Inorganica Chimica Acta 376 (2011) 525–530

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Binuclear cyclopalladated pincer compounds bridged by ditopic nitrogenated ligands

Ruy Cervantes [a,*], Jorge Tiburcio [b], Hugo Torrens [a]

[a] División de Estudios de Postgrado, Facultad de Química, Universidad Nacional Autónoma de México, Cd. Universitaria 3000, 04360 México, DF, Mexico
[b] Departamento de Química, Centro de Investigación y de Estudios Avanzados, Avenida IPN 2508, Zacatenco, 07360 México, DF, Mexico

ARTICLE INFO

Article history:
Received 18 February 2011
Received in revised form 7 July 2011
Accepted 12 July 2011
Available online 23 July 2011

Keywords:
Pincer complexes
Bridging ligands
Chemical topology

ABSTRACT

The binuclear cyclopalladated compounds [(SCS)Pd-*pz*-Pd(SCS)][BF_4]$_2$ (*pz* = pyrazine) **2a**, [(SCS)Pd-*bipy*-Pd(SCS)][BF_4]$_2$ (*bipy* = 4,4′-bipyridine) **2b**, [(SCS)Pd-*dcb*-Pd(SCS)][BF_4]$_2$ (*dcb* = 1,4-dicyanobenzene) **2c** and [(SCS)Pd-*tmeda*-Pd(SCS)][BF_4]$_2$ (*tmeda* = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) **2d** (SCS = {C_6H_3-2,6-($CH_2SC_6H_4F$-4)$_2$}) were synthesized by a substitution reaction between the pincer unit [Pd(C_6H_3-2,6-($CH_2SC_6H_4F$-4)$_2$)Cl] **1** and the corresponding bidentate nitrogenated ligands. The topology of the bridging ligand between both pincer units induces the aggregation of the organometallic cations in the solid state. The X-ray diffraction molecular structures of complexes **2a** and **2d** are also reported.

1. Introduction

Bridging two or more transition metals for the construction of more complex structures in nanometric scale has been the motivation of many research groups [1]. Controlling and predicting the molecular structure may lead to important contributions in areas such as material science and chemical topology.

The type of molecule that has been used most frequently as bridging ligand between transition metals has been the pyridine family. The self-assemble of two-dimensional molecular polygons and three-dimensional metal–organic polyhedra requires a rigid and linear conformation of the bridging ligand [2–6]. On the other hand, pincer type complexes have been well investigated [7] and they have found applications in different areas such as efficient catalyst precursors [8–11], in the construction of second generation dendrimers for surface modification [12], in the generation of supramolecular polymers acting as cross-linking moieties [13–15], as the recognition component in self-assembly of polymer backbones [16] and in the synthesis of amphiphilic copolymers and their subsequent self-assembly into well defined nanostructures [17]. Binuclear bridged pincer compounds are relative rare, but they have shown versatility in diverse areas. For instance, as luminescent materials [18], in the elucidation of dehydrogenation reactions [19], as building blocks with defined molecular shapes [20] and in the study of the reactivity of metal-coordinated radical anions [21].

The inclusion of aliphatic moieties in the structure of the bridging ligand, which can adopt multiple configurations, might induce non-planar geometries in binuclear pincer type compounds. Until now, structures with a –CH_2CH_2– functionalization in the bridging pyridine-type ligand between two pincer units had adopted a coplanar arrangement in the solid state [22,20,23].

As part of our interest in the structural behavior in solution and in solid state of fluorosulfur containing pincer type palladacycles [24,25] we have synthesized binuclear cyclopalladated pincer compounds bridged by nitrogenated bidentate ligands with different topologies. In this paper, we report the synthesis and characterization of the binuclear compounds [(SCS)Pd-*pz*-Pd(SCS)][BF_4]$_2$ (*pz* = pyrazine) **2a**, [(SCS)Pd-*bipy*-Pd(SCS)][BF_4]$_2$ (*bipy* = 4,4′-bipyridine) **2b**, [(SCS)Pd-*dcb*-Pd(SCS)][BF_4]$_2$ (*dcb* = 1,4-dicyanobenzene) **2c** and [(SCS)Pd-*tmeda*-Pd(SCS)][BF_4]$_2$ (*tmeda* = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) **2d** (SCS = {C_6H_3-2,6-($CH_2SC_6H_4F$-4)$_2$}) as well as the X-ray structures of **2a** and **2d** with significant differences in their aggregation in the solid state.

2. Experimental

2.1. General

All reactions were carried out under inert atmosphere using conventional Schlenk glassware and techniques. Solvents were dried using established procedures and distilled under nitrogen immediately prior to use. The IR spectra were measured on a

---

* Corresponding author. Present address: Departamento de Química, Centro de Investigación y de Estudios Avanzados, Avenida IPN 2508, Zacatenco, 07360 México, DF, Mexico. Tel.: +52 55 57473721; fax: +52 55 50613389.

E-mail addresses: rcervantes@cinvestav.mx (R. Cervantes), jtiburcio@cinvestav.mx (J. Tiburcio), torrens@unam.mx (H. Torrens).

0020-1693/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2011.07.019

Table 1
Crystallographic data, solution and refinement parameters for single crystal structure determinations of compounds **2a** and **2d**.

	2a	**2d**
Formula	$C_{44}H_{34}B_2F_{12}N_2Pd_2S_4$	$C_{52}H_{58}B_2F_{12}N_2O_2Pd_2S_4$
Formula weight	1181.39	1333.66
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P\,21/n$
T (K)	293(2)	173(2)
a (Å)	10.722(3)	11.082(2)
b (Å)	15.336(3)	18.653(4)
c (Å)	16.079(4)	14.000(3)
α (°)	81.87(2)	
β (°)	78.18(1)	109.426(3)
γ (°)	70.49(2)	
V (Å^3)	2431.6(10)	2729.2(10)
Z	2	2
D_{calc} (g/cm^3)	1.614	1.623
μ (mm^{-1})	0.991	0.895
Reflections collected	11 492	25 797
Unique reflections	8330	4807
$[I > 2\sigma(I)]$[a]	$R_1 = 0.0614$, $wR_2 = 0.1422$	$R_1 = 0.0842$, $wR_2 = 0.2084$
R_1/wR_2 (all data)[b]	0.1099/0.1735	0.1209/0.2253
Goodness-of-fit (GOF) on F^2	1.009	1.119
Parameters/restrains	595/0	343/0
Minimum/maximum residual density (e/Å^3)	0.91/−0.80	1.05/−1.31

[a] $R_1 = \Sigma||F_o| - |F_c||\Sigma|F_o|$.
[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, where $w = q[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$.

Perkin–Elmer 1600 FT-IR spectrometer. ^1H, ^{13}C and ^{19}F NMR spectra were recorded at 299.69, 75.36 and 281.96 MHz, respectively with a Varian Unity Inova 300 spectrometer. Chemical shifts are relative to TMS $\delta = 0$ (^1H, ^{13}C) and $CFCl_3$ $\delta = 0$ (^{19}F) using CD_3CN and CD_3COCD_3 as solvents obtained from Aldrich Chemical Co. FAB+ mass spectra were recorded on a Jeol JMS-SX102A mass spectrometer. Elemental analyses were determined using a Fisons EA1108 instrument. Bridging ligands pyrazine, 4,4′-bipyridine, 1,4-dicyanobenzene and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine were obtained from Aldrich Chemical Co. and used without further purification. Pincer unit $[Pd\{1,3\text{-}C_6H_3(SC_6H_4F\text{-}4)_2\}Cl]$ **1** was prepared according to published procedures [25].

2.2. Synthesis

Pincer unit $[Pd\{1,3\text{-}C_6H_3(SC_6H_4F\text{-}4)_2\}Cl]$ **1** (0.125 g, 0.25 mmol) was dissolved in 20 mL of dry THF and one equivalent of silver tetrafluoroborate (0.049 g, 0.25 mmol) was added and stirred for 30 min. Silver chloride was filtered off and 0.125 mmol of the corresponding bidentate nitrogenated ligand was added to the solution. The mixture stirred for 4 h. Solvent was removed under vacuum and the residue recrystallized in a mixture of acetone/hexane.

Compound [(SCS)Pd-*pz*-Pd(SCS)] **2a**. White crystalline solid; yield: 85%. M.p. dec. 185 °C. IR (KBr): ν = 1056, 1490, 1233, 1161, 833, 1586, 516 cm^{-1}. FAB(+)-MS: *m/z* (%) = 1180 [M$^+$] (1), 947 (12), 463 (100), 367 (5). ^1H NMR (CD_3CN; δ, ppm): 4.74 (br-s, 8H, CH_2SR_f), 7.09 (m, 6H, Pd-Ar), 7.26 (m, 8H, *m*-SR_f), 7.89 (m, 8H, *o*-SR_f), 8.54 (br-s, 4H, pz). $^{13}C\{^1H\}$ NMR (CD_3CN; δ, ppm): 51.84, 118.22 (d, $^2J_{C,F} = 22.7$ Hz), 124.39, 127.29, 127.30, 135.67 (d, $^3J_{C,F} = 9.1$ Hz), 146.59, 151.17, 165.10 (d, $J_{C,F} = 249.4$ Hz). ^{19}F NMR (CD_3CN; δ, ppm): −105.70 (br-s, 4F), −146.97 (s, 8F). *Anal.* Calc. for $C_{44}H_{34}F_{12}B_2S_4N_2Pd_2$ (1181.5): C, 44.73; H, 2.90; S, 10.85; N, 2.37. Found: C, 42.98; H, 2.77; S, 10.42; N, 2.34%.

Compound [(SCS)Pd-*bipy*-Pd(SCS)] **2b**. White solid; yield: 75%. M.p. dec. 145 °C. IR (KBr): ν = 1056, 1490, 1231, 1586, 1161, 815, 1607, 836, 1417 cm^{-1}. FAB(+)-MS: *m/z* (%) = 1171 [M-BF$_4$]$^+$ (1), 947 (3), 619 (30), 463 (100), 367 (15). ^1H NMR (CD_3CN; δ, ppm): 4.81 (br-s, 8H, CH_2SR_f), 7.11 (m, 6H, Pd–Ar), 7.19 (m, 8H, *m*-SR_f), 7.61 (d, 4H, β-bipy), 7.83 (m, 8H, *o*-SR_f), 8.51 (br-s, 4H, α-bipy). $^{13}C\{^1H\}$ NMR (CD_3CN; δ, ppm): 52.41, 118.15 (d, $^2J_{C,F} = 22.8$ Hz), 123.96, 124.27, 127.15, 127.29 (d, $^4J_{C,F} = 3.2$ Hz), 135.64 (d, $^3J_{C,F} = 9.2$ Hz), 151.06, 152.22, 157.61, 165.03 (d, $J_{C,F} = 250.6$ Hz). ^{19}F NMR (CD_3CN; δ, ppm): −105.665 (br-s, 4F), −146.931 (s, 8F). *Anal.* Calc. for $C_{50}H_{38}F_{12}B_2S_4N_2Pd_2$ (1257.5): C, 47.75; H, 3.04; S, 10.19; N, 2.22. Found: C, 46.59; H, 3.07; S, 9.20; N, 2.30%.

Compound [(SCS)Pd-*dcb*-Pd(SCS)] **2c**. Yellowish solid; yield: 73%. M.p. dec. 135 °C. IR (KBr): ν = 1055, 1491, 1009, 1238, 837, 1162, 1586, 516, 2270 cm^{-1}. FAB(+)-MS: *m/z* (%) = 1055 (5), 947 (5), 591 (3), 463 (100), 367 (5). ^1H NMR (CD_3COCD_3; δ, ppm): 4.89 (br-s, 8H, CH_2SR_f), 7.11 (m, 6H, Pd–Ar), 7.33 (m, 8H, *m*-SR_f), 8.07 (m, 8H, *o*-SR_f), 8.04 (s, 4H, dcb). $^{13}C\{^1H\}$ NMR (CD_3COCD_3; δ, ppm): 50.41, 117.45, 118.13 (d, $^2J_{C,F} = 22.3$ Hz), 118.30, 124.48, 126.94, 127.59, 134.17, 135.66 (d, $^3J_{C,F} = 9.1$ Hz), 151.16, 152.97, 164.91 (d, $J_{C,F} = 249.4$ Hz). ^{19}F NMR (CD_3COCD_3; δ, ppm): −109.97 (br-s, 4F), −150.69 (s, 8F). *Anal.* Calc. for $C_{48}H_{34}F_{12}B_2S_4N_2Pd_2$ (1229.5): C, 46.89; H, 2.79; S, 10.43; N, 2.28. Found: C, 44.35; H, 2.67; S, 9.36; N, 2.48%.

Compound [(SCS)Pd-*tmeda*-Pd(SCS)] **2d**. White crystalline solid; yield: 68%. IR (KBr): ν = 1055, 1489, 1226, 1160, 835, 1585, 520 cm^{-1}. FAB(+)-MS: *m/z* (%) = 579 (7), 463 (100), 117 (50). ^1H NMR (CD_3CN; δ, ppm): 2.59 (br-s, 12H, N-$(CH_3)_2$), 3.07 (br-s, 4H, N-$(CH_2)_2$), 4.81 (br-s, 8H, CH_2SR_f), 6.99 (m, 6H, Pd–Ar), 7.30 (m, 8H, *m*-SR_f), 8.09 (m, 8H, *o*-SR_f).

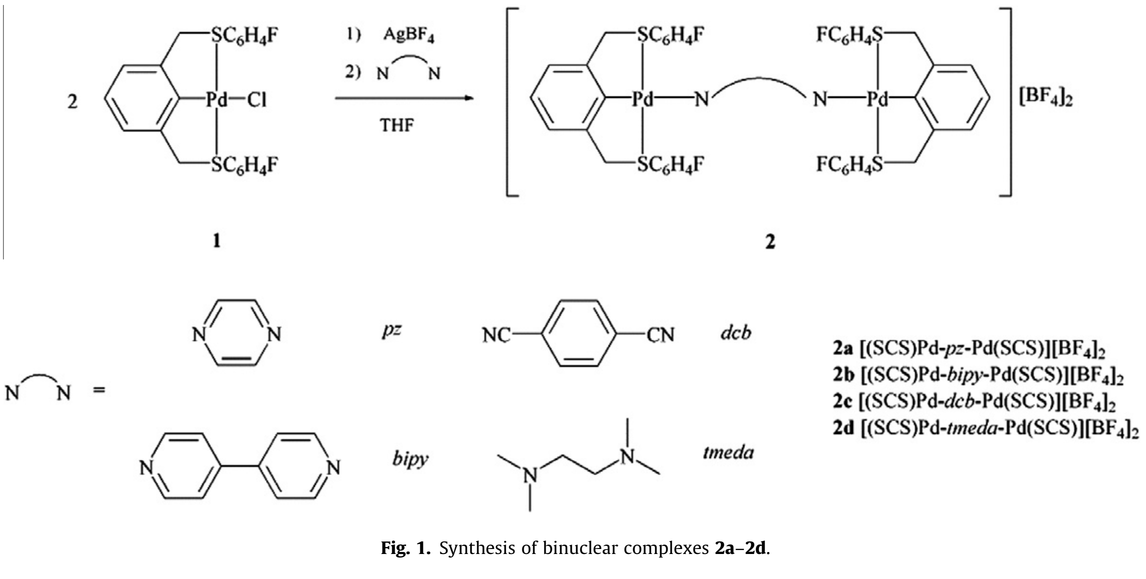

Fig. 1. Synthesis of binuclear complexes **2a–2d**.