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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsrt20</u>

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Version of record first published: 23 Mar 2012.

To cite this article: Guangming Nan , Yuancheng Qin & Zhijun Wei (2012): Bidentate Chelating N-Heterocyclic Carbene Complexes of Palladium: Synthesis and Structure, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42:2, 285-290

To link to this article: <u>http://dx.doi.org/10.1080/15533174.2011.610018</u>

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Bidentate Chelating N-Heterocyclic Carbene Complexes of Palladium: Synthesis and Structure

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The new cyclometalated racemic-chelated N-heterocyclic carbene palladium (II) complexes F_{a-b} derived from G have been prepared. The structure of cyclometalated race-chelated bidentate NHC-palladium (II) complexes F_{a-b} was characterized by ¹H NMR, ¹³C NMR X-ray, MS, and crystal diffraction.

Keywords crystal, N-heterocyclic carbine, palladium complexes, synthesis

INTRODUCTION

N-heterocyclic carbenes (NHCS) are the strong σ -donors bonding with metals and their greater stability toward heat, air, and moisture are compared to metal-phosphine complexes.^[1] With unique ligating properties, catalysts that incorporate NHCS as ligands have been applied to a broad range of reactions including olefin metathesis, hydrosylilation, and Pd-catalyzed cross-coupling reactions.^[2] Among these versatile catalysts, chelating bis(carbene) palladium (II) dihalide complexes are the efficient catalysts for various C–C and C–N coupling reactions.^[3] It is generally accepted that the chelate effect imparted on their metal complexes offers extra stability for the generation of robust metal complexes, which are highly desirable for catalytic applications, especially those requiring harsh reaction conditions.^[4]

Palladium-catalyzed coupling has become an indispensable tool for organic synthesis and there is a wide range of synthetically valuable transformations that can be catalyzed by palladium.^[5] However, chelating carbenes have not been as widely investigated in catalysis as monodentate NHCS.^[6–8] Several kinds of NHC-containing chelating type ligands; bisimidazolium salts **A**, **B**; and transition-metal complexes of chelating ligands with a linker, **C**, **D**, and **E** (Figure 1), have been reported.

In this article, we wish to report the synthesis and characterization of a novel cyclometalated biphenyl-chelated bidentate NHC-palladium (II) complex **F**. This biphenyl framework has certain unique characteristics, which allow making subtle alterations to its geometric, steric, and electronic properties.^[9] A chelate effect imparted on their metal complexes offers extra stability for the generation of robust metal complexes and their palladium(II) dihalide complexes are efficient catalysts for various C–C and C–N coupling reactions.

EXPERIMENTAL

General Procedures

Unless otherwise noted, all manipulations were performed under an argon atmosphere using standard Schlenk techniques. All chemicals were obtained from commercial sources and were generally used without further purification. All solvents were dried according to standard procedures. (Race)-2-amino-2'-nitro-6,6'-dimethyl-1,1'-biphenyl (G) was prepared according to literature.^[9] Melting points were determined with XRC-1 melting point apparatus and were uncorrected. ¹H (400 MHz, 600 MHz) and ¹³C (100 MHz, 150 MHz) NMR spectra were recorded using Bruker instruments. All NMR spectra were acquired at room temperature. X-ray structural analysis was carried out in Sichuan University.

X-ray Crystal Structure Determination and Refinement

X-ray single-crystal diffraction data for $\mathbf{F_a}$ were collected on an Enraf-Nonius CAD-4 diffractometer at 294(2) K with Mo K α radiation ($\lambda = 0.71073$ Å) by $\omega/2\theta$ scan mode. The structures were solved with direct methods using SHELXS-97 and refined by full-matrix least-squares refinement on F^2 with SHELXL-97.^[10] All atoms except hydrogen atoms were refined with anisotropic displacement parameters. In general, hydrogen

Received 15 May 2010; accepted 30 July 2011.

The authors thank the Natural Science Foundation of China for financial support (No. 20962022). They are also grateful to the Analytical & Testing Center of Sichuan University for support in NMR, MS, and X-ray crystal structure analyses.

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FIG. 1. The structure of NHC ligands and transition-metal complexes.

atoms were fixed at calculated positions, and their positions were refined by a riding model.

Crystal/refinement data for **F**_a: formula C₄₀H₄₂N₄Br₂Pd, M = 847.03, size 0.46 × 0.42 × 0.40 mm, monoclinic, space group C 2/c, a = 23.163(4) Å, b = 11.430(3) Å, c = 21.000(3) Å, $\alpha = 90^{\circ}$, $\beta = 91.57(3)^{\circ}$, $\gamma = 90^{\circ}$, F(000) = 2632, V = 5558 (2) Å³, T = 294(2) K, Z = 4, D (Calcd.) = 1.580 mg/m³, μ = 2.383 mm⁻¹, Max of h, k, l = 27, 13, 24, respectively. Reflection collected 4920, Independent Reflections 4639 [R (int) = 0.0066], refinement method full-matrix least-squares on F^2 with SHELXL-97.

(Race)-2-imidazole-1-yl)-2'-nitro-6,6'-dimethyl-1, 1'-biphenyl (H)

40% aqueous glyoxal (725 mg, 5.0 mmol) and 37% aqueous formaldehyde (405 mg, 5.0 mmol) was added to 25 ml acetic acid. The mixture was heated with stirring to 85°C, and then G ((Race)-2-amino-2'-nitro-6,6'-dimethyl-1,1'biphenyl)^[9] (484 mg, 2 mmol) was added dropwise along with 15 ml acetic acid, 5 ml water, and ammonium acetate (385 mg, 5.0 mmol) for 30 min. The mixture was stirred 8 h at 85°C and cooled to room temperature. A saturated aqueous solution of NaHCO₃ was added and adjusted pH of 7-8. The mixture was extracted with dichloromethane $(3 \times 30 \text{ ml})$. The fractions were combined, dried over MgSO₄, and filtered. After solvent was evaporated, the residue was purified by flash chromatography on silica gel (CH₂Cl₂/MeOH = 30/1). H was eluted with vield: 504 mg, 86%, pale vellow solid, mp 79–80°C. ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3, \text{TMS}): \delta = 1.97 \text{ (s, 3H, ArCH}_3), 2.02 \text{ (s, 3H, ArCH}_3)$ ArCH₃), 6.84 (s, 1H, imi-H), 6.91 (s, 1H, imi-H), 7.23–7.26 (m, 1H, NCHN), 7.36–7.45 (m, 5H, Ar-H). 7.778–7.78 (d, J = 0.8 Hz, 1H, Ar-H). ¹³C NMR (400 MHz, CDCl₃): δ 149.73, 138.87, 137.65, 137.30, 135.76, 134.98, 132.36, 130.78, 130.56, 129.07, 128.93, 124.12, 122.18, 120.31, 20.06 (CH₃), 19.85 (CH₃). MS (ESI): *m/z* 294.1 ([M + H]⁺).

(Race)-2-imidazole-1-yl -2'-amino-6,6'-dimethyl-1, 1'-biphenyl (I)

H (586 mg, 2.0 mmol), active carbon (590 mg), and FeCl₃·6H₂O (10 mg, 0.04 mmol) were added to methanol (30 ml) and the mixture was heated with stirring to reflux. hydrazine hydrate was added dropwise for 1 h. The solvent was refluxed for 17 h and filtered. The filtrate was dried over MgSO₄ and filtered. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (petroleum ether / EtOAc : 9/1). I was eluted with yield: 463 mg, 88%, white solid, mp 170–171°C. ¹H NMR (400 MHz, DMSO-d₆): $\delta = 1.60$ (s, 3H, ArCH₃), 2.00 (s, 3H, ArCH₃), 4.53 (s, 2H, $ArNH_2$),6.36–6.38 (d, J = 7.2 Hz, 1H, imi-H), 6.56–6.58 (d, J = 8.0 Hz, 1H, imi-H), 6.79 (s, 1H, Ar-H), 6.87–6.91 (t, J = 7.8 Hz, 1H, Ar-H), 7.12–7.13 (t, J = 1.2 Hz, 1H, NCHN), 7.30–7.33 (m, 1H, Ar-H), 7.43–7.47 (m, 2H, Ar-H), 7.54 (s, 1H, Ar-H). ¹³C NMR (400 MHz, CDCl₃): δ 143.86, 139.50, 137.28, 137.03, 136.31, 132.66, 130.34, 128.87, 128.82, 128.79, 123.67, 121.79, 120.19, 120.08, 112.66, 19.74 (CH₃). MS (ESI): m/z 263.1 ([M $+ H^{+}).$

(Race)-2,2'-bis(imidazole-1-yl)-6,6'-dimethyl-1, 1'-biphenyl (J)

J was prepared in the similar way to **H** from **I** (526 mg, 2.0 mmol). **J** was purified by flash chromatography on silica gel (CH₂Cl₂/MeOH = 20/1) and was eluted with yield: 565 mg, 90%. mp 129–131°C. ¹H NMR (400 MHz, CDCl₃): δ = 2.21 (s, 6H, ArCH₃), 6.39 (s, 2H, imi-H), 6.87 (s, 2H, imi-H), 6.93 (s, 2H, Ar-H), 7.05–7.07 (m, 2H, NCHN), 7.36–7.37 (t, J = 3 Hz, 4H, Ar-H). ¹³C NMR (400 MHz, CDCl₃): δ 138.91, 136.84,

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135.60, 131.49, 130.17, 129.38, 128.75, 123.58, 119.77, 20.01 (CH₃). MS (ESI): *m/z* 314.2 ([M + H]⁺).

(Race)-2,2'-bis[3-(2,4,6-trimethylbenzyl)imidazolium-1yl]-6,6'-dimethyl-1,1'-biphenyl dibromide (K_a)

J (361 mg, 1.15 mmol), 2-(bromomethyl)-1,3,5trimethylbenzene (1224 mg, 5.75 mmol) were dissolved in dioxane (5 ml). Under argon, the mixture was heated to 85°C and stirred for 1 h, and a white precipitation was formed and stirred for another 8 h. The solid K_a was obtained after filtration and washed with diethyl ether (2 \times 20 ml). The K_a was purified by flash chromatography on silica gel (CH2Cl2: MeOH = 10: 1). K_a was eluted with yield: 791 mg, 93%. white solid. mp 250°C. ¹H NMR (400 MHz, CDCl₃): $\delta = 2.14$ (s, 6H, ArCH₃), 2.28 (s, 6H, ArCH₃), 2.30 (s, 12H, ArCH₃), 5.66-5.70 (d, J = 14.8 Hz, 2H, ArCH₂), 5.95-5.99 (d, J = 14.8 Hz, 2H, ArCH₂), 6.88 (s, 4H, imi-H), 7.10–7.14 (d, J = 16.4, 4H, Ar-H), 7.51–7.54 (m, 4H, Ar-H), 7.58–7.62 (t, J = 7.8, 2H, Ar-H), 10.11 (s, 2H, NCHN). ¹³C NMR (400 MHz, DMSO-d₆): *δ* 139.51, 139.24, 138.53, 135.87, 133.36, 133.23, 130.91, 129.88, 129.76, 126.78, 125.43, 123.80, 123.41, 47.89 (CH₂), 21.09 (CH₃), 19.89 (CH₃), 19.73 (CH₃). MS (ESI): m/z 290.2 ([(M -2Br) /2]⁺).

(Race)-2,2'-bis(3-benzylimidazolium-1-yl)-6,6'-dimethyl-1,1'-biphenyl dibromide (K_b)

 K_b was prepared in the same way as K_a from J (361 mg, 1.15 mmol) and 1-(bromomethyl) benzene (983 mg, 5.75 mmol)

in dioxane (5 ml). **K**_b was eluted with yield: 693 mg, 92%. white solid, mp 250°C. ¹H NMR (400 MHz, DMSO-d₆): δ = 2.07 (s, 6H, ArCH₃),5.40 (s, 4H, ArCH₂), 7.21–7.23 (dd, J = 2.0 Hz, J = 7.6 Hz, 4H, imi-H), 7.27–7.28 (t, J = 1.6 Hz, 2H, Ar-H),7.41–7.47 (m, 6H, Ar-H), 7.56–7.69 (m, 6H, Ar-H), 9.11–9.12 (t, J = 1.4, 2H, NCHN). ¹³C NMR (400 MHz, DMSO-d₆): δ 139.18, 136.05, 134.31, 132.96, 132.80, 130.50, 129.12, 128.94, 128.77, 128.43, 124.62, 123.27, 123.03, 51.74 (CH₂), 19.74 (CH₃). MS (ESI): m/z 248.1 ([(M -2Br)/2]⁺).

(Race)-2,2'-bis(3-(2,4,6-trimethylbenzyl)imidazolin-2yliden-1-yl)-6,6'-dimethyl-1,1'-biphenyl dibromide palladium (F_a)

K_a (74 mg, 0.1 mmol), Pd(OAc)₂ (22 mg, 0.1 mmol), KO'Bu (17 mg, 0.15 mmol) was refluxed in THF or dioxane (10 ml) for 8 h. The solvent was removed under reduced pressure and the residue was separated by silica gel chromatography (CH₂Cl₂/MeOH = 10/1) to give Pd(II)-NHC complex **F**_a: 52 mg, 62%. yellow solid, mp 250°C. ¹H NMR (600 MHz, CDCl₃): $\delta = 1.92$ (s, 6H, ArCH₃), 2.09 (s, 12H, ArCH₃), 2.28 (s, 6H, ArCH₃), 5.15–5.18 (d, J = 14.4 Hz, 2H, ArCH₂), 6.07–6.10 (d, J = 16.2 Hz, 2H, ArCH₂), 6.38–6.46 (m, 4H, imi-H), 6.85 (s, 4H, Ar-H), 7.19–7.21 (d, J = 7.2 Hz, 2H, Ar-H), 7.36–7.39 (t, J = 7.5 Hz, 2H, Ar-H), 7.55–7.56 (d, J = 7.2 Hz, 2H, Ar-H). ¹³C NMR (400 MHz, CDCl₃): δ 159.01, 139.27, 139.03, 138.60, 137.54, 134.47, 131.14, 129.66, 129.18, 127.75, 124.19, 120.23, 52.21 (CH₂), 21.02 (CH₃), 20.61 (CH₃), 19.73 (CH₃). MS (ESI): *m/z* 844.1 ([M]⁺).



SCH. 1. Synthesis of the biphenyl-Linked Bis-NHC Chelate Ligands Ka-b.





(Race)-2,2'-bis(3-benzylimidazolin-2-yliden-1-yl)-6,6'dimethyl-1,1'-biphenyl dibromide palladium (F_b)

K_b (66 mg, 0.1 mmol), Pd(OAc)₂ (22 mg, 0.1 mmol), KO'Bu (17 mg, 0.15 mmol) was refluxed in THF or dioxane (10 ml) for 8 h. The solvent was removed under reduced pressure and the residue was seperated by silica gel chromatography (CH₂Cl₂/MeOH = 10/1) to give Pd(II)-NHC complex **F**_b: 51 mg, 67%. yellow solid, mp 250°C. ¹H NMR (600 MHz, CDCl₃): $\delta = 1.91$ (s, 6H, ArCH₃), 5.43–5.45 (d, J = 15.0 Hz, 2H, ArCH₂), 6.01–6.03 (d, J = 15.0 Hz, 2H, ArCH₂), 6.49–6.55 (d, J = 37.2 Hz, 4H, imi-H), 7.09–7.17 (m, 8H, Ar-H), 7.27–7.43 (m, 8H, Ar-H). ¹³C NMR (400 MHz, CDCl₃): δ 159.84, 139.00, 137.44, 135.29, 134.48, 130.93, 129.68, 129.32, 128.72, 128.29, 124.08, 123.28, 121.67, 58.02 (CH₂), 19.72 (CH₃). MS (ESI): *m/z* 762.0 ([(M]⁺).

RESULTS AND DISCUSSION

Proligand Synthesis

The synthetic bisimidazolium salt precursors **G-K** used to prepare the complexes are shown in Scheme 1.

Initially, (Race)-2-amino-2'-nitro-6,6'-dimethyl-1,1'-biphenyl (G) was prepared according to literature.^[9] Racemic H was obtained by one-pot synthesis starting from G, glyoxal and formaldehyde. The yield of the reaction can be arrived at 86%. Racemic H, active carbon, FeCl₃·6H₂O were added to methanol and the mixture was heated with stirring to reflux. Hydrazine hydrate was added dropwise. The corresponding racemic I in 88% yield was obtained. With the same procedure as racemic **H**, racemic **J** was produced at 90%. The desired bisimimidazolium salts $\mathbf{K_{a\cdot b}}$ were obtained in 93–92% yields by the racemic **J** with $\mathbf{R_{a\cdot b}}$ -X in dioxane under inert Ar at 85°C. ¹H and ¹³C NMR spectroscopic data for $\mathbf{K_{a\cdot b}}$ obtained show spectra consistent with C₂ symmetry, and in the ¹H NMR spectra, characteristic signals of the bisimidazolium salt NC(H)N protons are observed in the region among δ 10.11 and 9.11 ppm. These values fall in the range observed for related bisimidazolium salts.¹¹ We used other ways to obtain $\mathbf{K_{a\cdot b}}$ conveniently but it was unsuccessful as was shown in Scheme 2.

Metal Complex Synthesis

Under Ar protection, The reaction of the obtained bisimidazolium salts $\mathbf{K_{a-b}}$ with Pd(OAc)₂ under reflux in THF or dioxane produced the corresponding cyclometalated racemic-chelated N-heterocyclic carbene palladium(II) complexes $\mathbf{F_{a-b}}$ in 62% and 67%, respectively (Scheme 3). The products were isolated as air- and moisture-stable yellow solid in moderate yields. Their structures were fully characterized by spectroscopic data.

For example, the presence of racemic-chelated N-heterocyclic carbene palladium(II) complexes F_{a-b} was evidenced from its ¹³C NMR spectrum, with two NCN signals at δ 159.01 and 159.84. ¹² Also, The absence of the NC(H)N proton resonances in the ¹H NMR spectra, which demonstrate that the ligand is coordinated to palladium in dianionic bis-NHC form. In addition, yellow single crystals of complex F_a suitable for X-ray crystal structure analysis were grown from a solvent of



SCH. 3. Synthesis of the biphenyl-Linked Bis-NHC Chelate palladium(II) complexes Fa-b.



FIG. 2. Molecular structure of complex $\mathbf{K}_{a.}$ shows 30% probability displacement ellipsoids. H atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Pd (1)-C (1) = 1.830(19), Pd (1)-C (1)^{#1} = 1.830 (19), Pd (1)-Br (1) = 2.499(2), Pd (1)-Br (1)^{#1} = 2.499(2), C (1)-Pd (1)-Br (1) = 90.0(4), C (1)-Pd (1)-Br (1)^{#1} = 166.8(6), C (1)^{#1}-Pd (1)-C (1) = 93.1(8).

CHCl₃. On the basis of X-ray diffraction, the structure of complex F_a was unambiguously determined. Its molecular structure is depicted in Figure 2.

As expected, the dianionic ligand is coordinated to palladium in a dentate fashion by the two carbene atoms, forming a ninemembered chelate rings. X-ray analysis of these crystals showed the geometry of the ligand around the metal to be distorted square planar. The Pd (1)-C (1) bond length was 1.830 Å and Pd (1)-Br (1) bond length was 2.499 Å. The C (1)-Pd-C (1') bond angle was determined to be 93.1°. The Br (1)-Pd (1)-(Br') bond angle was 89.9°.

CONCLUSION

In summary, we have synthesized a new class of biphenylchelated bidentate-type NHC ligand precursors and cyclometalated biphenyl-chelated bidentate NHC-palladium (II) complexes F_{a-b} . On the basis of X-ray diffraction, the structure of the complexes was determined. Complexes F_{a-b} are stable under moisture and air at room temperature. The present ligands are versatile because they can be further modified by changing the aromatic ring substituents or N-substituents in the imidazole moiety, thus tuning either the sterics or the electronics, which are very promising for the construction of highly active transition-metal catalysts.

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