PALLADIUM AND RUTHENIUM DERIVATIVES STABILISED BY BIS-SULFONE LIGAND

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ABSTRACT. The synthesis and characterization of new palladium and ruthenium derivatives using the bis-sulfone 1,3-bis{(4-methylphenyl)sulfonyl}-5-tert-butylbenzene ligand is presented. The new compounds were characterized in solution by multinuclear NMR spectroscopy and for the palladium derivative the molecular structure in solid state was also determined by single crystal X-ray diffraction. The work was completed with a DFT study in order to better understand the electronic effect in the stabilization of the new complexes containing *bis*-sulfone ligand.

Keywords: bis-sulfone, palladium and ruthenium derivatives, NBO analysis

INTRODUCTION

Inorganic and organometallic chemistry developed significantly in the last period, mainly due to the possibility to control the properties of designed compounds by using versatile ligands with modulated structures connected to the central atom.

Structural modifications of the ligand backbone and its functional groups allowed access to a large number of compounds whose properties change depending on the connection mode to the metal atom.[1–4] Additionally, the metallic center plays also an important role in the properties of the new compounds; this fact must to be considered at the design of new species. It is well known that organometallic derivatives containing a transition metal

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are used mainly in various catalytic processes[5,6] as compounds with biological activity[7–10] or used as building blocks for obtaining of inorganic polymers or supramolecular structures,[6,11–14] these important applications being the reason for significant developments of this field of chemistry in the last period. There are numerous examples of palladium and ruthenium complexes obtained with different ligands whose coordination modes determine not only the stability of the species but also the chemical properties they display. Among the large variety of ligands used for these complexes are for example different phosphines,[15] sulfoxides,[16] Schiff bases[17] or pincer ligands.[13,14,18–20]

Furthermore, the preparation of ligands with properties modulated by the presence of several functional groups like: metallylenes,[21–23] oxathia- derivatives,[24] germil-aminophosphoric esters,[25] phophaalkenyl derivatives[26–28] or organometallic halogenated derivatives[29–31] as well as their study for the stabilization of transition metals derivatives of palladium, ruthenium, gold, tungsten, etc., is a continuous concern in our team.

Recently, we highlighted the utility of the bis-sulfone ligand 1,3-bis{(4-methylphenyl)sulfonyl}-5-tert-butylbenzene, containing two sulfonyl groups, as a pincer ligand for the stabilization of metallylenes and their transition metal compounds and cycloadducts.[32,33] In order to evaluate the properties and stability of organometallic derivatives containing a heavy *p-block* element or transition metal, additionally the effect induced by a ligand containing sulfonyl groups was studied. It's worth mentioning that in the literature there are several examples for transition metal containing derivatives stabilized by sulphur based, sulfonyl or sulfinyl containing ligands, where the transition metal is bonded either through the coordination of the sulphur or the oxygen atom,[16,34–37] however, there are only a few examples for such compounds containing a bis-sulfonyl ligand.[37]

Herein, we present the results obtained with the before mentioned bis-sulfone ligand in the synthesis of new palladium and ruthenium derivatives.

RESULTS AND DISCUSSIONS

The 1,3-bis{(4-methylphenyl)sulfonyl}-5-tert-butylbenzene ligand, hereafter named bis-sulfone **1**, was synthetized according to the previously described procedure.[32] For this study, compound **1** was tested to obtain transition metal complexes with the aim to further investigate the connection ability of **1** towards transition metals. The synthetic pathway to obtain the palladium and ruthenium derivative is shown in Scheme 1.

In the case of both palladium **2** and ruthenium **3** derivatives, the ^{1}H NMR spectra indicate the formation of the new compounds by the disappearance of the signal for the H1 proton from bis-sulfone **1** (Scheme 1) at 8.90 ppm. The signals for the *ortho* protons of the tolyl groups are downfield shifted to 8.55 ppm for palladium complex **2** and to 8.61 ppm for ruthenium complex **3** from 7.82 ppm in bis-sulfone **1**, while an upfield shift can be observed for the signals corresponding the *meta* protons H3 and H5 of the central aromatic ring to 8.06 ppm for palladium complex **2** and 7.32 ppm for ruthenium complex **3** from 8.25 ppm in bis-sulfone **1**. For the palladium complex **2** in the ^{1}H NMR spectrum signals at 2.48, 2.81 ppm and 5.44, 6.38 ppm can be seen, suggesting that the cyclooctadiene is still linked to the metal center. In the case of the ruthenium complex **3**, the signals at 6.87-7.03, 7.84, 7.55 ppm corresponding to 30 protons indicate the presence of two triphenylphosphine groups bonded to the ruthenium atom.
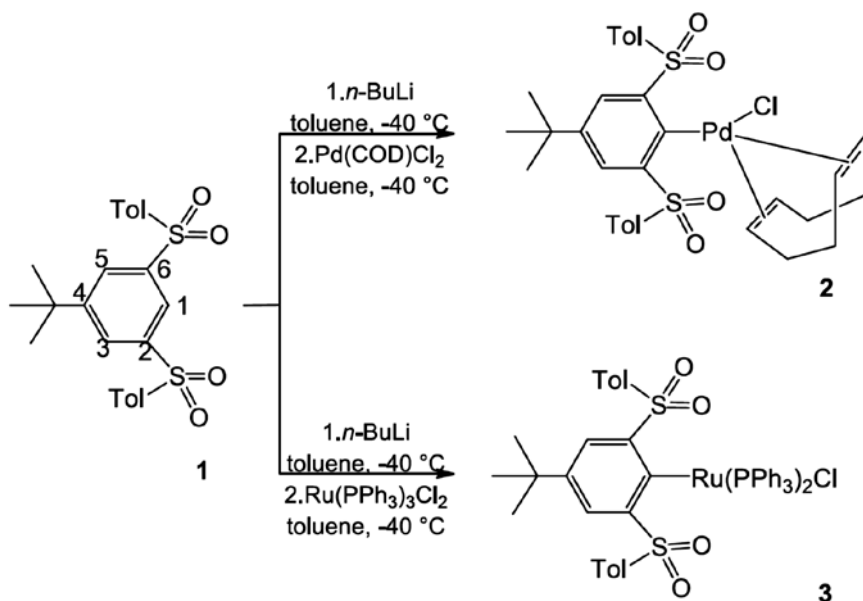

Scheme 1. *Synthesis of palladium complex **2** and ruthenium complex **3***

The ^{31}P{H} NMR of the ruthenium derivative **3** presents two doublet signals at 52.3 ppm ($^2J_{P-P}$=23.39 Hz) and 25.4 ppm (d, $^2J_{P-P}$=23.45 Hz), also confirming that two triphenylphosphine groups are linked to the metal. The ^{13}C NMR data for both derivatives **2** and **3** support these observations. All the NMR data are presented in the experimental part.

Crystals of palladium complex **2** were obtained by diffusion of pentane in dichloromethane solution and were analyzed by single crystal X-ray diffraction; the solid state molecular structure of compound **2** is shown in Figure 1.

The solid state molecular structure confirms the formation of the complex, where the palladium atom is linked to the C1 carbon atom of the bis-sulfone ligand. It also confirms the structure deduced from the ^{1}H and ^{13}C NMR spectra, that not only a chlorine atom is linked to the palladium atom, but also the cyclooctadiene group remains coordinated.

The palladium atom is four coordinated, with the usual square planar geometry. The geometrical features are in agreement with values from the literature for other palladium complexes with similar ligands.[13,14,19,20] The tolyl groups are situated on the same side of the central aromatic ring, not on opposite sides, as seen in the case of the previously reported metallylenes, as a consequence of the steric hindrance of the cyclooctadiene group. This effect was also observed in the previously reported transition metal complexes of the metallylenes.[32]
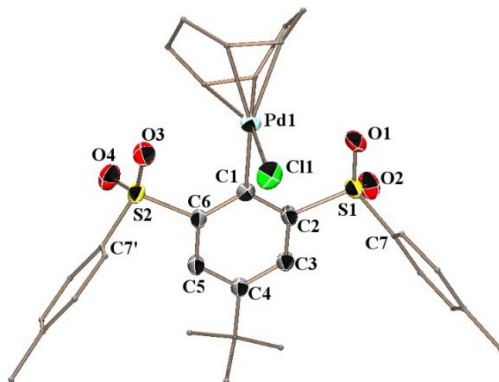

Figure 1. Molecular structure of compound **2** the solid state (50 % probability level for the thermal ellipsoids). For clarity, hydrogen atoms are omitted, tolyl and *t*-butyl and cyclooctadiene groups are simplified. Selected bond distances [Å] and bond angles [deg]: S1-O1 1.433(4), S1-O2 1.450(4), S2-O3 1.440(3), S2-O4 1.422(4), Pd1-C1 2.004(5), Pd1-Cl1 2.343(2), C1-Pd1-Cl1 86.04(14), C2-S1-C7 105.7(2), C6-S2-C7' 106.1(2), Pd1-C1-C2 122.7(3), Pd1-C1-C6 122.1(3)

The distance O1-Pd1 is 2.803(4) Å, while O3-Pd1 is 2.806(3) Å, values almost equal and significantly larger than the sum of the covalent radii of the Pd and O atoms (2.05).[38–40] The C1-Pd1, S1-O1, S2-O3 bonds are situated roughly in the same plane with the central aromatic ring (S1-O1 0.074 Å, S2-O3 0.277 Å out of the plane), arrangement favorable for interaction between the oxygen and palladium atoms. However, interaction

cannot be possible because of the presence of the cyclooctadiene group, thus in this case the bis-sulfone ligand **1** does not function as a pincer ligand as in the case of the previously reported metallylenes and their transition metal derivatives.

Furthermore, the oxygen atoms being a hard donor while the palladium atom a soft one, also effects the formation a coordinative bond. However, in the literature, a few examples can be found where an oxygen atom coordinates to a palladium atom.[20] The molecular structure of palladium compound **2** was additionally analyzed through DFT calculations. The calculated lengths of selected Pd-C (2.023 Å), Pd-Cl (2.353 Å) chemical bonds are in agreement with the solid-state data, as well as the Pd-O distances (2.855 Å and 2.867 Å). For the two η^2(C=C)→Pd coordinative bonds, the distances between the palladium atom and the centroids of the C=C bonds, have calculated values of 2.179 Å for the one oriented in *trans* with respect to the Pd-Cl bond, and of 2.290 Å for the other one. These lengths indicate strong interactions between the palladium atom and cyclooctadiene group.

NBO calculations, carried-out on the optimized structure of species **2**, revealed also strong η^2(C=C)→Pd interactions. According to these calculations, the energy corresponding to the short (C=C)→Pd coordinative bond (with calculated length of 2.179 Å) was computed to be around 78 kcal/mol, with about 64.1 kcal/mol corresponding to the π(C=C)→Pd interactions and 13.9 kcal/mol to the σ(C-C)→Pd ones; the NB orbitals involved within these donor-acceptor interactions are illustrated in Figure 2. For the other (C=C)→Pd chemical bonding, NBO data revealed an interaction energy of about 49.5 kcal/mol, with 11.9 kcal/mol arising from σ(C-C)→Pd, and the rest up to the total amount from the π(C=C)→Pd electron departures.

a b c
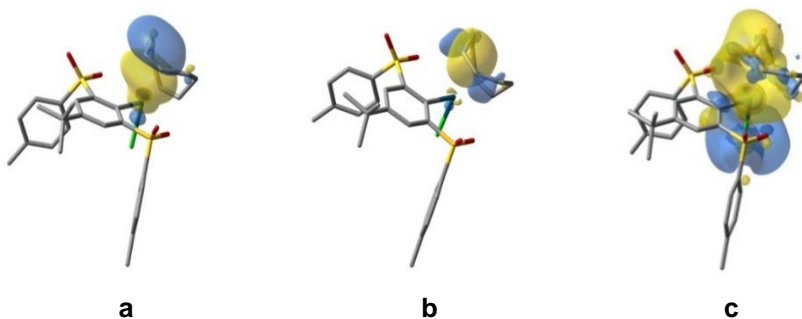
Figure 2. NB orbitals involved in the charge transfer interactions of the type η^2(C=C)→Pd for one of the two coordinative bonds; a) π(C=C) donor component on cyclooctadienyl species; b) σ(C-C) donor component on cyclooctadienyl species; c) acceptor orbital situated on the palladium atom; H atoms were omitted for clarity. NBOs with similar shapes were obtained for the other η^2(C=C)→Pd chemical bonding.

A potential chemical reaction involving palladium derivative **2** (see Figure 3) could be of interest due to the formation of a chelated O,C,O-coordinating pincer-type Pd complex, **2_a**. DFT calculations, performed on species **2_a**, indicate Pd-O bond lengths of 2.173 Å and 2.176 Å. According to NBO analyses, the calculated energies corresponding to these O→Pd chemical bondings is around 78 kcal/mol for each contact (77.4 kcal/mol and 78.1 kcal/mol, respectively).
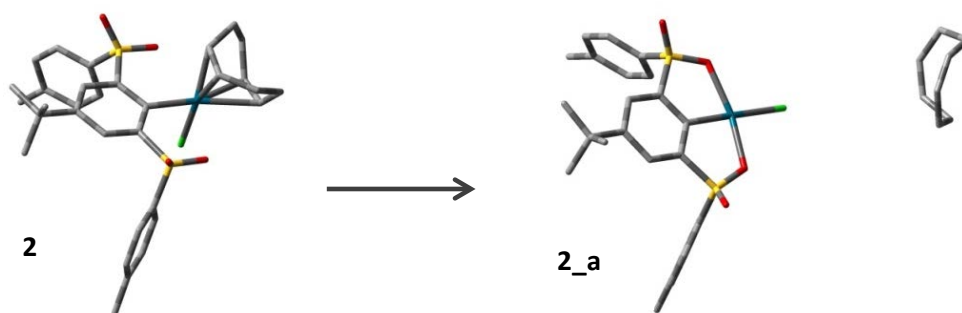
Figure 3. Potential chemical decomposition of complex **2** into a pincer-type palladium complex, **2_a**, and the cyclooctadiene group; hydrogen atoms were omitted for clarity.

The total energy corresponding to the O→Pd interactions in complex **2_a** (155.5 kcal/mol) is with 28 kcal/mol higher than the one calculated for the η^2(C=C)→Pd ones within derivative **2** (127.5 kcal/mol). According to the calculated energies of the investigated species, the reaction presented in Figure 3 is not thermodynamically favorable. Thus, the calculated energy of complex **2** is with 38.8 kcal/mol lower than the sum of the computed energies of **2_a** and of the free cyclooctadiene group (zero-point energy – ZPE – corrections were included in all cases). However, this energy difference could be significantly overestimated due to possible basis set superposition error.

The ruthenium complex **3** was also investigated by using DFT analysis. The optimized structure of **3** indicates a *quasi*-octahedral arrangement around the ruthenium atom with strong Ru-P bonds with calculated lengths of 2.393 Å, for the Ru-bond displaced in *trans* with respect to the Ru-C chemical bonding, and 2.261 Å for the one placed in the *cis* position. Short bond length was also calculated for the Ru-C bond (2.005 Å) while the Ru-Cl one has a calculated length of around 2.533 Å. For the Ru-O contacts, distances of 2.212 - 2.214 Å were obtained.

CONCLUSIONS

New palladium and ruthenium complexes were obtained using a bis-sulfone ligand. Both complexes, **2** and **3**, were characterized by NMR spectroscopy in solution and complex **2** also by single crystal X-ray analysis. It was shown that the bis-sulfone ligand **1** is also suitable to obtain transition metal derivatives; these compounds are the first examples of complexes with this ligand, opening the road to a new class of derivatives supported by sulfone based ligands. NBO analysis brought further explanations to the formation of the obtained palladium derivative. Furthermore, DFT calculations also supported the formation of the ruthenium complex

EXPERIMENTAL PART

All manipulations were realized in a dry, oxygen-free argon atmosphere using Schlenk-line and glove-box techniques. All the solvents were purified with a MBRAUN SBS-800 apparatus. The NMR spectra were recorded with a Bruker Avance II 300 apparatus: ^{1}H (300.13 MHz), ^{13}C (75.48 MHz), ^{31}P (121.51 MHz, reference H_3PO_4) at 298 K. High-resolution mass spectrometry (HRMS) spectra were measured with a GCT Premier Waters in DCI mode (CH_4). The X-ray data were collected at 193(2) K on a Bruker - AXS APEX II Quazar diffractometer, equipped with a 30 W air-cooled microfocus source using MoK$_\alpha$ radiation (wavelength = 0.71073 Å). Phi- and omega- scans were used. The data were integrated with SAINT[41] and an empirical absorption correction with SADABS[42] was applied. The structures were solved by direct methods using SHELXS-97[43] and refined using a least-squares method on F^2. All non-H atoms were refined with anisotropic displacement parameters. CCDC 1829298 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via *www.ccdc.cam.ac.uk/data_request/cif*

Computational Chemistry calculations were performed within the Density Functional Theory (DFT) framework. The hybrid functional used was B3LYP[44,45] in conjunction with Grimme's D3 dispersion correction,[46] along with the triple-zeta Def2-TZVP basis set[47] and Stuttgart effective core potentials[47] for the relativistic core electrons of the Pd atom. Optimization criteria were set to tight, vibrational analysis being performed on the optimized structures. The integration grid used was of 99 radial shells and 950 angular points for each shell (99,950). All the calculations were carried out using the Gaussian 09 package.[48] Natural Bond Orbital (NBO)[49-51] *single-point* calculations were performed using the Gaussian implemented version of the NBO Program.[52]

Synthesis of (2,6-(para-tolylsulfonyl)-4-tert-butylphenyl)-palladium-η^2-cyclooctadienyl chloride **2**

To a solution of bis-sulfone **1** (150 mg, 0.34 mmol) in 6 mL toluene cooled to -40°C, *n*-butyl lithium (0.22 mL, 0.36 mmol, 1.6 M in hexane) was added dropwise. The deep red solution was stirred 20 minutes at this temperature then was added over a suspension of $Cl_2Pd(COD)$ (97 mg, 0.34 mmol) in 2 mL toluene at -40°C. The dark red reaction mixture was stirred for 15 minutes at this temperature then allowed to warm slowly to room temperature and stirred for 18 hours, to become a black solution. After the evaporation of the volatiles, the compound was washed with Et_2O and obtained as a dark grey powder. (135 mg, yield=58%) Colourless crystals suitable for X-ray analysis were obtained by slow diffusion of pentane in CH_2Cl_2 solution.

^{1}H NMR (CDCl$_3$) δ = 1.05 (s, 9H, *t-Bu*), 2.37 (s, 6H, Me), 2.95 and 3.12 (m, CH_2 COD) 5.54 (m, 2H, CH COD), 6.34 (m, 2H, CH COD), 7.26 (d, 4H, $^3J_{HH}$ = 7.98 Hz, *m*-CH Tol), 7.56 (s, 2H, *m*-CH Ph), 8.08 (d, 4H, $^3J_{HH}$ = 8.30 Hz, *o*-CH Tol).

^{1}H NMR (C$_6$D$_6$) δ = 0.86 (s, 9H, *t-Bu*), 1.73 (s, 6H, Me), 2.48 and 2.81 (m, CH_2 COD) 5.44 (m, 2H, CH COD), 6.38 (m, 2H, CH COD), 6.75 (d, 4H, $^3J_{HH}$ = 7.96 Hz, *m*-CH Tol), 8.06 (s, 2H, *m*-CH Ph), 8.55 (d, 4H, $^3J_{HH}$ = 8.28 Hz, *o*-CH Tol).

^{13}C NMR (C$_6$D$_6$) δ = 21.8 (Me), 30.8 (*t*-Bu), 34.4 (C *t*-Bu), 28.2 and 31.3 (CH_2 COD), 107.4 and 122.4 (CH COD), 128.8 (*o*-CH Tol), 129.8 (*C3, C5*), 131.8 (*m*-CH Tol), 139.0, 140.4, 144.1, 147.7, 149.7.

HR-MS (DCI CH$_4$): (C$_{32}$H$_{37}$O$_4$S$_2$PdCl) [M-Cl]$^+$ calcd: 655.1179, found: 655.1182.

Synthesis of (2,6-(para-tolylsulfonyl)-4-tert-butylphenyl)-ruthenium-bis(triphenyphosphine) chloride **3**

To a solution of bis-sulfone **1** (150 mg, 0.34 mmol) in 6 mL toluene cooled to -40°C, *n*-butyl lithium (0.22 mL, 0.36 mmol, 1.6 M in hexane) was added dropwise. The deep red solution was stirred 20 minutes at this temperature then was added over a suspension of (PPh$_3$)$_3$RuCl$_2$ (325 mg, 0.34 mmol) in 1 mL toluene at -40°C. The dark red solution was allowed to warm slowly to room temperature and stirred for 18 hours. After the evaporation of the volatiles, the compound was washed with Et_2O and pentane to obtain it as a light brown powder. (110 mg, yield=30%).

^{1}H NMR (C$_6$D$_6$) δ = 0.85 (s, 9H, *t-Bu*), 1.77 (s, 6H, Me), 6.71 (d, 4H, $^3J_{HH}$ = 8.09 Hz, *m*-CH Tol), 6.87-7.03 (m, PPh$_3$), 7.32 (d, 2H, *J* = 1.37 Hz, *m*-CH Ph), 7.55 (m, PPh$_3$), 7.85 (m, PPh$_3$), 8.61 (d, 4H, $^3J_{HH}$ = 8.38 Hz, *o*-CH Tol).

^{13}C NMR (C$_6$D$_6$) δ = 21.2 (Me), 31.1 (*t*-Bu), 34.5 (C *t*-Bu), 130.5 (*C8, C12*), 127.1 (d, J = 2.28 Hz, *C3, C5*), 129.8 (*C9, C11*), 144.7 (C7), 145.8 (C2, C6),

136.8, (*C10*), 148.3 (d, J = 1.87 Hz, C4), 186.7 (dd, J = 10.09 and 76.09 Hz, C1), 127.3, 127.4, 127.6, 127.8, 129.6 (PPh₃), 134.2 (d, $^3J_{PC}$ = 9.33 Hz, PPh₃), 135.4, 135.7 (PPh₃), 135.5 (d, $^3J_{PC}$ = 10.99 Hz, *o,m-C*H PPh₃), 136.2 (d, $^3J_{PC}$ = 10.82 Hz, *o,m-C*H PPh₃), 138.3 (d, $^1J_{PC}$ = 28.11 Hz, *ipso*-PPh₃).
³¹P NMR (C₆D₆) δ = 52.3 (m), 25.4 (m)
³¹P{H} (C₆D₆) δ = 52.3 (d, $^2J_{P-P}$=23.39 Hz), 25.4 (d, $^2J_{P-P}$=23.45 Hz)
IR (nujol) ν (cm⁻¹) = 1595, 1465, 1377, 1321, 1261, 1187, 1146, 1106, 1058, 1009, 814, 741, 695, 662, 586, 520

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