Organometallics **2003,** *22,* 3025−3027 3025

Synthesis and Structural Characterization of a Novel Dipalladium Complex with an Unprecedented PdCN Bonding Motif

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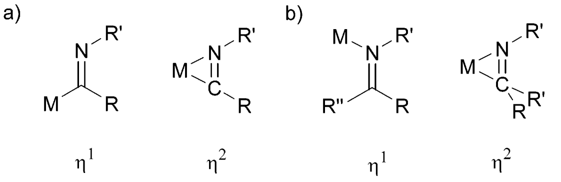
Received April 1, 2003

Summary: Removal of the chloride atom from $Pd\{C({=}NXy)CH_3\}(Cl)(Bu^t{}_2bipy)$ *initiates a series of reactions that lead to the formation of the novel dipalladium complex* $[Pd(Bu^t{}_2bipy)\{\eta^2\text{-}[Pd(Bu^t{}_2bipy)\{N(Xy){=}C(CH_3)\text{-}C(CH_3){=}NXy\}]\}][BF_4]_2$*. In this process, two imidoyl groups undergo a C−C coupling reaction generating a bis-imino ligand that coordinates to two palladium centers, one of which is bound to a C−N bond of the ligand giving an unprecedented three-membered PdCN ring.*

Insertion of small molecules such as CO, C_2H_4, and CNR into metal−carbon bonds has proven to be an efficient route for the synthesis of novel organic species and polymeric materials.[1,2] The migratory insertion of isocyanides (which are generally regarded as better σ-donors and weaker π-acceptors than CO)[3] into metal−carbon bonds yields imidoyl groups, which, in principle, can be coordinated to the metal in either an η^1- or η^2-fashion (see Scheme 1). While the lanthanides, actinides, and early transition metals tend to form η^2-complexes,[4] with the softer late transition metals η^1-coordination is usually observed. In group 10, for example, only nickel complexes have been reported to display η^2-coordination to the imidoyl group.[5] The first fully characterized example of this type of complex—with a nickel(II) center—was reported in 1990 by Carmona et al.[5a] Similarly, imines tend to form η^1 (σ-coordinated) complexes with the late transition metals rather than η^2-species. In group 10, although several nickel(0) complexes with η^2-coordination of imines have been reported,[6] very few are known with palladium[7] or platinum.[8]

Scheme 1. Possible Coordination Modes of Metal−Imidoyl (a) and Metal−Imine (b) Moieties



As part of a systematic investigation into metal-mediated C−C and C−N bond formation,[9] we have recently studied the reactivity of palladium−imidoyl complexes with a range of unsaturated species (such as olefins and isocyanates). By analogy with the work recently reported by Sen[10] and Arndtsen,[11] we investigated the possibility of inserting imines into the palladium−imidoyl bond of $Pd\{C({=}NXy)CH_3\}(Cl)(Bu^t{}_2bipy)$ (**2**) (where $Bu^t{}_2bipy$ = 4,4′-di-*tert*-butyl-2,2′-dipyridyl; Xy = 2,6-dimethylphenyl isocyanide). In the course of these

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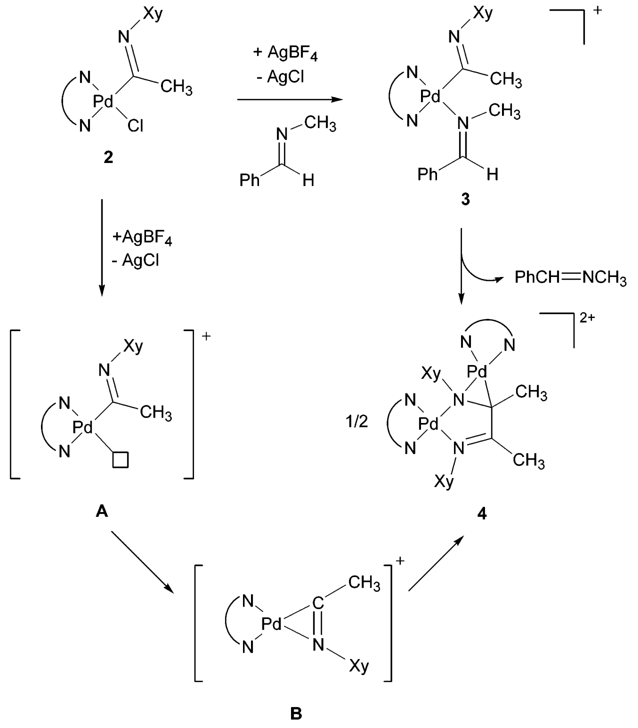
10.1021/om030235u CCC: $25.00
Publication on Web 06/25/2003

Scheme 2. Reaction Scheme Showing the Two Routes for the Synthesis of 4



studies the formation of the unprecedented dipalladium species [Pd(Bu$^t_2$bipy){η^2-[Pd(Bu$^t_2$bipy){N(Xy)═C(CH$_3$)-C(CH$_3$)═NXy}]}][BF$_4$]$_2$ (**4**) was observed and is herein reported (see Scheme 2). In this complex one of the palladium centers is η^2-coordinated to an imidoyl group, representing the first structurally characterized example of such a coordination mode for palladium.

The palladium−iminoacyl complex Pd{C(═NXy)CH$_3$}-(Cl)(Bu$^t_2$bipy) (**2**) was prepared by reacting Pd(CH$_3$)-(Cl)(Bu$^t_2$bipy) (**1**) with CNXy (following the method reported by Vrieze[12]). The IR spectrum of **2** shows an intense band at 1616 cm^{-1} associated with the characteristic ν(C═N) of inserted isocyanides. The ^{1}H NMR spectrum shows the expected resonances for the protons present in **2**; particularly indicative of the insertion process is a singlet at 2.27 ppm corresponding to the methyl protons of the −C(═NXy)CH$_3$ fragment (the same protons in the starting material appear at 0.82 ppm). The ^{13}C NMR spectrum also shows the expected signals for the proposed formulation. Two singlets at 29.1 and 163.5 ppm—assigned to the −*C*H$_3$ and *C*═NXy carbon atoms of the −C(═NXy)CH$_3$ moiety—indicate that the insertion of CNXy has taken place. The formulation was further confirmed by FAB(+) mass spectrometry (which showed the molecular peak at 556 amu corresponding to **2**) and elemental analyses.

With the aim of inserting an imine into the palladium−iminoacyl bond, complex **2** was reacted with 1 equiv of PhCH═NCH$_3$ in the presence of 1 equiv of AgBF$_4$. This reaction produced the new palladium complex [Pd{C(═NXy)CH$_3$}(Bu$^t_2$bipy){N(CH$_3$)═CHPh}]-[BF$_4$] (**3**), where the imine is σ-coordinated to the vacant site left upon removal of the chloride atom.[13] The IR spectrum of **3** showed the characteristic stretching frequencies associated with the iminoacyl group and the σ-coordinated imine (intense and broad bands between 1617 and 1587 cm^{-1}). The ^{1}H NMR spectrum shows all the expected resonances associated with the imine, the iminoyl groups, and the Bu$^t_2$bipy chelating ligand. Particularly indicative of the presence of the coordinated imine are the singlets at 8.65 and 3.91 ppm, which correspond to the CH and methyl protons in PhC*H*═NC*H*$_3$, respectively. The formulation of **3** was further confirmed by FAB(+) mass spectrometry (which showed the molecular peak at 641 amu corresponding to **3** − BF$_4$) and by elemental analyses. The spectroscopic characterization of this compound unambiguously demonstrated the coordination of the imine; however it did not show any evidence of insertion.

With the aim of obtaining single crystals of **3** for structural characterization, the crude solid was redissolved in CH$_2$Cl$_2$ and a layer of diethyl ether was added. The solution was left to stand for 2 days, after which time yellow-orange crystals were formed. Surprisingly, these crystals proved to have a different formulation than the original compound **3**. A single-crystal X-ray study of this material[14] revealed it to be the novel dipalladium species [Pd(Bu$^t_2$bipy){η^2-[Pd(Bu$^t_2$bipy)-{N(Xy)═C(CH$_3$)C(CH$_3$)═NXy}]}][BF$_4$]$_2$ (**4**). The unusual bimetallic structure of **4** comprises two "Pd(Bu$^t_2$bipy)" units linked by an organic fragment formed by the coupling of two iminoacyl units from the starting material (see Scheme 2 and Figure 1). The geometry at Pd(1) is distorted square planar with Pd−N bonds in the range 2.038(7)−2.059 Å, each of the two five-membered chelate rings being planar to within 0.038 Å. The coordination at Pd(2) comprises a conventional chelation to a Bu$^t_2$bipy ligand and an unprecedented coordination to a C−N bond from one of the coupled "iminoacyl" groups to give a three-membered PdCN ring, the nitrogen atom bridging the two palladium centers. The Pd(2)−N bonds to the Bu$^t_2$bipy ligand [2.109(7) Å to N(5) and 2.129(8) Å to N(6)] are both ca. 0.06 Å longer than their counterparts to Pd(1). The bond to N(6) is slightly longer than that to N(5), reflecting the different *trans* influences of carbon versus nitrogen. Within the three-membered ring the Pd(2)−N(4) and Pd(2)−C(1) distances of 2.092(8) and 2.054(10) Å are unexceptional, but the C(1)−N(4) distance of 1.431(10)

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[13] Synthesis of [Pd{C(═NXy)CH$_3$}(Bu$^t_2$bipy){N(CH$_3$)═CHPh}]-[BF$_4$] (**3**): To a solution of Pd{C(═NXy)CH$_3$}(Cl)(Bu$^t_2$bipy) (0.25 g, 0.45 mmol) in CH$_2$Cl$_2$ (25 mL) were added PhCH═NCH$_3$ (52 μL, 0.45 mmol) and AgBF$_4$ (0.09 g, 0.45 mmol). The reaction mixture was stirred for 30 min, during which time a fine precipitate (AgCl) was formed. The mixture was filtered to remove the silver salt and then concentrated under reduced pressure to ca. 10 mL. Upon addition of hexane (20 mL) a bright yellow solid precipitated and was isolated by filtration. Yield: 0.25 g, 0.34 mmol, 76%. Anal. Found: C, 59.55; H, 6.29; N, 7.69 (calcd for C$_{36}$H$_{45}$N$_4$PdBF$_4$: C, 59.48; H, 6.24; N, 7.71). IR (KBr): ν 1617 br, 1587 (C═N), 1058 (BF$_4$). ^{1}H (CDCl$_3$): δ 1.40 (s, 9H, ^{t}Bu), 1.46 (s, 9H, ^{t}Bu), 1.99 [br s, 9H, {6H, C$_6$H$_3$(C*H*$_3$)$_2$} + {3H, Pd(C═NR)C*H*$_3$}], 3.91 [br, s, 3H, N(C*H*$_3$)═CPhH], 6.72 [m, 1H, C$_6$*H*$_3$(CH$_3$)$_2$], 6.86 [m, 2H, C$_6$*H*$_3$(CH$_3$)$_2$], 7.48 [m, 5H, {3,3′-bipy} + {3,4,5-N═C(C$_6$*H*$_5$)H}], 7.91 [d, 1H, {2-bipy}, $^3J_{HH}$ = 5 Hz], 8.16 [s, 1H, 5-bipy], 8.20 [s, 1H, 5′-bipy], 8.49 [d, 1H, {2′-bipy}, $^3J_{HH}$ = 5.5 Hz], 8.65 [s, 1H, N═CPh*H*], 8.75 [m, 2H, {2,6-N═C(C$_6$*H*$_5$)H}]. MS (FAB)$^+$ *m*/*z* (rel int): 641 (3) [M − BF$_4$]$^+$, 520 (100) [M − BF$_4$ − imine]$^+$.

[14] Crystal data for **4**: [C$_{56}$H$_{72}$N$_6$Pd$_2$][BF$_4$]$_2$·1.5C$_6$H$_{13}$, M = 1343.4, monoclinic, $C2/c$ (no. 15), a = 34.094(3) Å, b = 16.575(2) Å, c = 24.868(2) Å, β = 113.15(1)°, V = 12922(2) Å^3, Z = 8, D_c = 1.381 g cm^{-3}, μ(Cu Kα) = 5.04 mm^{-1}, T = 203 K, yellow-orange needles; 8899 independent measured reflections, F^2 refinement, R_1 = 0.071, wR_2 = 0.163, 6368 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 120°], 680 parameters. CCDC 211066.

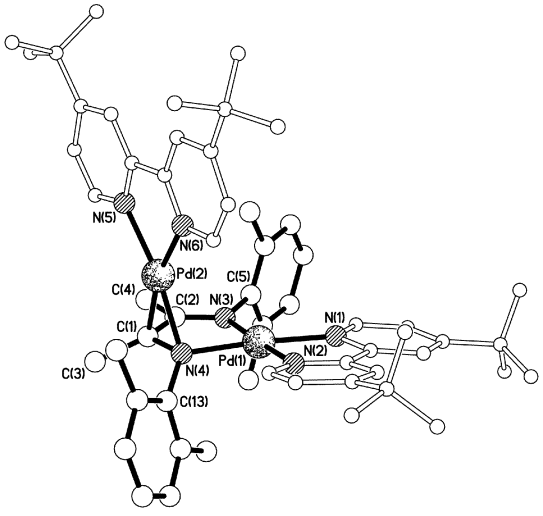

Figure 1. Molecular structure of **4**.

Å emphasizes its single-bond character. The three-membered ring is inclined approximately orthogonally (ca. 86°) to the ring formed by Pd(1) and the coupled "iminoacyl" moiety. The organic unit formed by the coupling of two iminoacyl groups can be regarded as a bis-imino ligand which chelates to Pd(1) and on coordination to Pd(2) loses the double-bond character of one of its original C═N linkages [C(1)−N(4)], while the other [C(2)═N(3) 1.306(11) Å] remains as an imino group. We believe that this is the first structurally characterized example of a three-membered PdCN ring. Indeed we have identified only one structurally characterized example of an analogous ring system occurring for platinum.[15] Examples involving nickel are more commonplace, but the C−N bond length in these systems is usually appreciably shorter and indicative of a partial π-coordination.[16,17]

The spectroscopic and analytical characterization of **4** is consistent with the structure revealed by X-ray crystallography. The IR spectrum shows the presence of intense (and broad) C═N stretching frequencies in the region between 1630 and 1549. These can be associated with the two different C═N(Xy) bonds and with the C═N bonds present in the $\text{Bu}^t{}_2$bipy ligand. The relatively low ν(C═N) value associated with the η^2-coordinated imidoyl group (in comparison to the value of around 1700 cm^{-1} for other metal η^2-imidoyl complexes)[5] is probably due to the coordination of this group, in **4**, to a second palladium center. The FAB(+) mass spectrum shows the molecular peak at 1127 amu, which corresponds to $[\mathbf{4} - \text{BF}_4]^+$. The ^{1}H NMR spectrum shows several broad singlets in the region between 1.34 and 2.75 ppm. These singlets correspond to the several methyl groups present in **4**, i.e., those associated with the $\text{Bu}^t{}_2$bipy ligand and with the Xy and $\text{C(CH}_3)$ methyl groups of the two different $-\text{C(C}H_3)\text{═NXy}$ moieties. The integration of these signals and those present in the aromatic region is consistent with the formulation of **4** (which was also confirmed by elemental analyses).

The conversion of **3** to the novel binuclear complex **4** implies the decoordination of the imine from the original compound and the carbon−carbon coupling of two iminoacyl fragments (which come from two different molecules of **3**). Consequently, **4** should also be formed by "dimerization" of the cationic species $[\text{Pd}\{\text{C(═NXy)CH}_3\}(\text{Bu}^t{}_2\text{bipy})]^+$ (**A** in Scheme 2). Thus, it was of interest to study the stability of **2** in solution upon removal of its chloride ligand. When **2** was dissolved in CH_2Cl_2 and 1 equiv of AgBF_4 was added to remove the chloride, a yellow-orange solution was obtained. After 30 min the solution was filtered to remove the AgCl, and upon addition of hexane a yellow-orange solid was obtained and characterized as **4** on the basis of ^{1}H NMR and IR spectroscopy, elemental analyses, and FAB(+) mass spectrometry (all of which gave the same data as the product obtained from **3** in CH_2Cl_2).[18]

The details of the pathway by which $[\text{Pd}\{\text{C(═NXy)CH}_3\}(\text{Bu}^t{}_2\text{bipy})]^+$ is converted into the novel dipalladium species **4** are not yet known. However, a mechanism for this process is likely to involve, first, the transformation of the η^1-imidoyl complex **A** into the η^2-imidoyl species **B** (see Scheme 2). The latter can then undergo a Pd−C bond cleavage followed by dimerization of two of these intermediate species via formation of new C−C and Pd−N bonds. The exact mechanism by which these events occur is not obvious, and further investigations will be carried out to elucidate it.

Acknowledgment. We are very grateful to EPSRC for financial support (G.R.O.) and Johnson Matthey PLC for a loan of palladium.

Supporting Information Available: Details about the syntheses of compounds **1**−**4** and the X-ray crystal structure, including ORTEP diagrams, and tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **4**, are available free of charge via the Internet at http://pubs.acs.org.

OM030235U

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(18) Synthesis of $[\text{Pd}(\text{Bu}^t{}_2\text{bipy})\{\eta^2\text{-}[\text{Pd}(\text{Bu}^t{}_2\text{bipy})\{\text{N(Xy)═C(CH}_3)\text{-C(CH}_3)\text{═NXy}\}]\}][\text{BF}_4]_2$ (**4**): To a solution of $\text{Pd}\{\text{C(═NXy)CH}_3\}(\text{Cl})(\text{Bu}^t{}_2\text{bipy})$ (0.16 g, 0.29 mmol) in CH_2Cl_2 (20 mL) was added AgBF_4 (0.06 g, 0.30 mmol). The resulting mixture was stirred for 30 min, during which time a fine precipitate (AgCl) was formed. The reaction mixture was filtered to remove the silver salt, and the yellow-orange filtrate was concentrated (to ca. 10 mL) under reduced pressure. Upon addition of hexane (15 mL), a yellow-orange solid was obtained. Yield: 0.12 g, 0.194 mmol, 68%. Anal. Found: C, 55.28; H, 5.96; N, 6.86 (calcd for $\text{C}_{56}\text{H}_{72}\text{N}_6\text{Pd}_2\text{B}_2\text{F}_8$: C, 55.33; H, 5.97; N, 6.91). IR (KBr): $\nu = 1617$ (C═N), 1549 (C═N), 1059 (BF_4). ^{1}H NMR (CD_2Cl_2): δ 1.34−1.45 [m, 42H, {4 × 9H, $\text{C(CH}_3)_3$} + {2 × 3H, N-$\text{C(CH}_3)$}], 2.45 [s, 3H, {$\text{C}_6\text{H}_3(\text{C}H_3)_2$}], 2.53 [s, 3H, {$\text{C}_6\text{H}_3(\text{C}H_3)_2$}], 2.59 [s, 3H, {$\text{C}_6\text{H}_3(\text{C}H_3)_2$}, 2.75 [s, 3H, {$\text{C}_6\text{H}_3(\text{CH}_3)$], 7.34−8.44 [m, 18H, [2 × 3H, {$\text{C}_6H_3(\text{CH}_3)_2$}] + [4 × 3H, {2,3,5-pyridine-H}]. MS (FAB)$^+$ m/z (rel int): 1127 (15) $[\text{M} - \text{BF}_4]^+$, 1041 (4) $[\text{M} - 2\text{BF}_4]^+$, 896 (20) $[\text{M} - 2\text{BF}_4 - \{\text{C(CH}_3)\text{═NXy}\}]^+$, 665 (26) $[(\text{Bu}^t{}_2\text{bipy})\text{Pd}\{\text{C(CH}_3)\text{═NXy}\}_2]^+$, 520 (78) $[(\text{Bu}^t{}_2\text{bipy})\text{Pd}\{\text{C(CH}_3)\text{═NXy}\}]^+$, 374 (100) $[(\text{Bu}^t{}_2\text{bipy})\text{Pd}]^+$.