Isocyanide Insertion into the Palladium−Carbon Bond of Complexes Containing Bidentate Nitrogen Ligands: A Structural and Mechanistic Study

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Insertion of the isocyanides 2,6-dimethylphenyl isocyanide (DIC), *tert*-butyl isocyanide (TIC) and tosylmethyl isocyanide (TosMIC) into the Pd−Me bond of complexes (N⌒N)Pd(Me)Cl (N⌒N = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 2,2′-bipyrimidine (bpm)) afforded quantitatively (N⌒N)Pd(C(=N−R)Me)Cl (R = 2,6-$Me_2C_6H_3$, *t*-Bu, CH_2Tosyl). The course of the reaction has been shown to proceed via the intermediates [(N⌒N)Pd(CN−R)(Me)]Cl (N⌒N = bpy, phen; R = 2,6-$Me_2C_6H_3$, *t*-Bu, CH_2Tosyl), which have been characterized at 250 K by NMR and IR spectroscopies and conductivity measurements. The mechanism of the insertion reaction involves substitution of the halide by the isocyanide followed by a rate-determining methyl migration to the precoordinated isocyanide. Kinetic measurements of the isocyanide insertion reaction, which provided the reaction rate constants of the isocyanide association (k_1), isocyanide dissociation (k_{-1}), and methyl migration reaction (k_2), have demonstrated that the migration rate of the methyl group to the precoordinated isocyanide increases with increasing electrophilicity of the isocyanide. Methyl migration in the intermediate complexes [(N⌒N)Pd(CN−R)(Me)]Cl (N⌒N = bpy, phen; R = 2,6-$Me_2C_6H_3$, *t*-Bu, CH_2Tosyl) also occurs in the solid state. The complexes (N⌒N)Pd(C(=N−R)Me)X (N⌒N = bpy, phen; R = *t*-Bu, CH_2Tosyl; X = Cl, Br) show a fluxional behavior due to a site exchange of the nitrogen donor atoms. Spin saturation transfer ^{1}H NMR experiments showed that the mechanism of this process involves Pd−N bond breaking and subsequent isomerization via a Y-shaped intermediate.

Introduction

Carbon monoxide insertion into metal−carbon bonds constitutes a key step in many transition-metal-catalyzed processes.[1−4] One of these involves the palladium-catalyzed copolymerization of CO and alkenes[5−11] involving a perfectly alternating insertion of CO and alkenes.[12−14] The mechanism of CO insertion into Pd−C bonds has been studied extensively for many systems both experimentally[15−19] and theoretically.[20−24]

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It has been generally accepted that precoordinated CO and the hydrocarbyl group should be *cis* in the reacting complex[15,25,26] and that the hydrocarbyl group migrates to CO rather than *vice versa*.[27,28] Our study on the carbonylation of organopalladium compounds, such as (L⌒L)Pd(Me)X, showed that the choice of ligands has a large influence on the reaction. Unexpectedly, it appeared that insertion of CO into the Pd−C bond of the neutral complexes (N⌒N)Pd(Me)X,[12,18] of which the bidentate nitrogen ligands are both flexible and rigid with a small bite angle, is usually faster than insertion of CO into the Pd−C bond of the analogous complexes (P⌒P)Pd(Me)X, of which the diphosphine ligands are flexible with a small or large bite angle.[29] Surprisingly, the insertion of CO in the complex {σ^3-N,N′,N″-2,2′:6′,2″-terpyridyl}methylpalladium(II) chloride containing a terdentate nitrogen ligand is very fast.[30]

The CO insertion process in the case of (N⌒N)Pd(Me)X may involve halide or nitrogen dissociation upon coordination of CO. The latter possibility might well occur as structural studies on Pd−η^3-allyl complexes and (2,9-dimethyl-1,10-phenanthroline)Pt(X)$_2$L complexes (L = C_2H_4, CO, PPh_3, ONPh) revealed monodentate coordination of a nitrogen ligand for flexible ligands as well as for rigid ones.[31−33]

To obtain more insight into the mechanism of CO insertion, we turned our attention to insertion of the isoelectronic isocyanides. Isocyanides might allow the observation of intermediate complexes and variation of electronic and steric factors by variation of the R group on the nitrogen atom, and moreover, it would be of great interest to look at the possibility for the direct synthesis of the polyimine analogue of polyketone. Since it is known that complexes having bidentate nitrogen ligands allow fast insertions of CO and olefins,[12−14,18,32,34] we wished to explore the prospect of copolymerization of isocyanides and olefins. Isocyanide insertion into Pd−C bonds has been extensively studied,[35−37] but mainly for complexes containing phosphine ligands.[38−43] We describe in this report, of which a preliminary account has already appeared,[44] the insertion of isocyanides into the Pd−Me bond of (N⌒N)Pd(Me)Cl complexes, the characterization of the reaction intermediates, and a detailed kinetic study of the isocyanide association, isocyanide dissociation, and methyl migration reaction.

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 and ^{13}C NMR spectra were recorded on a Bruker AMX 300 and DRX 300 spectrometer (300.13 and 75.48 MHz respectively). Elemental analyses were carried out by 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.

The complexes (bpm)Pd(Me)Cl,[10] (bpy)Pd(Me)Cl,[18] and (phen)Pd(Me)Cl[18] were synthesized according to previously reported procedures. The isocyanides 2,6-dimethylphenyl isocyanide (DIC), *tert*-butyl isocyanide (TIC), and tosylmethyl isocyanide (TosMIC) were purchased from Fluka and used without purification.

General Procedure for Insertion of DIC and TosMIC Providing Complexes (N⌒N)Pd(C(=N−R)Me)Cl (N⌒N = bpy (1), phen (2), bpm (3); R = 2,6-Me$_2$C$_6$H$_3$ (a), CH$_2$-Tosyl (c)). To a solution of (N⌒N)Pd(Me)Cl (100 mg, 0.22 mmol) in dichloromethane (20 mL) the appropriate isocyanide (0.22 mmol) was added, after which the mixture was stirred for 2 h. The volume of the solution was concentrated to 5 mL, and hexane (30 mL) was added. The crystalline material was collected by centrifugation.

(bpy)Pd(C(=N−2,6-Me$_2$C$_6$H$_3$)Me)Cl (1a). Yield: 84 mg; 0.19 mmol; 86% ^{1}H NMR (300 MHz, $CDCl_3$) (numbering scheme of the protons is presented in Figure 1): δ 9.15 (d, ^3J = 4.9 Hz, 1H, H6), 9.09 (d, ^3J = 4.9 Hz, 1H, H6′), 8.04 (m, 4H, H4, H4′, H3, H3′), 7.53 (m, 2H, H5, H5′), 6.98 (d, ^3J = 7.4 Hz, 2H, H_{meta}), 6.84 (dd, ^3J = 7.4 Hz, 1H, H_{para}), 2.29 (s, 3H, C(=NR)CH_3), 2.26 (s, 6H, (CH_3)$_2$Ph). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 183.7 (C=N), 155.6, 152.6 (C6, C6′), 151.9, 149.6, 148.1, 139.3, 139.1, 128.0, 127.0, 126.3, 122.7, 122.4, 121.7 (C_{phen}, C_{Ar}), 29.1 (C(=NR)CH_3), 19.5 ((CH_3)$_2$Ph). Elemental Analysis Found (calcd) for $C_{20}H_{20}ClN_3Pd\cdot CH_2Cl_2$: C, 46.91 (47.66); H, 4.17 (4.19); N, 7.88 (7.94). FAB MS Found (calcd) for $C_{20}H_{20}ClN_3Pd$: 444 (444). IR ν(C=N) (KBr): 1623 cm^{-1}.

(phen)Pd(C(=N−2,6-Me$_2$C$_6$H$_3$)Me)Cl (2a). Yield: 93 mg; 0.20 mmol; 89%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.45 (d, ^3J = 3.9 Hz, 1H, H6), 9.41 (d, ^3J = 3.9 Hz, 1H, H6′), 8.55 (d, ^3J = 8.2 Hz, 1H, H4), 8.44 (d, ^3J = 8.2 Hz, 1H, H4′), 7.96 (d, ^3J = 8.2 Hz, 1H, H7), 7.95 (d, ^3J = 8.2 Hz, 1H, H7′), 7.87 (dd, ^3J = 8.2, 4.8 Hz, 1H, H5), 7.79 (dd, ^3J = 8.2 Hz, 1H, H5′), 6.99 (d, ^3J = 7.4 Hz, 2H, H_{meta}), 6.84 (dd, ^3J = 7.4 Hz, 1H, H_{para}), 2.38 (s, 3H, C(=NR)CH_3), 2.31 (s, 6H, (CH_3)$_2$Ph). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 183.4 (C=N), 152.5, 150.0 (C6, C6′), 148.1, 146.7, 144.3, 138.2, 137.8, 130.0, 129.4, 128.0, 127.8, 127.1,

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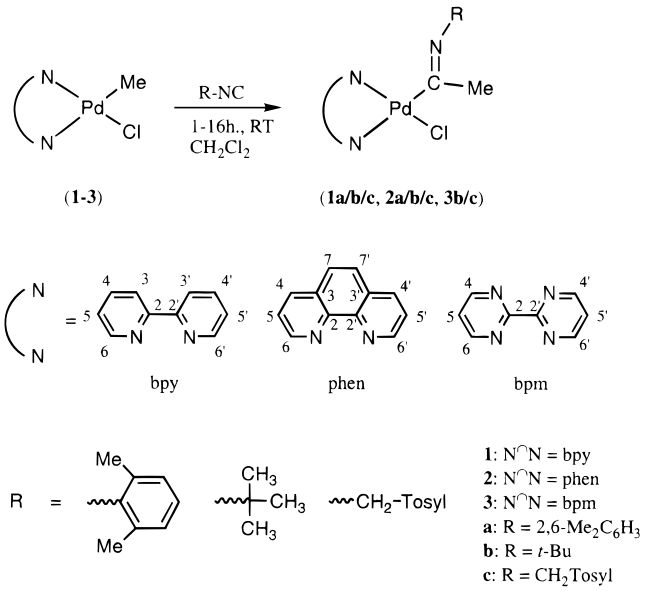

Figure 1. Isocyanide insertion in (N⌒N)Pd(Me)Cl complexes.

126.9, 125.3, 125.1, 122.4, 117.4, 117.2 (C_{phen}, C_{Ar}), 29.4 (C(=NR)CH_3), 19.7 ((CH_3)$_2$Ph). Elemental Analysis Found (calcd) for $C_{22}H_{20}ClN_3Pd\cdot{}^1/_2CH_2Cl_2$: C, 52.69 (52.91); H, 4.33 (4.15); N, 7.93 (8.23). FAB MS Found (calcd) for $C_{22}H_{20}ClN_3$-Pd: 468 (468). IR ν(C=N) (KBr): 1629 cm^{-1}.

(bpy)Pd(C(=N−CH$_2$Tosyl)Me)Cl (1c). Yield: 85 mg; 0.17 mmol; 76%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.02 (d, ^3J = 5.1 Hz, 1H, H6), 8.56 (d, ^3J = 5.1 Hz, 1H, H6′), 8.10 (m, 4H, H4, H4′, H3, H3′), 7.52 (m, 2H, H5, H5′), 7.88 (d, ^3J = 8.2 Hz, 2H, H_{ortho}), 7.33 (d, ^3J = 8.2 Hz, 2H, H_{meta}), 5.82 (d, ^3J = 13.9 Hz, 1H, CH_2SO_2), 5.27 (d, ^3J = 13.9 Hz, 1H, CH_2SO_2), 2.44 (s, 3H, Ph−CH_3), 2.44 (s, 3H, C(=NR)CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ C=N not observed, 155.3, 152.5, 139.1, 138.8, 129.3, 128.6, 127.1, 126.4, 122.0, 121.0 (C_{phen}, C_{Ar}), 31.1 (C(=NR)CH_3), 21.5 (Ph−CH_3). Elemental Analysis Found (calcd) for $C_{20}H_{20}ClN_3O_2SPd$: C, 46.43 (47.25); H, 4.02 (3.97); N, 8.07 (8.26). FD MS Found (calcd) for $C_{20}H_{20}ClN_3O_2SPd$: 509 (508). IR ν(C=N) (KBr): 1617 cm^{-1}.

(phen)Pd(C(=N−CH$_2$Tosyl)Me)Cl (2c). Yield: 89 mg; 0.17 mmol; 76%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.28 (d, ^3J = 4.6 Hz, 1H, H6), 8.81 (d, ^3J = 4.6 Hz, 1H, H6′), 8.59 (d, ^3J = 8.2 Hz, 1H, H4), 8.54 (d, ^3J = 8.2 Hz, 1H, H4′), 8.02 (d, ^3J = 8.2 Hz, 1H, H7), 8.01 (d, ^3J = 8.2 Hz, 1H, H7′), 7.89 (m, 2H, H5, H5′), 7.89 (d, ^3J = 8.2 Hz, 2H, H_{ortho}), 7.34 (d, ^3J = 8.2 Hz, 2H, H_{meta}), 5.99 (d, ^3J = 13.9 Hz, 1H, CH_2SO_2), 5.33 (d, ^3J = 13.9 Hz, 1H, CH_2SO_2), 2.71 (s, 3H, Ph−CH_3), 2.43 (s, 3H, C(=NR)CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ C=N not observed, 154.0, 149.7 (C6, C6′), 145.1, 145.0, 138.8, 138.5, 130.5, 130.1, 129.9, 129.2, 127.9, 127.4, 126.3, 125.8 (C_{phen}, C_{Ar}), 32.3 (C(=NR)CH_3), 22.1 (Ph−CH_3). Elemental Analysis Found (calcd) for $C_{22}H_{20}ClN_3O_2SPd$: C, 48.84 (49.63); H, 3.81 (3.79); N, 7.70 (7.89). FAB MS Found (calcd) for $C_{22}H_{20}ClN_3O_2SPd$: 532 (532). IR ν(C=N) (KBr): 1618 cm^{-1}.

(bpm)Pd(C(=N−CH$_2$Tosyl)Me)Cl (3c). Yield: 90 mg; 0.18 mmol; 80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.22 (m, 3H, C−H_{bpm}), 9.92 (dd, ^3J = 5.6, ^4J = 2.2 Hz, 1H, C-H_{bpm}), 7.74 (t, ^3J = 4.9 Hz, 1H, H5), 7.73 (t, ^3J = 4.9 Hz, 1H, H5′), 7.86 (d, ^3J = 8.2 Hz, 2H, H_{ortho}), 7.35 (d, ^3J = 8.2 Hz, 2H, H_{meta}), 5.93 (d, ^3J = 13.4 Hz, 1H, CH_2SO_2), 5.20 (dq, ^3J = 13.4 Hz, ^5J = 1.3 Hz, 1H, CH_2SO_2), 2.45 (d, ^5J = 1.3 Hz, 3H, C(=NR)CH_3), 2.45 (s, 3H, Ph−CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 196.2 (C=N), 160.4, 160.0, 159.4, 156.3, 124.7, 124.3 (C−H), 161.4, 159.8 (C_q), 145.0, 136.0, 130.0, 129.1 (C_{Ar}), 77.7 (CH_2SO_2), 31.4 (C(=NR)CH_3), 22.1 (Ph−CH_3). FAB MS Found (calcd) for $C_{18}H_{18}ClN_5O_2SPd$: 510 (510). IR ν(C=N) (KBr): 1619 cm^{-1}.

General Procedure for the Insertion of TIC Providing Complexes (N⌒N)Pd(C(=N−R)Me)Cl (N⌒N = bpy (1), phen (2), bpm (3); R = *t*-Bu (b)). To a solution of (N⌒N)-Pd(Me)Cl (100 mg, 0.22 mmol) in dichloromethane (20 mL) at 0 °C, TIC (19 mg, 0.22 mmol) was added. The solution was stirred for 15 min, after which it was warmed to room temperature and stirred for another 16 h. The volume of the solution was concentrated to 5 mL, and hexane (30 mL) was added. The crystalline material was collected by centrifugation.

(bpy)Pd(C(=N−C(CH$_3$)$_3$)Me)Cl (1b). Yield: 75 mg; 0.19 mmol; 82%. ^{1}H NMR (300 MHz, $CDCl_3$) (numbering scheme is presented in Figure 1): δ 9.08 (d, ^3J = 4.7 Hz, 1H, H6), 8.53 (d, ^3J = 4.7 Hz, 1H, H6′), 8.09 (m, 4H, H4, H4′, H3, H3′), 7.52 (m, 2H, H5, H5′), 2.49 (s, 3H, C(=NR)CH_3), 1.62 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 183.4 (C=N), 155.0, 152.6 (C6, C6′), 151.3, 148.7, 138.9, 126.5, 126.0, 122.9, 122.7, 121.6 (C_{phen}, C_{Ar}), 63.5 (*C*(CH_3)$_3$), 32.2 (C(*C*H$_3$)$_3$), 29.4 (C(=NR)-*C*H_3). FAB MS Found (calcd) for $C_{16}H_{20}N_3ClPd$: 396 (396). IR ν(C=N) (KBr): 1636 cm^{-1}.

(phen)Pd(C(=N−C(CH$_3$)$_3$)Me)Cl (2b). Yield: 70 mg; 0.17 mmol; 76%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.37 (d, ^3J = 4.7 Hz, 1H, H6), 8.79 (d, ^3J = 4.7 Hz, 1H, H6′), 8.60 (d, ^3J = 8.2 Hz, 1H, H4), 8.51 (d, ^3J = 8.2 Hz, 1H, H4′), 8.02 (d, ^3J = 8.2 Hz, 1H, H7), 8.00 (d, ^3J = 8.2 Hz, 1H, H7′), 7.88 (m, 2H, H5, H5′), 2.69 (s, 3H, C(=NR)CH_3), 1.71 (s, 9H, C(CH_3)$_3$). ^{13}C NMR data (75.48 MHz, $CDCl_3$); δ C=N not observed, 151.1, 149.3 (C6, C6′), 146.2, 144.2, 137.7, 137.4, 129.8, 129.2, 127.4, 126.5, 125.2 (C_{phen}, C_{Ar}), 32.2 (C(*C*H$_3$)$_3$), 30.2 (C(=NR)*C*H_3). FAB MS Found (calcd) for $C_{18}H_{20}N_3ClPd$: 420 (420). IR ν(C=N) (KBr): 1637 cm^{-1}.

(bpm)Pd(C(=N−C(CH$_3$)$_3$)Me)Cl (3b). Yield: 61 mg; 0.15 mmol; 70%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.30 (dd, ^3J = 5.0 Hz, ^4J = 2.2 Hz, 1H, H6′), 9.24 (dd, ^3J = 5.0 Hz, ^4J = 2.2 Hz, 1H, H4), 9.17 (dd, ^3J = 5.0 Hz, ^4J = 2.2 Hz, 1H, H4′), 8.76 (d, ^3J = 5.0 Hz, 1H, H6), 7.71 (d, ^3J = 5.0 Hz, 1H, H5′), 7.67 (d, ^3J = 5.0 Hz, 1H, H5), 2.48 (s, 3H, C(=NR)CH_3), 1.63 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 190.5 (C=N), 161.4, 160.0, 159.6, 159.3, 158.5, 156.7, 124.5, 124.2 (C_{bpm}), 68.3 (*C*(CH_3)$_3$), 32.9 (C(*C*H$_3$)$_3$), 32.8 (C(=NR)*C*H_3). FAB MS Found (calcd) for $C_{14}H_{18}N_5ClPd$: 398 (398). IR ν(C=N) (KBr): 1648 cm^{-1}.

Synthesis of (bpm)Pd(C(=N−C(CH$_3$)$_3$)Me)Br. The complex (bpm)Pd(C(=N−*t*-Bu)Me)Cl (100 mg, 0.25 mmol) and KBr (166 mg, 1.4 mmol) were dissolved in acetone (40 mL) and stirred for 2 h. The solvent was evaporated, and the residue was washed twice with THF. The volume of the solvent was concentrated and hexane (30 mL) was added, providing a yellow crystalline material, which was collected by centrifugation. Yield: 100 mg; 0.22 mmol; 90%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.42 (dd, ^3J = 5.0 Hz, ^4J = 2.2 Hz, 1H, H6′), 9.25 (dd, ^3J = 4.6 Hz, ^4J = 2.0 Hz, 1H, H4), 9.16 (dd, ^3J = 4.7 Hz, ^4J = 2.2 Hz, 1H, H4′), 8.78 (d, ^3J = 3.2 Hz, 1H, H6), 7.72 (d, ^3J = 4.8 Hz, 1H, H5′), 7.68 (d, ^3J = 4.8 Hz, 1H, H5), 2.50 (s, 3H, C(=NR)CH_3), 1.62 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ C=N not observed, 160.8, 160.3, 158.7, 157.8, 157.6, 156.9, 123.8, 123.6 (C_{bpm}), 55.4 (*C*(CH_3)$_3$), 32.4 (C(*C*H$_3$)$_3$), 30.3 (C(=NR)*C*H_3). FAB MS Found (calcd) for $C_{14}H_{18}N_5BrPd$: 442 (442). IR ν(C=N) (KBr): 1648 cm^{-1}.

Characterization of the Intermediate Complexes [(N⌒N)Pd(CN−R)(Me)]Cl (N⌒N = bpy (4), phen (5); R = 2,6-Me$_2$C$_6$H$_3$ (a), *t*-Bu (b), CH$_2$-Tosyl (c)) by ^{1}H NMR Spectroscopy. To a solution of (N⌒N)Pd(Me)Cl (5 mg, 13 μmol) in 0.5 mL of $CDCl_3$ was added the appropriate amount of a stock solution of isocyanide (13 μmol) in $CDCl_3$ at 250 K after which the color of the solution turned from yellow to colorless. The solution was transferred to a precooled 5 mm NMR tube. The intermediates **4a**, **4b**, and **5a** at temperatures higher than 273 K turned out to be in equilibrium with the starting complex and isocyanide, as intermediate complex **4a** could be observed together with starting complex **1** and uncoordinated DIC. Intermediate complex **4b** could be observed together with starting complex **1** and uncoordinated TIC, and intermediate **5a** could be observed together with

starting complex **2** and uncoordinated DIC. This equilibrium was shifted to the right for complexes **4c**, **5b**, and **5c**, as they are the only observed species in the temperature ranging from 250 to 320 K.

Elemental analyses and mass spectrometry could not be performed since complexes **4a**−**c** and **5a**−**c** reacted in the solid state to give complexes **1a**−**c** and **2a**−**c**, respectively, at room temperature.

[(bpy)Pd(CN−2,6-Me$_2$C$_6$H$_3$)(Me)]Cl (4a). ^{1}H NMR (300 MHz, $CDCl_3$, 223 K): δ 9.46 (d, ^3J = 8.8 Hz, 1H, H3), 9.43 (d, ^3J = 8.8 Hz, 1H, H3′), 8.60 (d, ^3J = 4.8 Hz, 1H, H6), 8.56 (d, ^3J = 4.8 Hz, 1H, H6′), 8.38 (t, ^3J = 7.7 Hz, 1H, H4), 8.34 (t, ^3J = 7.7 Hz, 1H, H4′), 7.72 (t, ^3J = 6.1 Hz, 1H, H5), 7.66 (t, ^3J = 6.1 Hz, 1H, H5′), 7.36 (t, ^3J = 7.4 Hz, 1H, H_{para}), 7.23 (d, ^3J = 7.4 Hz, 2H, H_{meta}), 2.54 (s, 6H, $(CH_3)_2$Ph), 1.12 (s, 3H, Pd−CH_3).

[(bpy)Pd(CN−C(CH$_3$)$_3$)(Me)]Cl (4b). ^{1}H NMR (300 MHz, $CDCl_3$, 223 K): δ 9.30 (d, ^3J = 8.2 Hz, 1H, H3), 9.25 (d, ^3J = 8.2 Hz, 1H, H3′), 8.48 (d, ^3J = 5.6 Hz, 1H, H6), 8.46 (d, ^3J = 5.6 Hz, 1H, H6′), 8.33 (m, 2H, H4, H4′), 7.69 (m, 2H, H5, H5′), 1.69 (s, 9H, $C(CH_3)_3$), 0.93 (s, 3H, Pd−CH_3).

[(bpy)Pd(CN−CH$_2$Tosyl)(Me)]Cl (4c). ^{1}H NMR (300 MHz, $CDCl_3$, 223 K): δ 8.90 (br, 1H, H6), 8.73 (br, 1H, H6′), 8.31 (br, 2H, H4, H4′), 8.10 (br, 1H, H3), 7.83 (br, 1H, H3′), 7.67 (br, 1H, H5), 7.47 (br, 1H, H5′), 8.00 (br, 2H, H_{ortho}), 7.47 (br, 2H, H_{meta}), 6.11 (s, 2H, CH_2SO_2), 2.42 (s, 3H, Ph−CH_3), 0.66 (s, 3H, Pd−CH_3).

[(phen)Pd(CN−2,6-Me$_2$C$_6$H$_3$)(Me)]Cl (5a). ^{1}H NMR (300 MHz, $CDCl_3$, 223 K): δ 9.01−8.92 (m, 4H, H6, H6′, H5, H5′), 8.21 (d, ^3J = 7.3 Hz, 1H, H4), 8.17 (d, ^3J = 7.3 Hz, 1H, H4′), 8.28 (s, 2H, H7, H7′), 2.61 (s, 6H, $(CH_3)_2$Ph), 1.32 (s, 3H, Pd−CH_3).

[(phen)Pd(CN−C(CH$_3$)$_3$)(Me)]Cl (5b). ^{1}H NMR (300 MHz, $CDCl_3$, 223 K): δ 8.98−8.86 (m, 4H, H6, H6′, H5, H5′), 8.24 (d, ^3J = 7.3 Hz, 1H, H4), 8.12 (d, ^3J = 7.3 Hz, 1H, H4′), 8.24 (s, 2H, H7, H7′), 1.79 (s, 9H, $C(CH_3)_3$), 1.11 (s, 3H, Pd−CH_3).

[(phen)Pd(CN−CH$_2$Tosyl)(Me)]Cl (5c). ^{1}H NMR (300 MHz, $CDCl_3$, 223 K): δ 9.21 (d, ^3J = 8.0 Hz, 1H, H3), 8.92 (d, ^3J = 8.0 Hz, 1H, H3′), 8.50 (m, 2H, H6, H6′), 8.15−7.96 (m, 4H, H4, H4′, H_{ortho}), 7.85 (s, 2H, H7, H7′), 7.50 (d, ^3J = 7.8 Hz, 2H, H_{meta}), 6.22 (s, 2H, CH_2SO_2), 2.49 (s, 3H, Ph−CH_3), 0.90 (s, 3H, Pd−CH_3).

Reaction in the Solid State of the Intermediate Complexes 4a−c and 5a−c Providing the Complexes 1a−c and 2a−c. The intermediate complexes were synthesized as described above, after which precooled (250 K) hexanes (5 mL) was added. The crystalline material was collected by centrifugation and dried in vacuo. The conversion of intermediate complexes in the solid state to the products at 293 or 320 K was followed by ^{1}H NMR spectroscopy in precooled $CDCl_3$.

Kinetic Measurements of Insertion of Isocyanide by ^{1}H NMR Spectroscopy. The intermediate complexes in $CDCl_3$ were synthesized as described above, after which the NMR tube was transferred to a prethermostated NMR spectrometer. The relative concentrations of the compounds in the solution were determined as a function of time.

Determination of the Kinetic Constants for Reaction of 2 with DIC. The reaction rate constants of the elementary isocyanide association, dissociation, and methyl migration steps with the rate constants k_1, k_{-1}, and k_2, respectively, were determined for each set of data by fitting the composition of the reaction mixture by a nonlinear regression. The composition of the reaction mixture was determined by means of ^{1}H NMR during the reaction time. The minimum objective function, which was the sum of squares of the residual concentrations of **1**, DIC, **5a**, and **2a**, is the difference between the observed and calculated value:

$$\phi = \sum_{i=1}^{n} (C_j^{\text{obs}} - C_j^{\text{calcd}})^2$$

where C_j is the concentration of component j and n is the number of the components.

The least-squares fitting was performed using a modified Powell algorithm[45] to find the minimum in the objective function.

The concentration of the components were calculated via numerical integration of a set of coupled ordinary differential equations describing the concentrations as a function of time. The governing equations are the following in the case of the isocyanide insertion:

$$\mathbf{2} + \text{DIC} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{5a} \xrightarrow{k_2} \mathbf{2a}$$

$$\frac{\mathrm{d}[\mathbf{2}]}{\mathrm{d}t} = -k_1[\mathbf{2}][\text{DIC}] + k_{-1}[\mathbf{5a}]$$

$$\frac{\mathrm{d}[\text{DIC}]}{\mathrm{d}t} = -k_1[\mathbf{2}][\text{DIC}] + k_{-1}[\mathbf{5a}]$$

$$\frac{\mathrm{d}[\mathbf{5a}]}{\mathrm{d}t} = k_1[\mathbf{2}][\text{DIC}] - k_{-1}[\mathbf{5a}] - k_2[\mathbf{5a}]$$

$$\frac{\mathrm{d}[\mathbf{2a}]}{\mathrm{d}t} = k_2[\mathbf{5a}]$$

The differential equations were solved numerically with the EPISODE method.[45] This algorithm is suited for integration of stiff equations, *i.e.*, in the case of the occurrence of both very fast and slow chemical reactions.

Spin Saturation Transfer Measurements. The lattice relaxation times were obtained using standard inversion recovery methods with 10 data points and a 90°/180° pulse width. The T_1 was measured at the lowest and highest temperature for which a spin saturation transfer measurement was carried out and varied from ca. 1.5−3 s in the temperature range from 273 to 334 K. The temperature of the NMR sample was checked externally with CH_3OH with an accuracy of 0.6 °C. The spin saturation transfer measurements were carried out using the Forsén−Hoffman method[46] with a $(T_d-\pi/2)_n$ pulse sequence (presaturation time T_d = 0.1−25 s, presaturation power 70 dB, relaxation delay d_1 = 25 s, eight scans per data point).

Crystal Structure Determination of 1a. Crystal and refinement data for complex **1a** and experimental details of the crystal structure determination have been published in a preliminary account of this work.[44] Atomic coordinates, bond lengths, bond angles, and thermal parameters have been deposited in the Supporting Information and at the Cambridge Crystallographic Data Centre.

Results

The isocyanides 2,6-dimethylphenyl isocyanide (DIC), *tert*-butyl isocyanide (TIC), and tosylmethyl isocyanide (TosMIC) inserted quantitatively into the Pd−C bond of the complexes (bpy)Pd(Me)Cl (bpy = 2,2′-bipyridine) (**1**), (phen)Pd(Me)Cl (phen = 1,10-phenanthroline) (**2**), and (bpm)Pd(Me)Cl (bpm = 2,2′-bipyrimidine) (**3**) when 1 equiv of isocyanide was added to a solution of the starting complex in dichloromethane (see Figure 1). The insertion reactions of DIC and TosMIC have been carried out at 294 K, while the insertion reactions of TIC with complexes **1**, **2**, and **3** were carried out by addition of TIC to a solution of the starting complex in dichloromethane at 273 K and slow warming of the reaction mixture from 273 to 294 K, since otherwise

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uncharacterized side products were formed. The reaction time strongly depends on the isocyanides; TosMIC, DIC, and TIC required 1, 3, and 16 h, respectively, before total conversion of the starting complex was reached. The reactions are highly selective under the mentioned conditions, since formation of other products has not been observed except for reaction of **3** with DIC in dichloromethane, which provided several uncharacterized side products in addition to the expected insertion product.

The solid products (bpy)Pd(C(=NR)Me)Cl (**1a**−**c**), (phen)Pd(C(=NR)Me)Cl (**2a**−**c**), and (bpm)Pd(C(=NR)-Me)Cl (**3b**,**c**) (R = 2,6-$Me_2C_6H_3$ (**a**), *t*-Bu (**b**), and tosylmethyl (**c**)) are stable under an atmosphere of nitrogen for weeks, while decomposition occurs in air within several days.

We have used the strongly σ-coordinating bidentate nitrogen ligands bpy, phen, and bpm, since other α-diimine ligands like bis(arylimino)acenaphthene (Ar-BIAN) and 1,4-diazabutadiene (R-DAB) are substituted by isocyanides. Substitution of the bidentate nitrogen ligands bpy, phen, and bpm has been observed when more than 1 equiv of isocyanide was added to the reaction mixture.

It appears that there is a difference in the σ-coordinating capabilities between the ligands phen, bpy, and bpm. Competition experiments showed that addition of 1 equiv of bpy to a solution of complex **3b** in $CDCl_3$ resulted in an immediate substitution of bpm by bpy, and as expected, addition of 1 equiv of bpm to a solution of **1b** in $CDCl_3$ did not give substitution of bpy by bpm. Analogous experiments with phen and bpy and their complexes demonstrated that coordination of phen toward Pd(II) is favored with respect to bpy. Therefore, we can conclude that the σ-coordinating capabilities increase in the order bpm < bpy < phen.

The products **1a**−**c**, **2a**−**c** and, **3b**,**c** have been fully characterized by ^{1}H and ^{13}C NMR and IR spectroscopies, mass spectroscopy, and elemental analysis and by an X-ray structure determination of complex **1a**.

The ^{1}H NMR signal of the methyl group on the palladium shifted upon insertion of the isocyanide from ca. 1 ppm in the starting complex to ca. 2.5 ppm in the carbo imine product, which has also been observed in the case of insertion of CO into the Pd−Me bond of complexes containing bidentate nitrogen ligands.[12,18] The C=N stretching frequencies of the products **1a**−**c**, **2a**−**c**, and **3b**,**c** occurred in the IR spectrum around 1630 cm^{-1}. In the ^{13}C NMR spectra, the ^{13}C chemical shift of the C=N fragments could be observed around 184 ppm.[47−51] The two methyne protons of the tosylmethyl group have been observed as two doublets in the ^{1}H NMR spectrum with a large coupling constant between those two protons of ^2J = 13.9 Hz. The magnetic inequivalency of these two protons indicates a hindered rotation of the carbo imine group around the Pd−C bond.

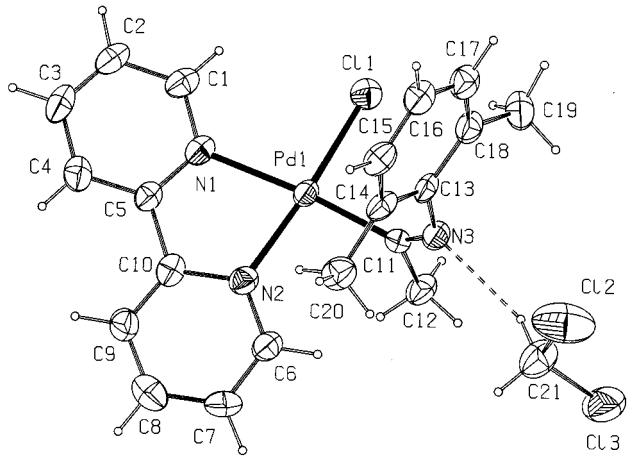

Figure 2. ORTEP plot at 50% probability level of complex (bpy)Pd(C(=N−2,6-$Me_2C_6H_3$)Me)Cl (**1a**).

Table 1. Bond Distances (Å) for (bpy)Pd(C(=N−2,6-$Me_2C_6H_3$)Me)Cl (1a) (with Esd's in Parentheses)

Pd(1)−Cl(1)	2.3081(18)	C(6)−C(7)	1.380(9)
Pd(1)−N(1)	2.146(5)	C(7)−C(8)	1.387(9)
Pd(1)−N(2)	2.066(5)	C(8)−C(9)	1.380(10)
Pd(1)−C(11)	1.976(5)	C(9)−C(10)	1.359(9)
N(1)−C(1)	1.323(9)	C(11)−C(12)	1.510(10)
N(1)−C(5)	1.348(7)	C(13)−C(14)	1.406(8)
N(2)−C(6)	1.320(8)	C(13)−C(18)	1.399(9)
N(2)−C(10)	1.380(7)	C(14)−C(15)	1.401(11)
N(3)−C(11)	1.258(8)	C(14)−C(20)	1.504(10)
N(3)−C(13)	1.416(9)	C(15)−C(16)	1.370(11)
C(1)−C(2)	1.386(9)	C(16)−C(17)	1.378(10)
C(2)−C(3)	1.350(10)	C(17)−C(18)	1.386(11)
C(3)−C(4)	1.376(10)	C(18)−C(19)	1.498(9)
C(4)−C(5)	1.399(8)	Cl(2)−C(21)	1.733(9)
C(5)−C(10)	1.482(9)	Cl(3)−C(21)	1.700(8)

Table 2. Bond Angles (deg) for (bpy)Pd(C(=N−2,6-$Me_2C_6H_3$)Me)Cl (1a) (with Esd's in Parentheses)

Cl(1)−Pd(1)−N(1)	96.69(13)	C(7)−C(8)−C(9)	118.9(7)
Cl(1)−Pd(1)−N(2)	172.77(14)	C(8)−C(9)−C(10)	119.9(6)
Cl(1)−Pd(1)−C(11)	89.55(18)	N(2)−C(10)−C(5)	115.4(5)
N(1)−Pd(1)−N(2)	78.91(19)	N(2)−C(10)−C(9)	121.5(6)
N(1)−Pd(1)−C(11)	173.5(2)	C(5)−C(10)−C(9)	123.1(5)
N(2)−Pd(1)−C(11)	95.1(2)	Pd(1)−C(11)−N(3)	128.5(5)
Pd(1)−N(1)−C(1)	127.1(4)	Pd(1)−C(11)−C(12)	112.3(4)
Pd(1)−N(1)−C(5)	113.3(4)	N(3)−C(11)−C(12)	119.2(5)
C(1)−N(1)−C(5)	119.0(5)	N(3)−C(13)−C(14)	121.0(6)
Pd(1)−N(2)−C(6)	126.4(4)	N(3)−C(13)−C(18)	117.6(5)
Pd(1)−N(2)−C(10)	115.4(4)	C(14)−C(13)−C(18)	120.8(6)
C(6)−N(2)−C(10)	117.9(5)	C(13)−C(14)−C(15)	117.5(6)
C(11)−N(3)−C(13)	127.4(5)	C(13)−C(14)−C(20)	121.7(6)
N(1)−C(1)−C(2)	122.0(6)	C(15)−C(14)−C(20)	120.8(6)
C(1)−C(2)−C(3)	120.1(7)	C(14)−C(15)−C(16)	121.9(7)
C(2)−C(3)−C(4)	118.8(6)	C(15)−C(16)−C(17)	119.6(7)
C(3)−C(4)−C(5)	119.3(6)	C(16)−C(17)−C(18)	121.0(7)
N(1)−C(5)−C(4)	120.9(6)	C(13)−C(18)−C(17)	119.0(6)
N(1)−C(5)−C(10)	116.1(5)	C(13)−C(18)−C(19)	120.9(7)
C(4)−C(5)−C(10)	123.0(5)	C(17)−C(18)−C(19)	120.1(6)
N(2)−C(6)−C(7)	123.5(5)	Cl(2)−C(21)−Cl(3)	115.6(4)
C(6)−C(7)−C(8)	118.3(6)		

Molecular Structure (bpy)Pd(C(=N−2,6-Me_2-C_6H_3)Me)Cl (1a). Crystals suitable for X-ray diffraction of complex **1a** were obtained from slow diffusion of hexanes into a solution of the complex in dichloromethane. The molecular structure is presented in Figure 2, while the bond lengths and bond angles of the non-hydrogen atoms are collected in Tables 1 and 2. This structure displays a square-planar geometry about the palladium atom with a bidentate coordinated bpy ligand, the chloride atom, and the carbon atom of the

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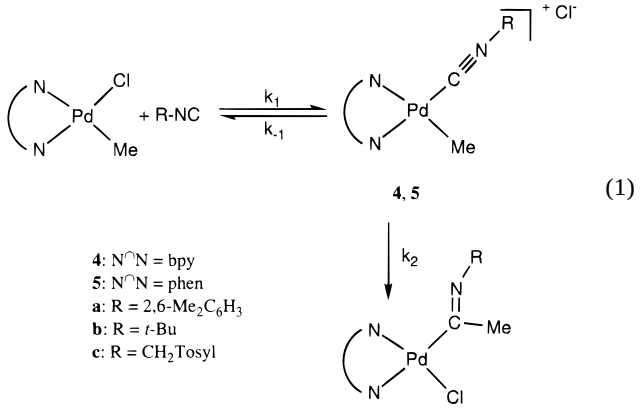
inserted isocyanide. It clearly shows that the plane C(12)−C(11)−N(3) makes an angle of 82.1(6)° with the coordination plane of palladium. This is analogous to the complex (bpy)Pd(C(O)Me)Cl, which shows that the C(O)Me plane is perpendicular to the coordination plane.[18] The Pd−N(1) distance (2.146(5) Å) is longer than the Pd−N(2) distance (2.066(5) Å), showing that the C(=N−R)Me group has a larger *trans* influence than the chloride atom. The N(3)−C(13) distance of 1.258(8) Å is comparable to other carbo imine bonds of palladium complexes formed by isocyanide insertion.[49,51]

It is interesting to note that the crystal lattice of complex **1a** contains one dichloromethane molecule per complex molecule, in which one hydrogen of dichloromethane is bonded to N(3) of the carbo imine group via a hydrogen bridge (N(3)−H(21) = 2.253(9) Å).

Identification of Intermediates of the Isocyanide Migratory Insertion Reaction. We monitored the reactions of complex **1** and **2** with the isocyanides DIC, TIC, and TosMIC by IR and NMR spectroscopies and conductivity measurements. After addition of DIC, TIC, or TosMIC to a solution of the complexes **1** or **2** in dichloromethane at 273 K, the IR spectrum shows a very intense vibration around 2200 cm^{-1} characteristic of an isocyanide σ-coordinated to the palladium atom,[40−42,48,51] while the ^{1}H NMR spectrum shows the formation of a new complex with a methyl signal around 1 ppm, characteristic of a methyl σ-coordinated to a Pd center.[12,18,34] Slowly warming the reaction mixture from 273 to 294 K shows a decreasing intensity of the σ-coordinated isocyanide and an increasing intensity of the imine C=N vibration around 1630 cm^{-1} in the IR spectrum. In the ^{1}H NMR spectrum, decreasing intensity of the signal around 1 ppm and increasing intensity of the signal around 2.4 ppm from the products **1a**−**c** or **2a**−**c** can be observed.

Addition of DIC, TIC, or TosMIC to complexes **1** or **2** in acetonitrile at 273 K showed an increase of the conductivity from around 4 to 160 Ω^{-1} cm^2 mol^{-1} in a few seconds, whereas in dichloromethane and chloroform the conductivity increases from around 0.04 to 20 and 2 Ω^{-1} cm^2 mol^{-1}, respectively. This indicates that during the reaction in acetonitrile, as well as in dichloromethane, the chloride is substituted by the isocyanide to form an ionic intermediate containing a σ-coordinated isocyanide (see eq 1). The low conductivity value for



(1)

the intermediate complexes in the moderately polar solvent chloroform might indicate the existence of contact ion pairs. Subsequent warming of the reaction mixture leads to a decrease in conductivity, as the ions recombine to the nonconducting species **1a**−**c** and **2a**−**c**.

The intermediate complexes [(N⌒N)Pd(CN−R)(Me)]Cl (N⌒N = bpy (**4**), phen (**5**); R = 2,6-$Me_2C_6H_3$ (**a**), *t*-Bu (**b**), and tosylmethyl (**c**)), as shown in eq 1, have been characterized by ^{1}H NMR spectroscopy (see Experimental Section) at 223 K, since at 273 K a fluxional process occurs in which both halves of the bidentate nitrogen ligands bpy and phen become magnetically equivalent on the NMR time scale.

The temperature at which the product forms is dependent on the isocyanide used, as intermediates **4a**−**c** and **5a**−**c** react to form the products **1a**−**c** and **2a**−**c** at 273 K for R = tosylmethyl, at 283 K for R = 2,6-$Me_2C_6H_3$, and at 293 K for R = *tert*-butyl.

An interesting observation is that at temperatures higher than 273 K, intermediates **4a**, **4b**, and **5a** (see eq 1) are in equilibrium with the starting complex and isocyanide, while this equilibrium is shifted to the right for complexes **4c**, **5b**, and **5c** in the temperature range from 250 to 320 K (see Experimental Section).

On the basis of these measurements, a mechanism for the isocyanide insertion into the palladium−carbon bond of (N⌒N)Pd(Me)Cl complexes may be postulated, as shown in eq 1.

It should be mentioned that intermediate **4a** could not be synthesized quantitatively at low temperature (250 K). Since free bpy ligand also (10% with regard to complex **4a**) appeared in the reaction mixture, probably intermediates are also formed containing two σ-coordinated isocyanides in addition to intermediate **4a**. Warming of the reaction mixture from 250 to 293 K, however, results in quantitative formation of product **1a**. Additionally, quantitative formation of the intermediates [(bpm)Pd(CN−*t*-Bu)(Me)]Cl and [(bpm)Pd(CN−CH_2-Tosyl)(Me)]Cl appeared to be impossible, as free ligand (50% with regard to the intermediate complexes) could also be observed in the reaction mixture of complex **3** with TIC and TosMIC at 270 K.

The intermediate complexes **4a**−**c** and **5a**−**c** can be precipitated from a solution in dichloromethane when hexane is added. Interestingly, these intermediates in the solid state quantitatively react to products **1a**−**c** and **2a**−**c**, although more slowly than in solution. Intermediates **4b** and **5b** convert within a few minutes in the solid state to the products **1b** and **2b**, respectively, upon heating to 320 K, while no product is formed when the solid is kept at room temperature. However, the intermediates **4a** and **5a** convert quantitatively to the products **1a** and **2a**, respectively, within 2 days at room temperature, while **4c** and **5c** in the solid state react quantitatively to **1c** and **2c** within 1 h at room temperature. Such a reaction in the solid state has been observed before for the complex [(PhNC)(Et_3P)$_2$PdCCPd(PEt_3)$_2$(CNPh)]Cl_2.[41]

Kinetics of the Migratory Insertion Reaction. Detailed kinetics of the isocyanide insertion into the Pd−C bond of (N⌒N)Pd(R)X complexes have been carried out. Determination of the migration rates of the methyl group to the precoordinated isocyanide, as described by the reaction constant k_2 (see eq 1), could readily be performed by measuring the concentration decay of the intermediate complexes **4c**, **5c**, and **5b** in time by means of ^{1}H NMR spectroscopy in a tempera-

Table 3. Migration Rates k_2 for Complexes 4c and 5a−c (with Esd's in Parentheses)

compound	T (K)[a]	k_2 (s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta G^{\ddagger}_{298}$ (kJ mol^{-1})
4c	264.2	0.00071(1)			
	268.3	0.001345(9)			
	273.4	0.00343(4)	98.4(2.1)	68.1(7.6)	78.1(4.3)
	277.6	0.0060(2)			
	282.7	0.0144(2)			
5a	288.9	0.00084(2)			
	294.1	0.00196(3)			
	296.2	0.00253(5)	110.0(1.9)	77.2(6.3)	87.0(3.8)
	299.2	0.0043(1)			
	304.4	0.0096(4)			
	309.6	0.018(1)			
5b	294.1	0.000190(5)			
	299.2	0.00039(1)			
	304.4	0.00081(2)	108.4(2.1)	52.3(7.1)	92.8(4.2)
	309.6	0.00186(7)			
	314.7	0.00360(8)			
5c	277.6	0.00085(7)			
	282.7	0.00175(4)	87.1(0.4)	10.7(1.4)	83.9(0.8)
	288.9	0.00392(5)			
	293.0	0.00664(7)			

[a] The standard deviation in T is 0.6 K.

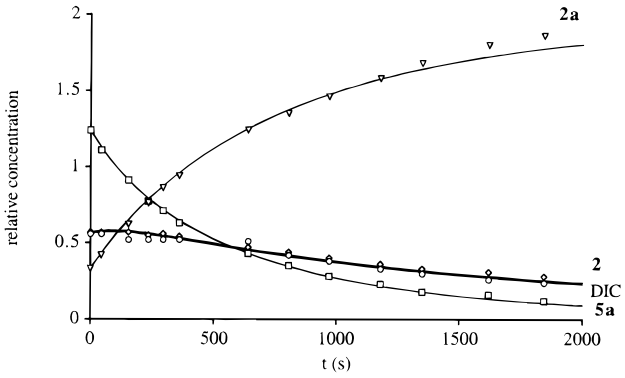


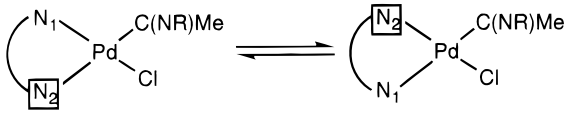
Figure 3. Nonlinear regression fitting of the composition of the reaction mixture **2** with DIC at 294.1 K. The experimental values for the relative concentrations of the components **2**, **2a**, DIC, and **5a** are displayed by the markers, while the result of the calculations are displayed by the extended lines.

ture range from 264 to 314 K (see Table 3). A logarithmic plot of these concentrations against time resulted in a straight line, which showed that the reactions are perfectly first order in palladium concentration for at least three half-lifes. Unfortunately, overlap of several signals in the ^{1}H NMR spectrum upon addition of TIC to complex **1** prevented determination of the kinetic data in this case. Since intermediate complex **5a** is in equilibrium with complex **2** and free DIC, the reaction rate constants of the elementary steps, *i.e.*, isocyanide association (k_1), dissociation (k_{-1}), and methyl migration (k_2), have been determined by fitting the composition of the reaction mixture by a nonlinear regression in the temperature range from 289 to 304 K. The composition of the reaction mixture was determined by ^{1}H NMR spectroscopy. The result of one of these calculations for the reaction of **2** with DIC at 294.1 K is displayed in Figure 3. The values for k_1 and k_{-1} are collected in Table 4, whereas the values for k_2 are shown in Table 3. The thermodynamic activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G_{298}{}^{\ddagger}$ (see Table 3) were obtained from an Eyring plot. Since the standard deviations in the values for k_1 and k_{-1} are rather large, no values for the thermodynamic activation parameters have been calculated.

Table 4. Values of k_1 and k_{-1} for Complex 5a (with Esd's in Parentheses)

T (K)	k_1 (M^{-1} s^{-1})	k_{-1} (s^{-1})
288.9	0.0027(7)	0.00064(17)
294.1	0.0037(6)	0.0012(3)
296.2	0.0070(21)	0.0022(8)
299.2	0.0088(51)	0.0035(28)
304.4	0.019(12)	0.011(9)
309.6	0.020 (22)	0.012(23)

Nitrogen Donor Atom Site Exchange in (N⁀N)-Pd(C(=NR)Me)Cl Complexes. Irradiation in the ^{1}H NMR spectrum of the H6 proton adjacent to the nitrogen of the bpy, phen, or bpm in complexes **1b**, **1c**, **2b**, **2c**, and **3b** caused a spin saturation transfer to the H6′ proton and *vice versa*. Exchange of protons H6 and H6′ with one another could be confirmed with EXSY ^{1}H NMR measurements, which can be explained by a process in which both nitrogen atoms of the bidentate nitrogen ligand change coordination sites, as shown in eq 2. Overlap of signals in the ^{1}H NMR spectrum



(2)

impeded a detailed study of the nitrogen donor atom exchange for complexes **1a**, **2a**, and **3c**. However, it is reasonable to assume that the process shown in eq 2 also occurs for these complexes. Fluxional behavior of this type has been reported before for the analogous complexes (bpy)Pd(C(O)Me)Cl[13] and (Ar-BIAN)Pd(C(O)-Me)Cl,[52] but evidence for the mechanism of this process could not be obtained for these compounds. A similar isomerization has been found by Pregosin *et al.* and Bäckvall *et al.*[53] for the complexes (N⁀N)Pd(η^3-allyl)X. In complexes where N⁀N = bpm, it could be shown that the process occurs via Pd−N bond breaking and subsequent isomerization, as has also been demonstrated for the complex [Rh(bpm)(nbd)]OTf.[54]

Therefore, we have investigated complex **3b** containing the ligand bpm in more detail to obtain more insight into the mechanism of the nitrogen donor exchange in (N⁀N)Pd(C(=NR)Me)Cl complexes. The ^{1}H NMR spectrum of complex **3b** shows four signals for H4, H6, H4′, and H6′ (the numbering scheme of the protons is presented in Scheme 1), of which the position in the ^{1}H NMR spectrum has been determined by ^{1}H NOE difference and ^{1}H decoupling experiments at 264 K. The methyl protons of the C(=N−*t*-Bu)Me group reveal a large NOE interaction with proton H6 of the bpm ligand *cis* to this group. The influence of the carbo imine group also results in a relatively large chemical shift difference between H6 and the other three protons H6′, H4, and H4′. From an EXSY ^{1}H NMR measurement of complex **3b**, it could be inferred that protons H4, H6, H4′, and H6′ are in exchange with one another.

The rates of the site exchange have been measured by the Forsén−Hoffman method[46] for complexes **1b**, **1c**,

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Scheme 1

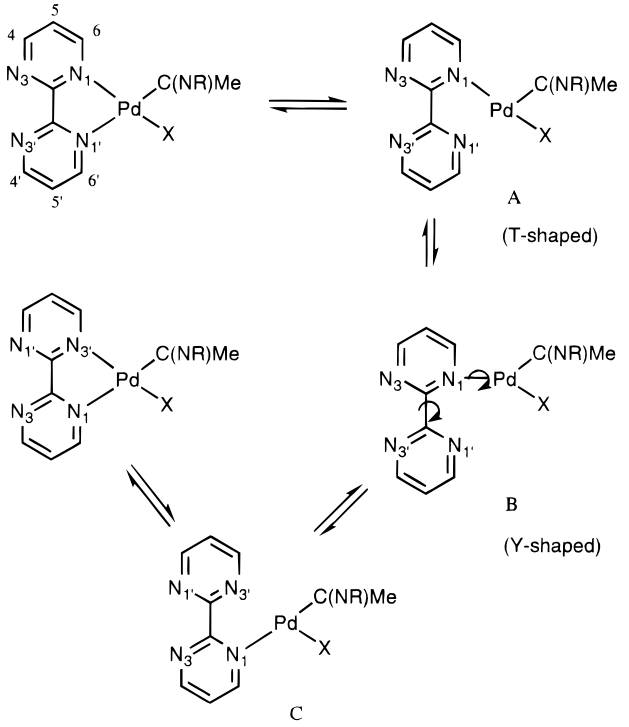

Table 5. Kinetic Data for Nitrogen Donor Exchange Processes (with Esd's in Parentheses)

compound	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta G^{\ddagger}_{298}$ (kJ mol^{-1})
1b	78.2(1.9)	7.7(1.6)	75.9(2.4)
1c	33.6(1.5)	−158.1(5.2)	80.7(3.0)
2b	82.6(1.4)	15.8(4.7)	77.9(2.8)
2c	49.3(1.7)	−107.1(5.3)	81.2(3.3)
3b	79.6(2.5)	28.1(8.6)	71.2(5.1)

2b, **2c**, and **3b** at different temperatures. The thermodynamic activation parameters for the mentioned complexes, derived from Eyring plots, have been collected in Table 5. The exchange rates are not influenced by the concentration of the complexes in $CDCl_3$ nor by the addition of Cl^- or free bidentate nitrogen ligand.

Discussion

Insertion of Isocyanide into Pd−C Bonds of (N⁀N)Pd(Me)Cl Complexes. The insertion of the isocyanides DIC, TIC, and TosMIC into the Pd−C bond of complexes **1**, **2**, and **3** resulted in the quantitative formation of the monoinsertion products **1a**−**c**, **2a**−**c**, and **3b**,**c**. This is rather surprising since in the case of complexes having phosphine ligands, multiple insertions take place rather than monoinsertion.[41,42,49,55−57] Quantitative product formation requires addition of exactly 1 equiv of the isocyanide with respect to the palladium complex, because an excess causes substitution of the bidentate ligand.

The structure shown in Figure 2 of complex **1a** exhibits some large similarities with the structure of complex (bpy)Pd(C(O)Me)Cl.[18] The Pd−N(1), Pd−N(2), and Pd−Cl(1) distances of complex **1a** are equal within the standard deviations as compared to those observed for complex (bpy)Pd(C(O)Me)Cl. The equal Pd−N(1) distances in complex **1a** and (bpy)Pd(C(O)Me)Cl indicate that the *trans* influence of the C(O)Me group and the C(=N−2,6-$Me_2C_6H_3$) group are comparable.

Kinetics of the Insertion Reaction. From the results, it is clear that the mechanism of isocyanide insertion involves coordination of the isocyanide to the metal via displacement of the chloride atom, followed by a rate-determining migration of the methyl group to the precoordinated isocyanide. Such a mechanism has been proposed before for isocyanide insertion into palladium− and platinum−carbon bonds.[39,41,58,59] The complex *trans*-[PdCl(2-pyrazyl)(PPh_3)$_2$][59] undergoes migratory insertion of TIC via Pd−X bond breaking, although there are indications for a mechanism involving Pd−P bond breaking.

It has been proposed that multiple insertion of isocyanides into Pd−C bonds of ($Ph_2P-C_2H_4-PPh_2$)Pd(CH=$CHCO_2Me$)Br[60] occurs via a five-coordinate transition state, while it has been proven that such a reaction with X(R_3P)$_2$PdCCPd(PR_3)X complexes takes place via Pd−X bond breaking.[41]

As substitution of the ligand bpm occurs upon addition of the isocyanides TIC and TosMIC to complex **3** at 250 K, also in this case other mechanisms may occur involving Pd−N bond breaking instead of Pd−X bond breaking.

The values for k_1 and k_{-1} could only be determined in the case of reaction of **2** with DIC, which showed that the rate of isocyanide association (k_1 = 0.0037(6) M^{-1} s^{-1} at 294.1 K, [DIC] = 0.03 M) is comparable with the rate of isocyanide dissociation (k_{-1} = 0.0012(3) s^{-1} at 294.1 K). As the pre-equilibrium in eq 1 for reactions of **1** with TosMIC and **2** with TIC and TosMIC lies close to the respective intermediates, we might conclude that in these cases the value for K_1 is much larger than that for reaction of **2** with DIC.

The rate of methyl migration to the precoordinated isocyanide, with rate constant k_2, increases along the series TIC < DIC < TosMIC. The migration rate is enhanced by R groups on the isocyanide having electron-withdrawing properties, such as a tosylmethyl group, and it is reduced by an electron-donating R group, such as *tert*-butyl. In earlier studies, it has already been shown that *p*-chlorophenyl isocyanide inserts with a higher rate than methyl isocyanide into the Pd−R′ bond of (PR_3)$_2$Pt(R′)X (R′ = CH_3, C_6H_5; X = Br, I),[58] and analogously, the insertion of isocyanides with electron-withdrawing R groups into the Pd−acetylide bond of the complexes X(R_3P)$_2$PdCCPd(PR_3)X is faster than the insertion of isocyanides having electron-donating R groups.[41]

As can be seen from Table 3, the migration step involves relatively high activation enthalpies and positive activation entropies. It can be expected that solvent molecules are more strongly ordered around the ionic intermediates **4** and **5** than around the neutral products **1a**−**c** and **2a**−**c**. During the migration step, the com-

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plex converts from an ionic species into a neutral species giving rise to disorder in the orientation of the solvent molecules and a positive value for ΔS. This indicates that the transition state of the migration reaction resembles the neutral final state and might, therefore, look like a five-coordinate neutral species having the halide atom coordinated to the metal center, as proposed previously for isocyanide insertion into $(PR_3)_2Pt(R)X$ complexes.[58]

The interesting observation that product formation occurs from intermediates **4a**−**c** and **5a**−**c** even in the solid state shows that in the crystal lattice movement of the methyl group to the precoordinated isocyanide and subsequent movement of the chloride atom from the second coordination sphere to the palladium atom occurs, albeit at a lower rate.

Comparison of the rate of CO insertion[18] with the rate of isocyanide insertion into the Pd−Me bond of (N⁀N)-Pd(Me)Cl complexes shows that the rates are of the same order of magnitude. The major difference between both reactions is that intermediate complexes such as [(N⁀N)Pd(Me)(CO)]Cl have never been observed for CO insertion reactions. Furthermore, we do not have any experimental indication for which of the steps in the CO insertion mechanism is the rate-determining one.

Nitrogen Donor Atom Site Exchange in (N⁀N)-Pd(C(=NR)Me)Cl Complexes. Analogous to what has been proposed for the complexes (bpm)Pd(η^3-allyl)-X[53] and [Rh(bpm)(nbd)]OTf,[54] the exchange in complex **3b** of the protons H4, H4′, H6, and H6′ with one another can be explained by a mechanism (see Scheme 1) in which during the site exchange of the two pyrimidine rings (*i.e.*, exchange of H4 with H4′ and H6 with H6′), the two rings undergo an internal rotation around the C−C bond (*i.e.*, exchange of H6 with H4 and H6′ with H4′). It is clear that the internal ligand rotation necessitates Pd−N bond breaking (see Scheme 1). In earlier studies on this exchange process,[53,54] it was proposed that internal ligand rotation may occur in a T-shaped intermediate **A** (Scheme 1). If this were so, internal ligand rotation and exchange of the pyrimidine rings are uncoupled processes and the exchange of H6′ and H4′ is independent of the exchange of H6′ and H6. However, spin saturation ^{1}H NMR experiments using a short presaturation time of 0.1 s upon irradiation of proton H6 or H6′ showed equal rates of spin saturation transfer to each of the protons H4, H6′, and H4′ (saturation of H6) or H4, H6, and H4′ (saturation of H6′). For these spin saturation experiments, complex (bpm)Pd(C(=N−*t*-Bu)Me)Br was used, as the chemical shift differences in the ^{1}H NMR spectrum between the protons H6′, H4, and H4′ is larger than those in complex **3b**. These measurements indicate that internal ligand rotation does not occur without exchange of the two pyrimidine rings. Therefore, we propose that subsequent to Pd−N1′ bond breaking *trans* to the carbo imine group (this group has a larger *trans* influence than chloride), *cis*−*trans* isomerization of N1 and N1′ occurs via a Y-shaped[61,62] intermediate **B**, which involves also internal ligand rotation (see Scheme 1).

We have studied the nitrogen donor atom site exchange in the carbo imine complexes **1b**,**c**, **2b**,**c**, and **3b** as a function of the R group on the carbo imine moiety, the bidentate nitrogen ligand, concentration of the carbo imine complexes in $CDCl_3$, and the presence of free bidentate nitrogen ligand and Cl^- in a solution of the carbo imine complexes in $CDCl_3$. A *t*-Bu substituent on the carbo imine group gives a higher exchange rate ($\Delta G_{298}^{\ddagger} = 75.9(2.4)$ kJ mol^{-1} for **1b**) than a tosylmethyl substituent ($\Delta G_{298}^{\ddagger} = 80.7(3.0)$ kJ mol^{-1} for **1c**). This is understandable as the *trans* influence of the carbo imine group will be enlarged by an electron-donating *t*-Bu group, thereby facilitating Pd−N bond breaking *trans* to the carbo imine group. The exchange process does not occur in the complexes **1** and **2**,[13] which can be explained by the smaller *trans* influence of a methyl group with respect to a carbo imine group or an acetyl group.[63] This indicates that destabilization of the initial state of the carbo imine complexes is an important factor contributing to the exchange process.

The $\Delta G_{298}^{\ddagger}$ values (75.9(2.4) kJ mol^{-1}) and the exchange rates ($k = 0.248$ s^{-1} in dichloromethane at 296.2 K) for complex **1b** are comparable with those for the complex (bpy)Pd(C(O)Me)Cl ($\Delta G_{298}^{\ddagger} = 75(4)$ kJ mol^{-1}; $k = 0.252$ s^{-1} in dichloromethane at 297 K), which is consistent with the similar *trans* influences of the acetyl and C(=N−2,6-Me$_2$C$_6$H$_3$)Me group.

The $\Delta G_{298}^{\ddagger}$ values for the bpy complexes **1b**,**c** ($\Delta G_{298}^{\ddagger} = 75.9(2.4)$ kJ mol^{-1} for **1b** and 80.7(3.0) kJ mol^{-1} for **1c**) are comparable with those for phen complexes **2b**,**c** ($\Delta G_{298}^{\ddagger} = 77.9(2.8)$ kJ mol^{-1} for **2b** and 81.2(3.3) kJ mol^{-1} for **2c**), whereas the $\Delta G_{298}^{\ddagger}$ value for complex **3b** containing bpm is lower (71.2(5.1) kJ mol^{-1} for **3b**), resulting in a faster exchange rate for this complex. The higher exchange rate for complex **3b** might be connected with the lower σ-coordinating capabilities of the ligand bpm with regard to the ligands bpy and phen, as mentioned in the results. It should be noted that the value for $\Delta S^{\ddagger}$ for complexes **1b**, **2b**, and **3b** is very small, while this value for the complexes **1c** and **2c** is largely negative. In addition, the values for $\Delta H^{\ddagger}$ for **1b**, **2b**, and **3b** are much larger than those for **1c** and **2c**, which we cannot readily explain.

Intermolecular ligand exchange as the source of the observed exchange can be excluded, since the exchange rates are not influenced by the concentration of the complex in $CDCl_3$ nor by the addition of free bidentate nitrogen ligand. Furthermore, as addition of 0.5−2 equiv of Cl anions to a mixture of complexes **1b**,**c**, **2b**,**c**, or **3b** in $CDCl_3$ at 294 K has no effect on the exchange rate, we might conclude that Pd−Cl bond breaking is not involved in the rate-determining step of the nitrogen donor exchange.

Conclusion

The neutral (N⁀N)Pd(Me)Cl complexes undergo facile and quantitative monoinsertion of isocyanides, which is the first step on the road to the polyimine analogue of polyketone. The mechanism of this reaction involves substitution of the halide by the isocyanide followed by a rate-determining methyl migration to the precoordinated isocyanide. A kinetic study on this reaction showed that the migration rate of the methyl group to

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the precoordinated isocyanide increases with increasing electrophilicity of the isocyanide.

The complexes (N⁀N)Pd(C(═N−R)Me)X show a fluxional behavior due to a site exchange of the nitrogen donor atoms. The mechanism of this process involves Pd−N bond breaking and subsequent isomerization via a Y-shaped intermediate.

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Supporting Information Available: Tables of crystal data, atomic coordinates, anisotropic thermal parameters, bond lengths, bond angles, and torsion angles of **29** (6 pages). Ordering information is given on nay current masthead page.

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