

SYNTHESIS AND CHARACTERIZATION OF FULLERENE-PYRIDYL ARENE RUTHENIUM COMPLEXES

DIVAMBAL APPAVOO^a, ROBERT DESCHENAUX^{a*},
BRUNO THERRIEN^{a*}

ABSTRACT. Association of [60]fullerene with arene ruthenium moieties has been achieved for the first time. Two fullerenopyrrolidine derivatives ($N_{\text{pyr}}\text{-C}_{60}$) were synthesized *via* a 1,3-dipolar cycloaddition, and coordinated to arene ruthenium complexes to form two half-sandwich complexes of the general formula (*p*-cymene)RuCl₂($N_{\text{pyr}}\text{-C}_{60}$). The coordination of the fullerenopyrrolidines to the arene ruthenium unit was evidenced by NMR spectroscopy and mass spectrometry, thus confirming the formation of these novel arene ruthenium complexes.

Keywords: fullerene; arene ligand; ruthenium; pyridyl ligand; half-sandwich complexes

INTRODUCTION

In the last 25 years, a lot of progress has been made to the chemistry of fullerenes [1]. However, the most stable and abundant member of the fullerene family, [60]fullerene (C_{60}), remains the most popular derivative [2]. In spite of this popularity, its direct application is often hampered by its poor solubility and processability. Functionalization of the C_{60} by reactions such as Bingel and 1,3-dipolar cycloaddition has allowed an expansion of the fullerene chemistry [3]. A wide range of fullerene derivatives have since been synthesized by combining the electron acceptor fullerene with various donors such as tetrathiafulvalenes, conjugated oligomers, porphyrins and ferrocenes [4]. The study of these materials for their intramolecular photo-induced energy and electron transfer processes has shown useful properties for applications in

^a *Université de Neuchâtel, Institut de Chimie, Avenue de Bellevaux 51, 2000 Neuchâtel, Switzerland.*

* *Corresponding authors: robert.deschenaux@unine.ch; bruno.therrien@unine.ch*

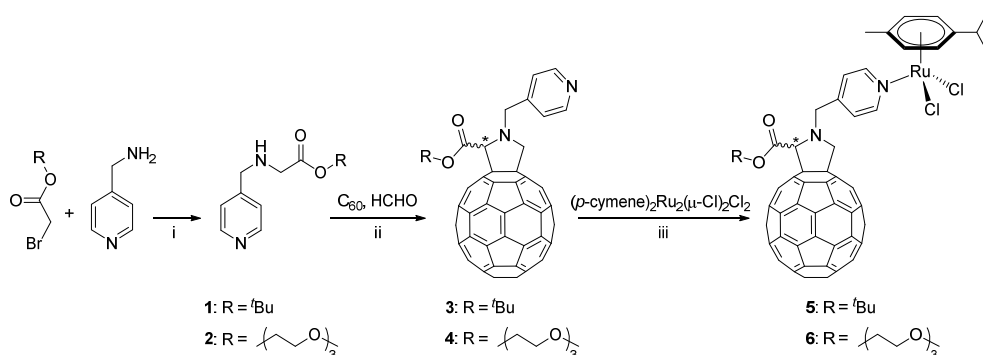
solar cell technologies [5]. This photochemical property of fullerene has been particularly interesting in systems containing coordinating metals. Complexes combining fullerene and d^6 or d^{10} metal ions have shown to exhibit long lived metal-to-ligand charge transfer excited state which stimulated photo-induced electron transfer to the fullerene sphere [6]. Such systems are good candidates for photovoltaic devices. For example, fullerene-based tris(2,2'-bipyridine)ruthenium(II) complexes have been found to possess good energy conversion efficiencies [7]. Other ruthenium-fullerene complexes have been synthesized, like $(\eta^5\text{-C}_{60}\text{Me}_5)\text{RuCl}(\text{CO})_2$, for potential applications in material science and catalysis, yet, the association of fullerene with ruthenium remains generally unexplored [8].

Half-sandwich arene ruthenium complexes, which are an important part of the ruthenium chemistry, have been increasingly used in the development of organometallic chemistry [9]. The arene ligand provides a better control for the coordination of ligands to the metal center and protects the ruthenium center from rapid oxidation [10]. These complexes adopt a pseudo-tetrahedral geometry, with the potential of coordinating three different ligands to the ruthenium center. Mono- and polydentate pyridyl-based ligands have been used extensively for coordination to arene ruthenium moieties, thus resulting in mono- and polynuclear supramolecular assemblies. Moreover, arene ruthenium complexes have found applications in different fields, including anticancer research [11], catalysis [12] and liquid-crystalline material [13].

Despite widespread studies in these two individual fields, to the best of our knowledge, the combination of fullerene with arene ruthenium unit has yet to be accomplished. We hereby report the synthesis and characterization of the first fullerene-based arene ruthenium complexes.

RESULTS AND DISCUSSION

The $N_{\text{pyr}}\text{-C}_{60}$ compounds **3** and **4** (Scheme 1) were synthesized under standard 1,3-dipolar cycloaddition conditions by the addition of the pyridine *N*-modified glycines **1** or **2** to [60]fullerene in the presence of formaldehyde. Compounds **1** and **2** were in turn prepared by reacting the commercially available 4-(aminomethyl)pyridine with the corresponding alkyl bromides, *tert*-butyl bromoacetate and 2-[2-(2-methoxyethoxy)ethoxy]ethyl bromoacetate, respectively. Treatment of **3** and **4** with 0.5 molar equivalent of $(p\text{-cymene})_2\text{Ru}_2(\mu\text{-Cl})_2\text{Cl}_2$ gave the neutral half-sandwich $(p\text{-cymene})\text{RuCl}_2(N_{\text{pyr}}\text{-C}_{60})$ complexes **5** and **6**, which were isolated in excellent yields as dark solids. The two complexes showed good solubility in organic solvents, but remained insoluble in water.



Scheme 1. Synthesis of complexes **5** and **6**, and the $N_{\text{pyr}}\text{-C}_{60}$ derivatives **3** and **4** starting from alkyl bromides and primary amines. Reagents and conditions: i. NEt_3 , THF, 0°C to rt, 16h, **1**: 60%, **2**: 32%, ii. toluene, 110°C , 16h, **3**: 51%, **4**: 24%, iii. CH_2Cl_2 , reflux, 24h, in the dark, **5**: 98%, **6**: 92%.

The ^1H NMR spectra of the $N_{\text{pyr}}\text{-C}_{60}$ derivatives **3** and **4** revealed the expected signals for this family of fulleropyrrolidines [15]. One characteristic feature of such compounds is that the methylene protons located in α positions with respect to the pyrrolidine nitrogen are diastereotopic due to the asymmetric carbon on the pyrrolidine unit (the asymmetric carbon being identified with an asterisk in Scheme 1). For instance, the protons of the CH_2 group linking the pyrrolidine to the pyridine, which appear as a doublet at $\delta = 3.30$ ppm in compound **1** (see experimental section), can be seen as two doublets in **3**, at $\delta = 4.93$ and 4.30 ppm, respectively. Similarly, the CH_2 protons of the pyrrolidine group ($\delta = 3.81$ ppm in **1**) are now observed as two doublets at $\delta = 4.69$ and 4.14 ppm in **3** (Figure 1). Moreover, complexation to the ruthenium center results in a major downfield shift of the signal corresponding to the protons of the pyridyl groups, mainly H_α ($\Delta\delta = +0.4$ ppm) and H_β ($\Delta\delta = +0.1$ ppm) (Figure 1). This is characteristic for the coordination of a pyridyl moiety to an arene ruthenium unit [16]. However, the other protons of the $N_{\text{pyr}}\text{-C}_{60}$ ligands **3** and **4** do not undergo any significant shift as a result of the complexation.

The formation of the complexes was also confirmed by electrospray mass spectrometry (ESI-MS). However, the two complexes behave differently under the ESI-MS conditions. Complex **5** showed a cationic species at $m/z = 1225.1$, which can be assigned to complex **5** after the loss of a chloride anion, $[\mathbf{5} - \text{Cl}]^+$, while in **6**, a sodium adduct was found at $m/z = 1363.2$, $[\mathbf{6} + \text{Na}]^+$. The loss of a chloride atom in dichloropyridyl arene ruthenium complexes is relatively common under ESI-MS conditions [17]. Similarly, the formation of sodium adducts has been observed previously [18]. In addition to the peak $[\mathbf{5} - \text{Cl}]^+$ for complex **5**, the mass peak observed at $m/z = 1475.3$ corresponds to a dinuclear species in which the ^tBu group is lost and insertion of a (*p*-cymene)RuCl unit occurs, thus giving rise to the adduct $[\mathbf{5} - ^t\text{Bu} + (\textit{p}\text{-cymene})\text{RuCl} + \text{H}]^+$ (Figure 2).

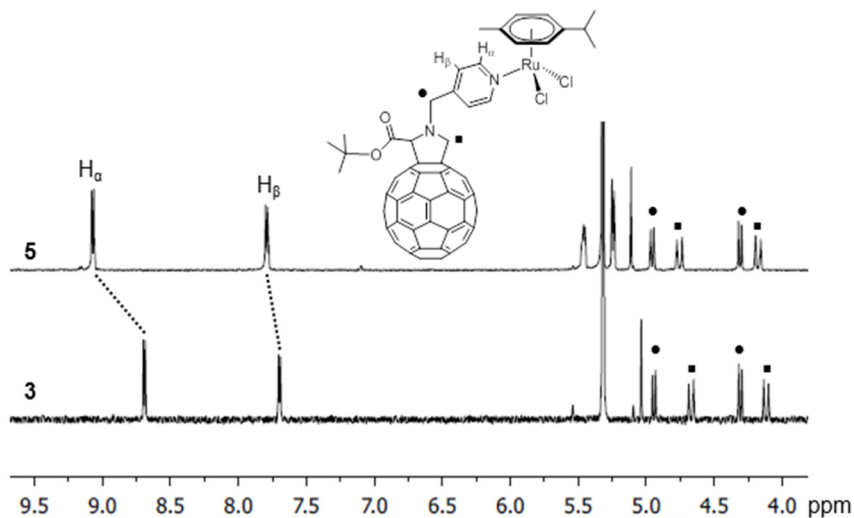


Figure 1. Comparative ¹H NMR spectra of compounds **3** and **5** (400 MHz, CD₂Cl₂). The pyrrolidine CH₂ protons and the exocyclic CH₂ are indicated with ■ and ●, respectively.

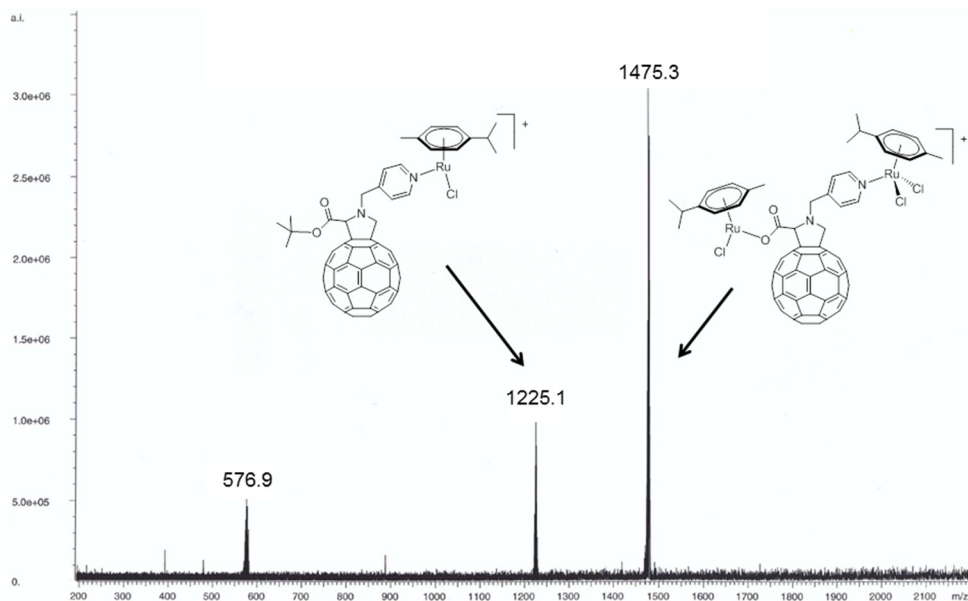


Figure 2. ESI mass spectrum of **5** (in CHCl₃/CH₃CN).

CONCLUSIONS

Two (*p*-cymene)RuCl₂(N_{pyr}-C₆₀) complexes have been synthesized and characterized by NMR spectroscopy and ESI mass spectrometry. These complexes can be exploited for further reactions to afford other derivatives (to be published). Such fullerene-based arene ruthenium complexes and their congeners can be of interest for applications in biomedical, catalysis and material science.

EXPERIMENTAL SECTION

Toluene (NaH, under N₂), THF (K and Na, under N₂) and CH₂Cl₂ (P₂O₅, under N₂) were distilled prior to use. [60]Fullerene (99.9%) was purchased from Materials and Electrochemical Research (MER) Corporation, Tucson (AZ), USA. 4-(Aminomethyl)pyridine and all other reagents were commercially available (Sigma-Aldrich), while (*p*-cymene)₂Ru₂(μ-Cl)₂Cl₂ was prepared according to literature [19].

Column chromatography was performed using silica gel (Chemie Brunschwig, Basel, Switzerland, 63-200, 60Å). Size exclusion chromatography was carried out using size exclusion gel Bio-Rad SX1 with the range of mass operation between 600 and 14000 Da. NMR spectra were measured in CDCl₃ or in CD₂Cl₂ on a Bruker AMX-400 (400 and 100 MHz) or a Bruker Advance-400 spectrometer and are reported in ppm on the δ scale. The mass spectrometry measurements were performed on a LCQ-IT Finnigan or on a Bruker FRMS 4.7T BioAPEX II for ESI.

Preparation of *tert*-butyl(pyridin-4-yl-methyl)glycinate, **1**

To a solution of 4-(aminomethyl)pyridine (0.81 g, 7.50 mmol) and triethylamine (1.52 g, 15.00 mmol) in dry THF (40 mL), a THF solution (25 mL) of *tert*-butyl bromoacetate (0.98 g, 5.00 mmol) was added dropwise at 0°C. After 16h of reaction at RT, the solvent was evaporated and the residue was dissolved in dichloromethane (50 mL). The organic phase was washed (H₂O), dried (MgSO₄) and evaporated. Purification of the residue by column chromatography (eluent CH₂Cl₂/MeOH 10/0.75) gave pure **1** as an orange/red liquid with a yield of 60% (0.66 g). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 8.54 (d, ³J_{H-H} = 6.0 Hz, 2H, H_α pyridine), 7.27 (d, ³J_{H-H} = 5.6 Hz, 2H, H_β pyridine), 3.81 (s, 2H, CH₂CO₂Bu), 3.30 (s, 2H, CH₂C_{pyridine}), 2.09 (s, 1H, NH), 1.46 (s, 9H, C(CH₃)₃). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 171.25, 149.54, 148.92, 123.18, 81.63, 51.89, 50.79, 28.12. MS (ESI(+)) = 223.3 [M + H]⁺.

Preparation of 2-(2-(2-methoxyethoxy)ethoxy)ethyl(pyridin-4-yl-methyl)glycinate, **2**

Compound **2** was prepared and purified as **1**, from 4-(aminomethyl)pyridine (0.16 g, 1.50 mmol), triethylamine (0.30 g, 3.00 mmol), 2-(2-(2-methoxyethoxy)ethoxy)ethyl bromoacetate (0.28 g, 1.00 mmol) and dry THF (80 mL). Product **2** was isolated as a pale yellow liquid with a yield of 32% (0.10 g). ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 8.56 (d, $^3J_{\text{H-H}} = 6.1$ Hz, 2H, H_α pyridine), 7.28 (d, $^3J_{\text{H-H}} = 6.1$ Hz, 2H, H_β pyridine), 4.30 (t, $^3J_{\text{H-H}} = 4.7$ Hz, 2H, H_{peg}), 3.87 (s, 2H, $\text{CH}_2\text{C}_{\text{pyridine}}$), 3.68-3.71 (m, 2H, H_{peg}), 3.63-3.66 (m, 6H, H_{peg}), 3.53-3.55 (m, 2H, H_{peg}), 3.45 (s, 2H, $\text{CH}_2\text{CO}_2\text{peg}$), 3.37 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ = 171.86, 149.27, 123.31, 71.90, 70.58, 68.96, 64.04, 61.64, 59.00, 51.72, 49.82. MS (ESI(+)) = 313.3 [$\text{M} + \text{H}$] $^+$.

Preparation of *tert*-butyl(*N*-ethylpyridine)fullerenopyrrolidine carboxylate, **3**

To a solution of [60]fullerene (0.36 g, 0.50 mmol) in dry toluene (300 mL), a suspension of **1** (0.11 g, 0.50 mmol) and *para*-formaldehyde (0.07 g, 2.50 mmol) in dry toluene (10 mL) was added. The mixture was stirred under reflux for 16h in the dark and evaporated to dryness. Purification of the solid by column chromatography (first with toluene to eliminate unreacted [60]fullerene, and then with toluene/MeOH 20:1) gave **3** as a shiny black solid with a yield of 51% (0.24 g). ^1H NMR (400 MHz, CD_2Cl_2 , ppm): δ = 8.69 (d, $^3J_{\text{H-H}} = 5.2$ Hz, 2H, H_α pyridine), 7.70 (d, $^3J_{\text{H-H}} = 5.3$ Hz, 2H, H_β pyridine), 5.04 (s, 1H, CHCO_2^tBu), 4.96 (d, $^3J_{\text{H-H}} = 9.3$ Hz, 1H, $\text{HCHC}_{\text{pyridine}}$), 4.69 (d, $^3J_{\text{H-H}} = 14.0$ Hz, 1H, $\text{HCH}_{\text{pyrrolidine}}$), 4.32 (d, $^3J_{\text{H-H}} = 9.3$ Hz, 1H, $\text{HCHC}_{\text{pyridine}}$), 4.14 (d, $^3J_{\text{H-H}} = 14.0$ Hz, 1H, $\text{HCH}_{\text{pyrrolidine}}$), 1.53 (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (100 MHz, CD_2Cl_2 , ppm): δ = 168.58, 154.49, 153.76, 152.44, 151.22, 150.14, 147.34, 146.95, 146.23, 146.01, 145.33, 145.21, 144.58, 144.44, 143.02, 142.56, 142.17, 142.11, 142.05, 142.04, 141.74, 140.18, 140.13, 138.69, 139.28, 136.33, 135.99, 132.27, 123.61, 83.16, 76.79, 72.76, 69.49, 67.73, 64.85, 54.73, 27.98. MS (ESI(+)) = 956.1 [$\text{M} + \text{H}$] $^+$.

Preparation of 2-(2-(2-methoxyethoxy)ethoxy)ethyl(*N*-ethylpyridine)fullerenopyrrolidine carboxylate, **4**

Compound **4** was prepared as **3**, from [60]fullerene (0.13 g, 0.16 mmol), *para*-formaldehyde (0.02 g, 0.70 mmol), and **2** (0.04 g, 0.14 mmol) in dry toluene (250 mL). Purification of the solid by column chromatography (first with toluene and then with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 20:1) and a size exclusion column of Bio-Rad SX1 (eluent toluene) afforded **4** as a brown solid with a yield of 24% (0.07 g).

^1H NMR (400 MHz, CD_2Cl_2 , ppm): δ = 8.69 (d, $^3J_{\text{H-H}} = 4.9$ Hz, 2H, H_α pyridine), 7.70 (d, $^3J_{\text{H-H}} = 5.6$ Hz, 2H, H_β pyridine), 5.23 (s, 1H, $\text{CH}_{\text{peg}}\text{CO}_2$), 4.97 (d, $^3J_{\text{H-H}} = 9.4$ Hz, 1H, $\text{HCH}_{\text{pyrrolidine}}$), 4.68 (d, $^3J_{\text{H-H}} = 14.1$ Hz, 1H, $\text{HCH}_{\text{pyrrolidine}}$), 4.44-4.48 (m, 2H, H_{peg}), 4.35 (d, $^3J_{\text{H-H}} = 9.5$ Hz, 1H, $\text{HCHC}_{\text{pyridine}}$), 4.14 (d, $^3J_{\text{H-H}} = 14.1$ Hz, 1H, $\text{HCHC}_{\text{pyridine}}$), 3.62-3.73 (m, 2H, H_{peg}), 3.54-3.45 (m, 8H, H_{peg}), 3.30 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, CD_2Cl_2 , ppm): δ = 170.12, 155.00, 150.79, 147.31, 146.87, 146.69, 145.65, 146.63, 146.37, 146.24, 146.21, 145.85, 145.83, 143.25, 143.22, 143.19, 142.83, 142.81, 142.67, 142.54, 142.39, 142.37, 142.36, 124.30, 77.12, 73.32, 72.45, 71.09, 70.99, 70.06, 69.44, 65.45, 65.19, 59.20, 55.40, 30.26. MS (ESI(+)) = 1045.4 $[\text{M} + \text{H}]^+$.

Preparation of dichloro(*p*-cymene)(*tert*-butyl(*N*-ethylpyridine)fullerenopyrrolidine carboxylate)ruthenium(II), **5**

A solution of (*p*-cymene) $_2\text{Ru}_2(\mu\text{-Cl})_2\text{Cl}_2$ (0.05 g, 0.10 mmol) and **3** (0.19 g, 0.20 mmol) in dry CH_2Cl_2 (50 mL) was stirred under reflux for 24h. After evaporation to dryness, product **5** was obtained as a brown solid with a yield of 98% (0.24 g). ^1H NMR (400 MHz, CD_2Cl_2 , ppm): δ = 9.08 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 2H, H_α pyridine), 7.79 (d, $^3J_{\text{H-H}} = 6.1$ Hz, 2H, H_β pyridine), 5.45-5.47 (m, 2H, H_{cymene}), 5.25 (d, $^3J_{\text{H-H}} = 6.0$ Hz, 2H, H_{cymene}), 5.11 (s, 1H, CHCO_2^tBu), 4.97 (d, $^3J_{\text{H-H}} = 9.4$ Hz, 1H, $\text{HCHC}_{\text{pyridine}}$), 4.77 (d, $^3J_{\text{H-H}} = 15.1$ Hz, 1H, $\text{HCH}_{\text{pyrrolidine}}$), 4.32 (d, $^3J_{\text{H-H}} = 9.4$ Hz, 1H, $\text{HCHC}_{\text{pyridine}}$), 4.20 (d, $^3J_{\text{H-H}} = 15.1$ Hz, 1H, $\text{HCH}_{\text{pyrrolidine}}$), 2.98 (sept, $^3J_{\text{H-H}} = 6.9$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 2.09 (s, 3H, $\text{CH}_3\text{C}_{\text{arom}}$), 1.53 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.33 (d, $^3J_{\text{H-H}} = 7.0$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (100 MHz, CD_2Cl_2 , ppm): δ = 169.09, 155.45, 150.82, 147.06, 146.86, 146.63, 146.38, 146.26, 146.19, 145.98, 145.83, 145.22, 145.02, 143.60, 143.23, 142.77, 142.66, 142.37, 140.78, 136.89, 136.64, 124.62, 103.86, 97.57, 84.01, 83.50, 83.38, 82.75, 82.72, 77.42, 73.28, 70.11, 65.44, 54.67, 53.46, 31.23, 30.24, 28.61, 22.57, 22.55, 18.53. MS (ESI(+)) = 1225.12 $[\text{M} - \text{Cl}]^+$.

Preparation of dichloro(*p*-cymene)(2-(2-(2-methoxyethoxy)ethoxy)ethyl(*N*-ethylpyridine)fullerenopyrrolidine carboxylate)ruthenium(II), **6**

Compound **6** was prepared and purified as **5**, from (*p*-cymene) $_2\text{Ru}_2(\mu\text{-Cl})_2\text{Cl}_2$ (0.01 g, 0.02 mmol), **4** (0.05 g, 0.04 mmol) in dry CH_2Cl_2 (5 mL). Product **6** was obtained as a black solid with a yield of 92% (0.05 g). ^1H NMR (400 MHz, CD_2Cl_2 , ppm): δ = 9.08 (d, $^3J_{\text{H-H}} = 6.7$ Hz, 2H, H_α pyridine), 7.80 (d, $^3J_{\text{H-H}} = 6.4$ Hz, 2H, H_β pyridine), 5.44-5.47 (m, 2H, H_{cymene}), 5.31 (s, 1H, $\text{CH}_{\text{peg}}\text{CO}_2$), 5.25 (d, $^3J_{\text{H-H}} = 5.9$ Hz, 2H, H_{cymene}), 4.98 (d, $^3J_{\text{H-H}} = 9.5$ Hz, 1H, $\text{HCH}_{\text{pyrrolidine}}$), 4.77 (d, $^3J_{\text{H-H}} = 15.1$ Hz, 1H, $\text{HCH}_{\text{pyrrolidine}}$), 4.44-4.47 (m, 2H, H_{peg}), 4.35 (d, $^3J_{\text{H-H}} = 9.4$ Hz, 1H, $\text{HCHC}_{\text{pyridine}}$), 4.20 (d, $^3J_{\text{H-H}} = 15.1$ Hz, 1H,

HCHC_{pyridine}), 3.71-3.60 (m, 2H, H_{peg}), 3.45-3.55 (m, 8H, H_{peg}), 3.31 (s, 3H, OCH₃), 2.95-3.02 (m, 1H, CH(CH₃)₂), 2.09 (s, 3H, CH₃C_{arom}), 1.33 (d, ³J_{H-H} = 6.9 Hz, 6H, CH(CH₃)₂). ¹³C NMR (100 MHz, CD₂Cl₂, ppm): δ = 170.04, 155.47, 154.99, 154.74, 153.71, 151.40, 150.60, 148.00, 149.86, 147.05-145.85, 145.23, 145.11, 144.96, 143.63, 143.21, 142.81, 142.68-142.44, 142.38, 140.88, 140.81, 140.29, 140.15, 138.25, 136.93, 136.82, 136.10, 124.66, 103.90, 97.55, 83.45, 83.36, 82.76, 77.09, 73.20, 72.43, 71.05, 70.97, 70.95, 70.05, 69.36, 65.42, 65.28, 59.20, 31.24, 22.56, 18.54. MS (ESI(+)) = 1363.2 [M + Na]⁺.

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REFERENCES

- [1]. J.L. Delgado, S. Filippone, F. Giacalone, M.Á. Herranz, B. Illescas, E.M. Pérez, N. Martín, *Topics in Current Chemistry*, **2014**, 350, 1.
- [2]. (a) H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, *Nature*, **1985**, 318, 162. (b) R.C. Haddon, L.E. Brus, K. Raghavachari, *Chemical Physics Letters*, **1986**, 125, 459. (c) R.C. Haddon, *Journal of the American Chemical Society*, **1997**, 119, 1797. (d) A. Hirsch, "Principles of Fullerene Reactivity", Vol. 199, Springer, Berlin, **1999**. (e) N. Martín, *Chemical Communications*, **2013**, 49, 1039.
- [3]. (a) C. Bingel, *Chemische Berichte*, **1993**, 126, 1957. (b) M. Maggini, G. Scorrano, M. Prato, *Journal of the American Chemical Society*, **1993**, 115, 9798. (c) M. Prato, M. Maggini, *Accounts of Chemical Research*, **1998**, 31, 519. (d) K. Kordatos, T. Da Ros, S. Bosi, E. Vázquez, M. Bergamin, C. Cusan, F. Pellarini, V. Tomberli, B. Baiti, D. Pantarotto, V. Georgakilas, G. Spalluto, M. Prato, *Journal of Organic Chemistry*, **2001**, 66, 4915.
- [4]. (a) D.M. Guldi, *Chemical Society Reviews*, **2002**, 31, 22. (b) M. Sawamura, Y. Kuninobu, M. Toganoh, Y. Matsuo, M. Yamanaka, E. Nakamura, *Journal of the American Chemical Society*, **2002**, 124, 9354. (c) M. Segura, L. Sánchez, J. de Mendoza, N. Martín, D.M. Guldi, *Journal of the American Chemical Society*, **2003**, 125, 15093. (d) D.M. Guldi, G.M. Aminur Rahman, V. Sgobba, C. Ehli, *Chemical Society Reviews*, **2006**, 35, 471.
- [5]. (a) B.C. Thompson, J.M.J. Fréchet, *Angewandte Chemie International Edition*, **2008**, 47, 58. (b) C.J. Brabec, S. Gowrisanker, J.J.M. Halls, D. Laird, S. Jia, S.P. Williams, *Advanced Materials*, **2010**, 22, 3839.

- [6]. (a) M. Maggini, A. Donò, G. Scorrano, M. Prato, *Journal of the Chemical Society; Chemical Communications*, **1995**, 846. (b) N. Armaroli, C. Boudon, D. Felder, J.-P. Gisselbrecht, M. Gross, G. Marconi, J.-F. Nicoud, J.-F. Nierengarten, V. Vicinelli, *Angewandte Chemie International Edition*, **1999**, *38*, 3730. (c) K. Barthelmes, J. Kübel, A. Winter, M. Wächtler, C. Friebe, B. Dietzek, U.S. Schubert, *Inorganic Chemistry*, **2015**, *54*, 3159.
- [7]. F. Cardinali, J.-L. Gallani, S. Schergna, M. Maggini, J.-F. Nierengarten, *Tetrahedron Letters*, **2005**, *46*, 2969.
- [8]. (a) Y. Matsuo, E. Nakamura, *Organometallics*, **2003**, *22*, 2554. (b) C.-H. Chen, C.-S. Chen, H.-F. Dai, W.-Y. Yeh, *Dalton Transactions*, **2012**, *41*, 3030. (c) F.L. Bowles, M.M. Olmstead, A.L. Balch, *Journal of the American Chemical Society*, **2014**, *136*, 3338. (d) W.-Y. Yeh, *Journal of Organometallic Chemistry*, **2014**, *751*, 351. (e) C.-H. Chen, A. Aghabali, C. Suarez, M.M. Olmstead, A.L. Balch, L. Echegoyen, *Chemical Communications*, **2015**, *51*, 6489.
- [9]. (a) B. Therrien, *Coordination Chemistry Reviews*, **2009**, *253*, 493. (b) A.K. Singh, D.S. Pandey, Q. Xu, P. Braunstein, *Coordination Chemistry Reviews*, **2014**, *270-271*, 31.
- [10]. (a) K. Severin, *Chemical Communications*, **2006**, 3859. (b) B. Therrien, *European Journal of Inorganic Chemistry*, **2009**, 2445.
- [11]. (a) A.F.A. Peacock, P.J. Sadler, *Chemistry: An Asian Journal*, **2008**, *3*, 1890. (b) G. Süß-Fink, *Dalton Transactions*, **2010**, *39*, 1673. (c) G.S. Smith, B. Therrien, *Dalton Transactions*, **2011**, *40*, 10793. (d) T.R. Cook, V. Vajpayee, M.H. Lee, P.J. Stang, K.-W. Chi, *Accounts of Chemical Research*, **2013**, *46*, 2464. (e) A.A. Nazarov, C.G. Hartinger, P.J. Dyson, *Journal of Organometallic Chemistry*, **2014**, *751*, 251.
- [12]. (a) L. Delaude, A. Demonceau, *Dalton Transactions*, **2012**, *41*, 9257. (b) A.L. Noffke, A. Habtemariam, A.M. Pizarro, P.J. Sadler, *Chemical Communications*, **2012**, *48*, 5219. (c) G. Süß-Fink, *Journal of Organometallic Chemistry*, **2014**, *751*, 2. (d) P. Kumar, R.K. Gupta, D.S. Pandey, *Chemical Society Reviews*, **2014**, *43*, 707.
- [13]. A. Pitto-Barry, N.P.E. Barry, V. Russo, B. Heinrich, B. Donnio, B. Therrien, R. Deschenaux, *Journal of the American Chemical Society*, **2014**, *136*, 17616.
- [14]. G. Porzi, S. Sandri, *Tetrahedron: Asymmetry*, **1996**, *7*, 189.
- [15]. (a) C.-H. Andersson, G. Berggren, S. Ott, H. Grennberg, *European Journal of Inorganic Chemistry*, **2011**, 1744. (b) C.-H. Andersson, L. Nyholm, H. Grennberg, *Dalton Transactions*, **2012**, *41*, 2374. (c) B. Jin, J. Shen, R. Peng, C. Chen, S. Chu, *European Journal of Organic Chemistry*, **2014**, 6252. (d) A. Parveen, V. Sughanya, S. Nagarajan, *RSC Advances*, **2015**, *5*, 20351.
- [16]. (a) P. Govender, N.C. Antonels, J. Mattsson, A.K. Renfrew, P.J. Dyson, J.R. Moss, B. Therrien, G.S. Smith, *Journal of Organometallic Chemistry*, **2009**, *694*, 3470. (b) N.P.E. Barry, M. Austeri, J. Lacour, B. Therrien, *Organometallics*, **2009**, *28*, 4894. (c) O. Zava, J. Mattsson, B. Therrien, P.J. Dyson, *Chemistry: A European Journal*, **2010**, *16*, 1428. (d) N.P.E. Barry, F. Edafe, B. Therrien, *Dalton Transactions*, **2011**, *40*, 7172.

- [17]. (a) T.-T. Thai, B. Therrien, G. Süß-Fink, *Journal of Organometallic Chemistry*, **2009**, *694*, 3973. (b) M. Auzias, J. Gueniat, B. Therrien, G. Süß-Fink, A.K. Renfrew, P.J. Dyson, *Journal of Organometallic Chemistry*, **2009**, *694*, 855. (c) M. Gras, B. Therrien, G. Süß-Fink, A. Casini, F. Edafe, P.J. Dyson, *Journal of Organometallic Chemistry*, **2010**, *695*, 1119.
- [18]. P. Govindaswamy, B. Therrien, G. Süß-Fink, P. Štěpnička, J. Ludvík, *Journal of Organometallic Chemistry*, **2007**, *692*, 1661.
- [19]. M.A. Bennett, T.-N. Huang, T.W. Matheson, A.K. Smith, *Inorganic Syntheses*, **1982**, *21*, 74.