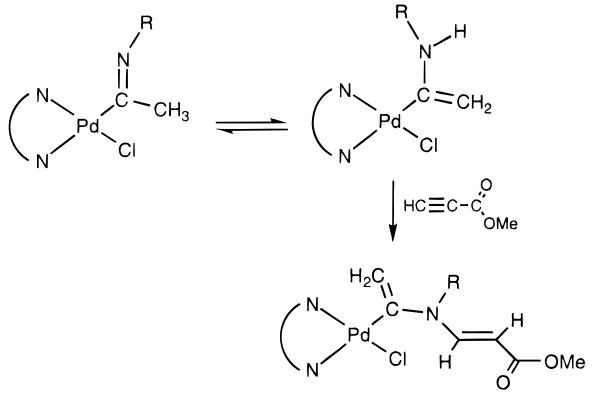
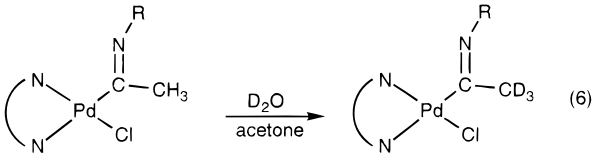


Figure 2. ORTEP plot[34] at 50% probability level of complex (bpy)Pd[C(=CH_2)N(2,6-$Me_2C_6H_3$)(CH=CHCOOMe)]-Cl (**13a**).

Scheme 2



close to the imine complex. We have obtained proof for the tautomerism in complex **1a** in a reaction with D_2O, since, when **1a** was stirred in acetone with excess D_2O, the methyl group on the imine carbon was quantitatively deuterated within 1 h (see eq 5).



Molecular Structure of (bpy)Pd[C(=CH_2)N(2,6-$Me_2C_6H_3$)(CH=CHCOOMe)]Cl (13a). Crystals of complex **13a** suitable for X-ray structure determination were obtained by slow diffusion of hexane into a solution of the complex in dichloromethane. The molecular structure of complex **13a** is presented in Figure 2, while selected bond lengths and bond angles have been collected in Table 3.

This structure displays a square planar surrounding of the palladium atom by a bidentate coordinated bpy ligand, the chloride atom and by carbon C(11). The Pd−N(1) distance of 2.125(14) Å is longer than the Pd−N(2) distance of 2.023(15) Å because of the higher *trans* influence of carbon C(11) with respect to the chloride atom.[48] The Pd−C(11) distance of 1.990(18) Å is comparable to other Pd−C(sp^2) bond distances of (N⁀N)-Pd(II) complexes.[42]

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Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for (bpy)Pd[C(=CH_2)N(2,6-$Me_2C_6H_3$)-(CH=CHCOOMe)]Cl (13a)[a]

bond distances (Å)		bond angles (deg)	
Pd−Cl	2.309(5)	Cl−Pd−N(1)	96.6(5)
Pd−N(1)	2.125(14)	Cl−Pd−C(11)	87.9(5)
Pd−N(2)	2.023(15)	N(1)−Pd−N(2)	78.1(6)
Pd−C(11)	1.990(18)	N(2)−Pd−C(11)	96.7(7)
C(11)−C(12)	1.32(2)	C(12)−C(11)−N(3)	119.6(16)
N(3)−C(11)	1.40(2)	C(11)−N(3)−C(21)	123.9(15)
N(3)−C(13)	1.47(2)	N(3)−C(21)−C(22)	130.0(16)
N(3)−C(21)	1.36(2)	C(21)−C(22)−C(23)	122.1(17)
C(21)−C(22)	1.34(2)		

[a] Esd's in Parentheses.

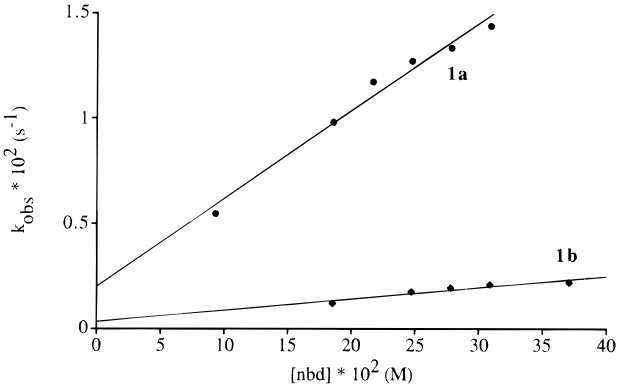

Figure 3. Dependence of the pseudo-first-order rate constants k_{obs} on the norbornadiene concentration for the reaction of complexes **1a** and **1b** with norbornadiene in CH_3CN at 304 K ([Pd] = 0.375 mM).

Kinetic Measurements of Norbornadiene Insertion. The kinetics of the norbornadiene insertion into the Pd−C bond of **1a**, **1b**, **2a**, and **3a** as shown in eq 1 were studied by monitoring the absorption in the range of 360−620 nm as a function of time in a UV−visible spectrometer. All reactions were carried out with a large excess (at least 10-fold) of norbornadiene as compared to the metal complex, i.e., under pseudo-first-order conditions. The conversion of the starting complexes is quantitative under these conditions, and in all cases, isosbestic points were obtained. The reaction rates k_{obs} (s^{-1}) were calculated from the slope of the plots $\ln\{(A_t - A_\infty)/A_0 - A_\infty)\}$ vs time. All reactions were found to be first order in the concentration of the metal complex for at least three half-lifes when the reaction was performed in acetonitrile, while, unfortunately, in dichloromethane no straight lines were obtained in a first-order plot. In fact, the rate of the reaction in dichloromethane increases during the reaction time, which may be ascribed to an increase of the polarity of the reaction mixture caused by formation of ionic insertion products. It should be mentioned that the reaction in the polar solvent acetonitrile is faster than in dichloromethane.

The pseudo-first-order rate constants k_{obs} gave straight lines when plotted against the concentration of norbornadiene with a nonzero intercept with the *y*-axis (see Figure 3), indicating that the usual[25,26] rate eq $k_{obs} = k_1 + k_2$[nbd] is obeyed. The reaction of norbornadiene with complex **1b** containing phen appeared to be much slower than the reaction with complex **1a** containing bpy (Figure 3). Therefore, we have only carried out kinetic measurements for the reaction of complex **1b** with nbd at 304 K. The rate constants k_1 and k_2 for reactions of the complexes **1a**, **1b**, **2a**, and **3a**, along with the values of the parameters of activation $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for reaction of complex **1a**, determined from the values of k_1 and k_2 measured in the temperature range of 293−304 K, have been collected in Table 4.

Table 4. Rate Constants k_1 and k_2 and the Enthalpy and Entropy of Activation for Reaction of Complexes (N⌒N)Pd(C(=N-2,6-$Me_2C_6H_3$)Me)Cl with Norbornadiene

N⌒N	X	T (K)	$k_1 \times 10^2$ (s^{-1})	$k_2 \times 10^2$ ($M^{-1}\,s^{-1}$)	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J $K^{-1}\,mol^{-1}$)
bpy (**1a**)	Cl	293.0	0.07(2)	1.68(8)		
		298.0	0.10(4)	2.58(18)	k_1 70.2(6.2)	k_1 −66(21)
		302.0	0.11(3)	3.30(14)	k_2 56.8(3.8)	k_2 −85(13)
		304.0	0.20(7)	4.18(31)		
phen (**1b**)	Cl	304.0	0.02(1)	0.56(4)		
bpy (**2a**)	Br	304.0	0.94(9)	7.89(42)		
bpy (**3a**)	I	304.0	1.58(23)	15.8(10)		

[a] Esd's in parentheses. Conditions: acetonitrile solvent; [Pd] = 0.375 mM.

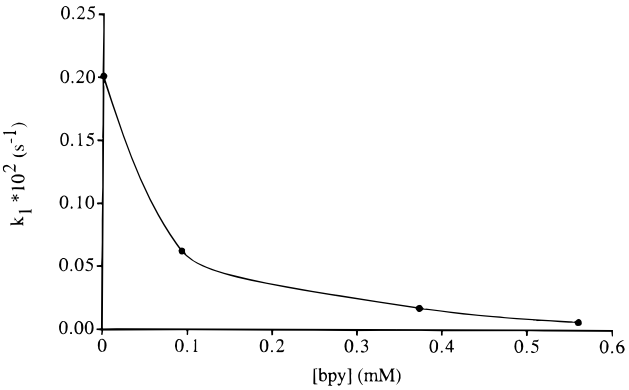

Figure 4. Effect of the concentration of excess bpy on the rate constant k_1 of the reaction of norbornadiene with **1a** in CH_3CN at 304 K ([Pd] = 0.375 mM).

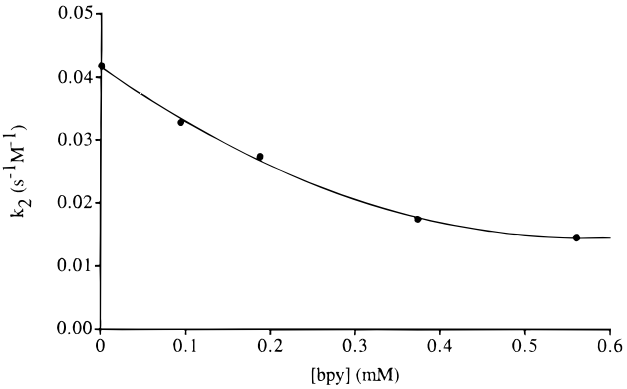

Figure 5. Effect of the concentration of excess bpy on the rate constant k_2 of the reaction of norbornadiene with **1a** in CH_3CN at 304 K ([Pd] = 0.375 mM).

The value for k_1 and k_2 for the reaction of (bpy)Pd(C(=N-2,6-$Me_2C_6H_3$)X (X = Cl (**1a**), Br (**2a**), I (**3a**)) with norbornadiene measured at 31 °C in acetonitrile increases in the order X = Cl < Br < I. However, the variations in the values for both k_1 and k_2 are relatively small.

Influence of Excess Free Bidentate Nitrogen Ligand and Chloride. In Figures 4 and 5, the influence of addition of excess free bpy to **1a** on the value of k_1 and k_2, respectively, is displayed. Interestingly,

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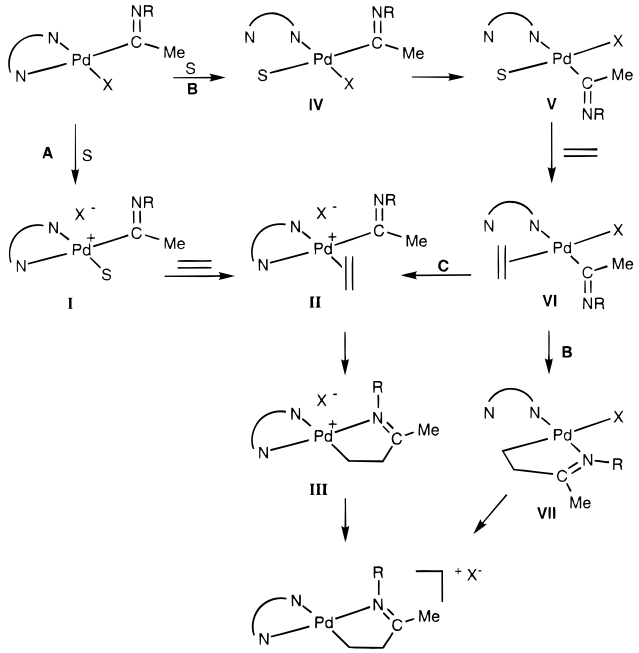
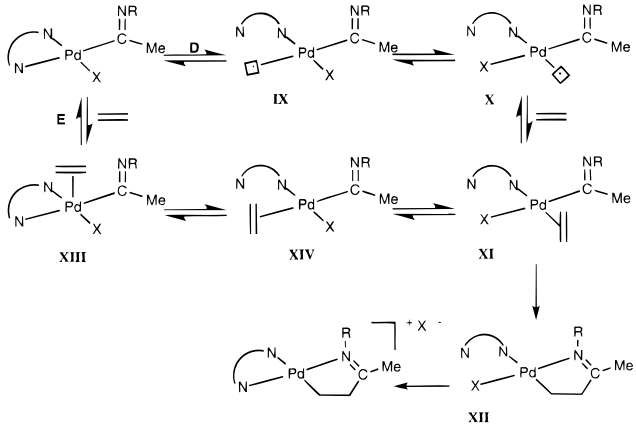
Scheme 3. Possible Routes for the Norbornadiene-Independent k_1 Pathway



Scheme 4. Possible Routes for the Norbornadiene-Dependent k_2 Pathway



the norbornadiene-independent pathway with rate constant k_1 is strongly retarded by addition of excess bpy. The value for k_1 decreases from 0.20×10^{-2} s^{-1} without excess ligand to 0.0064×10^{-2} s^{-1} with 1.5 equiv of excess ligand. This result is comparable to that obtained for the reaction of norbornadiene with (*p*-An-BIAN)Pd(C(O)Me)Cl.[25] Unexpectedly, the norbornadiene-dependent pathway with a rate constant k_2 is also retarded by excess ligand. The value for k_2 decreases from 0.042 M^{-1} s^{-1} without excess ligand to 0.015 M^{-1} s^{-1} with 1.5 equiv of excess ligand. It should be noted that the value of k_2 in the case of reaction of (*p*-An-BIAN)Pd(C(O)Me)Cl with norbornadiene appeared to be hardly affected by excess ligand.[25]

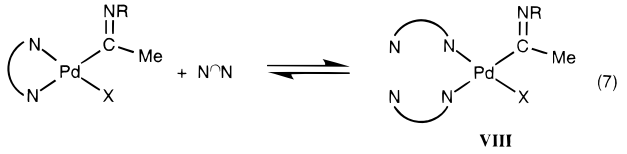
Addition of excess Cl$^-$ in the form of NEt_4Cl, while the ionic strength is maintained constant by addition of NEt_4OTf, influenced neither the value for k_1 nor for k_2. This has also been observed for the reaction of (*p*-An-BIAN)Pd(C(O)Me)Cl with norbornadiene.[25]

Mechanism of the Norbornadiene Insertion. From the kinetic measurements, it is clear that the norbornadiene insertion reaction with **1a**, **1b**, **2a**, and **3a** proceeds via two pathways: one that is independent of the norbornadiene concentration with a rate constant k_1 and one that is linearly dependent on the norbornadiene concentration with a rate constant k_2.

Alkene-Independent k_1 Pathway. For the reaction of (Ar-BIAN)Pd(C(O)R)X with norbornadiene we have recently reported the possible pathways A, B, and C (see Scheme 3),[25] involving a rate determining Pd−solvent bond-making reaction, which is more important than Pd−X bond breaking (pathway A) or Pd−N bond breaking (pathways B and C).

Pathways A, B, and C are in agreement with the absence of mass law retardation by halide ions and the small influence of the nature of the coordinated halide on the reaction rate.

The retardation of the k_1 pathway upon addition of free ligand may be explained by substitution of the weakly coordinating solvent molecule in intermediate **I**, **IV**, or **V** by free ligand, providing a species containing two nitrogen ligands coordinated in a monodentate way. Actually, we have observed the formation of a new complex in the ^{1}H NMR spectrum of a mixture of complex **1a** or **1b** and 1 equiv of free bpy or phen, respectively, in $CDCl_3$ at 230 K, which is most likely species **VIII** containing two nitrogen ligands (eq 6).



(7)

Since substitution of one of these ligands by norbornadiene in species **VIII** can be expected to be more difficult than substitution of a solvent molecule of species **I**, **IV**, or **V**, an apparent decrease of the value of k_1 might be observed.

Alkene-Dependent k_2 Pathway. The alkene-dependent k_2 pathway might occur either via an initial alkene association affording a square-pyramidal intermediate **XIII** (Scheme 4, pathway E), as we have previously reported for the norbornadiene insertion reaction in (Ar-BIAN)Pd(C(O)R)X[25] complexes, or via initial nitrogen dissociation (intermediate **IX**, pathway D), as we have recently proposed for the allene insertion reaction with (N⌒N)Pd(R)X complexes.[26]

Pathway D for the insertion into the Pd−carboimine bond seems most likely, since nitrogen donor atom site exchange in (N⌒N)Pd(C(=NR)Me)Cl complexes (N⌒N = bpy, phen, 2,2′-bipyrimidine; R = *t*-Bu, tosylmethyl) also involves Pd−N bond breaking.[29] Furthermore, kinetic measurements[29] showed that the exchange process is much faster (k_{obs} is ca. 0.5 s^{-1} at 303 K) than the norbornadiene insertion ($k_{obs} = 1.18 \times 10^{-2}$ s^{-1} at 304 K, [nbd] = 0.216 M, **1a**). A mechanism involving Pd−X bond breaking before or during the rate-determining step is not likely, since the difference in the value for k_2 of complexes **1a** (X = Cl), **2a** (X = Br), and **3a** (X = I) is not very large. Moreover, no mass law retardation upon addition of free halide is observed.

The retardation of the k_2 pathway upon addition of excess free ligand might be explained by coordination of the extra ligand instead of norbornadiene on the vacant site of intermediate **IX** or **X** leading to less reactive species. The observation that (N⌒N)Pd(C(=N-CH_2tosyl)Me)Cl (N⌒N = bpy, phen) does not react with

norbornadiene is consistent with a rate-determining migratory insertion step, as has also been proposed for the allene[29] and norbornadiene[25] insertion reactions. It is known that electron-withdrawing groups on a migrating R group (in this case the tosylmethyl group) retard migration, while electron-donating groups accelerate migration.[25,26,49−52]

In this study, we were able to study the influence of the flexibility of the ligand on the rate of norbornadiene insertion, while we have previously employed only the very rigid Ar-BIAN ligand.[25] From the results it is clear that the value for k_2 of complex **1a** ($4.18(31) \times 10^{-2}$ M^{-1} s^{-1}) containing the flexible ligand bpy is much larger than that of complex **1b** ($0.56(4) \times 10^{-2}$ M^{-1} s^{-1}) containing the very rigid ligand phenanthroline. One may imagine that the intermediates containing monodentate ligands such as **IX**, **X**, and **XI** are more readily formed for flexible ligands such as bpy than for rigid ligands such as phen, for which the dissociated nitrogen must stay in close proximity of the metal center.

Conclusion

The neutral and cationic (N⌒N)Pd(C(═NR)Me)X complexes undergo facile and quantitative insertion of strained and unstrained alkenes, allenes, and alkynes to give in most cases remarkably stable products. Unfortunately, we have not succeeded in direct formation of the polyimine analogue of polyketone. Nonetheless, we have been able to demonstrate the existence of the first two steps, i.e., isocyanide insertion into the Pd−C bond[29] and alkene insertion into the Pd−carboimine bond. Further insertions on the road to polyimine fragments do not occur owing to the strong coordination of the carboimine nitrogen to the metal center.

A kinetic study on the norbornadiene insertion reaction in (N⌒N)Pd(C(═NR)Me)X complexes showed that the reaction involves two pathways, one of which is independent and one dependent on the norbornadiene concentration. The alkene concentration-independent pathway may proceed via a rate-determining solvent-assisted halide or nitrogen dissociation, followed by alkene association and migratory insertion, while the alkene concentration-dependent pathway may occur via initial dissociation of a nitrogen donor followed by alkene association and a rate-determining migratory insertion.

Acknowledgment. Professor Dr E. Drent and Dr W. P. Mul (Koninklijke/Shell-Laboratorium, Amsterdam) are acknowledged for their helpful discussions and Shell Research BV for financial support. This work was supported in part (N.V. and A.L.S.) by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO). We thank J.-M. Ernsting for NMR spectroscopy assistance and R. H. Fokkens and J. W. H. Peeters for mass spectroscopy.

Supporting Information Available: Further details of the structure determinations, including tables of atomic coordinates, bond lengths and angles, and thermal parameters for **10b** and **13a** and the measured k_{obs}'s of all the kinetic reactions (17 pages). Ordering information is given on any current masthead page.

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