Research Article

Microwave-Assisted Synthesis and Characterization of $[\text{Rh}_2(\text{OAc})_4(\text{L})_2]$ Paddlewheel Complexes: A Joint Experimental and Computational Study

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The synthesis of four rhodium(II) paddlewheel complexes bearing axial aromatic amines and coumarin ligands, with formula $[\text{Rh}_2(\text{OAc})_4(\text{L})_2]$ ($\text{L} = \text{NH}_2\text{Mesityl}$ (**1**), NH_2Dip (**2**), NH_2Couma (**3**), coumarin (**4**)), prompted by microwave irradiation, was carried out successfully. All of the complexes were characterized by the melting point, elemental analysis, NMR, IR, and UV/Visible spectroscopy. Additionally, the structure of complexes **1-2** and **4** was corroborated by single-crystal X-ray diffraction. Cyclic voltammetry, ESI-MS, and tandem MS analyses were carried out in compound **1** for gaining further insight into its stability. Finally, a DFT study shows that complexes **1-4** are the thermodynamic products, having as intermediates complexes **1'-4'** which, under our experimental conditions, cannot be isolated.

1. Introduction

Rhodium complexes are one of the most important, versatile, and useful catalysts in organic synthesis. Their well-known reactivity has been exploited by catalytic or stoichiometric selective bond activation and C-C bond coupling reactions [1–5]. Wilkinson's complex is a milestone largely used in decarbonylation or in olefin hydrogenation reactions [6–8]. In this regard, the rhodium acetate complex $[\text{Rh}_2(\text{OAc})_4]$, **I**, has been recognized as (i) a valuable, stable, and easy-to-handle catalyst; and (ii) a linker in the synthesis of inorganic polymers and cages, **II** and **III**, respectively (Figure 1) [9–13]. The number of reports involving **I** in the fields of biochemistry [14–17], catalysis [18–20], and bioorganometallic [21, 22], inorganic [23–26], and organometallic chemistry [27–29] has been increased to an average of sixty papers per year in the last decade (according to SciFinder at 03-01-2017).

Early, in 1973, Paulissen et al. reported the insertion reaction of a carbenoid species, generated in situ from ethyl-diazoacetate, into O-H bonds catalyzed by **I**, under soft conditions [30]. Later, the works independently published by Hubert et al. among others showed the use of complex **I** as a catalyst for the cyclopropanation of olefins and allylic activation by diazo-esters [19, 20, 27–29, 31–39].

Furthermore, **I** and analogous complexes have been used as catalysts in the alkyne cyclopropanation or hydrophosphinylation reactions [40, 41], with concomitant mechanistic studies addressed to understand the role of the tetrabridged species in the catalytic process [41–45]. In the last decade, a work by Pirrung et al. showed that the chiral rhodium dimer, **IV** (Figure 1), can be easily synthesized and used as a catalyst for the enantioselective addition of ethyl-diazoacetate to terminal acetylenes [46–48]. In 2007, Gois and Jang groups reported, respectively, that the binuclear Rh(II) complex,

FIGURE 1: Rhodium paddlewheel complexes.

FIGURE 2: Alkyne hydroamination catalyzed by transition metals.

V, containing N-Heterocyclic Carbenes (NHC) as auxiliary ligands, can be a profitable tool in (i) the arylation of aldehydes and (ii) the allylic oxidation reaction [49, 50]. Recently, Werlé et al. reported that acetate rhodium derivatives like compound **VI** can be useful carbene transfer reagents [51].

On the other hand, the hydroamination (HA) of alkynes catalyzed by transition metal complexes is an important reaction, which involves the C-N bond formation. Based on the properties of the catalyst, this reaction can afford either the Markovnikov or anti-Markovnikov products (Figure 2) [52–58]. Furthermore, a few Rh species have been reported as excellent catalysts for this process [59–63]. However, to the best of our knowledge, complex **I** has not yet been reported as a catalytic precursor for this reaction. Therefore, we were initially motivated to investigate about the reactivity of **I** as a catalyst for the HA reaction, although we obtained the double ligand-insertion products into the binuclear Rh(II) complex which were not exactly as it was reported previously for this kind of complexes. Herein, we report about the characterization with different spectroscopic techniques and their reactivity as well as a computational study to rationalize our findings.

2. Results and Discussion

2.1. Attempts to Obtain the Hydroamination Products. Our first step was addressed to obtain the HA product from

TABLE 1: Attempts to obtain hydroamination products (see Scheme 1).

Entry ^a	Ar	[Cat]	Solvent	PPA%
1	Ms	[Rh ₂ (OAc) ₄]	Toluene	100
2	Dip	[Rh ₂ (OAc) ₄]	Toluene	100
3	Tri-Br	[Rh ₂ (OAc) ₄]	Toluene	100
4	Coumarin	[Rh ₂ (OAc) ₄]	Toluene	100
5	Ms	None	Toluene	n.o.
6 ^b	Ms	[Rh ₂ (OAc) ₄]	Toluene	n.o.
7 ^b	Tri-Br	[Rh ₂ (OAc) ₄]	Toluene	n.o.
8 ^b	Dip	[Rh ₂ (OAc) ₄]	Toluene	n.o.
9	None	[Rh ₂ (OAc) ₄]	Toluene	n.o.
10	Ms (Drop)	[Rh ₂ (OAc) ₄]	DMF	100

^a A mw tube was charged with HCCPh (0.1 g, 1 mmol), NH₂Ar (1.1 mmol), and [Rh₂(OAc)₄] (0.04 g, 0.001 mmol). The mixture was irradiated under mw at 110°C, 150 W and 0.5 h. ^b Reaction without HCCPh. n.o. = not obtained.

the reaction between phenylacetylene (PA) with the corresponding aromatic amine bearing electron donor and electron withdrawing groups, using (**I**) as catalyst, under microwave (mw) irradiation. Unexpectedly, an untreatable brown oil is obtained as the main product (Table 1, entries 1–4). The proton NMR spectrum of the reaction crude suggests that the formation of the desired hydroamination products, HA1 or HA2, does not take place. Instead, multiple signals are observed from 7.5 to 6.7 ppm, which are assigned to aromatic protons, attributed to the formation of oligo- and polyphenylacetylene (PPA) species, with a concomitant complete consumption of PA. Similar results have been reported using other rhodium mononuclear complexes as catalytic species [59–63]. At the same time, free amine is observed and quantitatively recovered.

TABLE 2: Selected spectroscopic data for complexes 1–4.

Compound	^1H	$^{13}\text{C}\{^1\text{H}\}$	IR ν (cm^{-1})	UV/Vis λ (nm), ϵ ($\text{M}^{-1}\text{cm}^{-1}$)	m.p. ($^{\circ}\text{C}$)
1	6.87 (s, 2H, CH_m); 5.42 (b.s., 2H, NH_2); 2.37 (s, 6H, CH_3 , Ar_o); 2.24 (s, 3H, CH_3 , Ar_p); 1.63 (OCH_3)	190.9 (C=O); 138.6 ($\text{C}_{\text{Ar}}\text{-NH}_2$); 130.0 (C_q); 129.0 (CH , Ar_m); 125.4 (C_q); 20.6 (CH_3 , Ar_p); 17.6 (CH_3 , Ar_o); 23.7 (OCH_3)	3372, 3308 ($\text{H}_2\text{N-Ar}$)	283, 36786	301
2	7.17 (d, 2H, CH , $^3J_{\text{H-H}} = 7.1$ Hz); 7.05 (t, 1H, CH , $^3J_{\text{H-H}} = 7.0$ Hz); 5.90 (b.s., 2H, NH_2); 3.48 (sept, 2H, $\text{CH}(\text{CH}_3)_2$, $^3J_{\text{H-H}} = 3.4$ Hz); 1.80 (OCH_3); 1.31 (d, 12H, CH_3 , $^3J_{\text{H-H}} = 3.4$ Hz)	190.6 (C=O); 138.2 ($\text{C}_{\text{Ar}}\text{-NH}_2$); 136.6 ($\text{C}_{\text{Ar}}\text{-iPr}$); 126.0 (CH_m); 121.7 (CH_p); 27.0 ($\text{CH}(\text{CH}_3)_2$); 23.2 ($\text{CH}(\text{CH}_3)_2$); 23.6 (OCH_3)	3402, 3334 ($\text{H}_2\text{N-Ar}$)	274, 20331	304
3	7.69 (d, 1H, CH_b , $^3J_{\text{H-H}} = 7.6$ Hz); 7.08 (d, 1H, CH_f , $^3J_{\text{H-H}} = 7.0$ Hz); 6.88 (m, 1H, CH_e , $^3J_{\text{H-H}} = 6.8$ Hz); 6.77 (d, 1H, CH_c , $^3J_{\text{H-H}} = 6.7$ Hz); 6.29 (d, 1H, CH_a , $^3J_{\text{H-H}} = 6.2$ Hz); 4.27 (b.s., 2H, NH_2); 1.76 (OCH_3)	208.7 (O-C=O); 192.1 (C=O); 147.5 (C_q , C_{Ar}); 145.8 ($\text{C}_q\text{-NH}_2$); 141.7 (C_b , CH); 122.3 (C_p , CH); 120.0 (C_q , C_{Ar}); 116.6 (C_c , CH); 116.5 (C_a , CH); 23.5 (OCH_3)	3346, 3275 ($\text{H}_2\text{N-Ar}$)	298, 36785	307
4	7.86 (d, 1H, CH_b , $^3J_{\text{H-H}} = 7.87$ Hz); 7.61 (d, 1H, CH_c , Ar , $^3J_{\text{H-H}} = 7.61$ Hz); 7.34 (t, 1H, CH_e , Ar , $^3J_{\text{H-H}} = 7.32$ Hz); 7.32 (m, 1H, CH_e , $^3J_{\text{H-H}} = 6.88$ Hz); 6.39 (d, 1H, CH_a , $^3J_{\text{H-H}} = 6.39$ Hz); 1.79 (OCH_3)	205.5 (O-C=O); 190.6 (C=O); 153.0 (C_q); 149.0 (C_b , CH); 137.1 (C_f , CH); 133.5 (C_e , CH); 129.8 (C_c , CH); 129.6 (C_d , CH); 126.4 (C_q); 121.7 (C_a , CH); 21.6 (OCH_3)	1669, 1590 (C=O)	370, 119602	300

SCHEME 1

On the other hand, when $[\text{Rh}_2(\text{OAc})_4]$, PA, or the aromatic amine was not added in three independent entries, it clearly affected the reaction pathway; the formation of PPA was not detected, recovering instead the quantitative reactants (Table 1, entries 5–9). Interestingly, when a drop of amine is added as an additive into the reaction mixture in a polar solvent as DMF, we observed a quantitative consumption of PA with a subsequent formation of PPA (Table 1, entry 10).

2.2. Synthesis and Characterization of Rh(II) Paddlewheel Complexes 1–4. On the other hand, after workup of each catalytic attempt, a colorful green-violet solid is obtained which was attributed to the formation of an adduct species with formula $[\text{Rh}_2(\text{OAc})_4(\text{L})_2]$, 1–4, ($\text{L} = \text{NH}_2\text{Ar}$; $\text{Ar} = \text{Ms}$ [2,4,6-tri- (CH_3) - C_6H_2] 1, Dipp [2,6-di- $(\text{CH}_3)_2\text{CH}$]- C_6H_3] 2, Couma [Coumarin] 3), respectively (Figure 3). Additionally, coumarin could also be used in the reaction as a ligand itself, resulting in the formation of complex 4. All of the compounds were isolated as deep purple-green solids in quantitative yields.

The structure of complexes 1–4 is based on the 1D and 2D NMR spectroscopy analysis. Thus, the proton NMR spectrum of compound 1 shows a singlet signal at 6.87 ppm, which was attributed to the aromatic protons, in accordance with the three singlet signals observed at 2.37 and 2.24 ppm, assigned to the methyl groups of the Ms substituents, and at 1.63 ppm corresponding to the OAc ligands (2 : 1 : 2 ratio). The amine protons were assigned to a broad signal observed at 5.42 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showed a singlet signal at 190.9 ppm which was assigned to the carbonyl groups. In the aromatic region, four signals from 138.6 to 125.4 ppm were attributed to the aromatic carbons. Furthermore, the signals observed at 20.6 and 17.6 ppm were assigned to the carbon atoms of the methyl groups of the mesityl substituents and the peak at 23.7 ppm belongs to the acetate fragments. The IR spectrum showed two vibration bands at 3372 and 3308 cm^{-1} assigned to the NH_2 functional group (Table 2). Additionally, in the UV/Vis spectrum, a maximum absorption longitude was found at 283 nm attributed to a ligand-metal charge transference transition [64–66]. Compounds 2–4 showed similar spectroscopic characteristics so they will not be discussed.

TABLE 3: X-ray diffraction selected data for compounds 1-2 and 4.

	1	2	4
Chemical formula	C ₂₆ H ₃₈ N ₂ O ₈ Rh ₂	C ₃₂ H ₅₀ N ₂ O ₈ Rh ₂	C ₂₆ H ₂₄ O ₁₂ Rh ₂
Formula weight	712.40	796.56	734.27
T [°K]	130(2)	130(2)	130(2)
λ [Å]	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P 21/c
Unit cell dimensions	$a = 8.0671(11) \text{ Å}$ $\alpha = 69.118(9)^\circ$ $b = 8.3981(6) \text{ Å}$ $\beta = 70.302(11)^\circ$ $c = 11.6427(14) \text{ Å}$ $\gamma = 89.701(8)^\circ$	$a = 8.2014(5) \text{ Å}$ $\alpha = 75.975(5)^\circ$ $b = 9.2294(6) \text{ Å}$ $\beta = 75.919(5)^\circ$ $c = 11.9557(7) \text{ Å}$ $\gamma = 82.881(5)^\circ$	$a = 11.616(2) \text{ Å}$ $\alpha = 90^\circ$ $b = 13.6577(17) \text{ Å}$ $\beta = 106.927(18)^\circ$ $c = 8.5475(15) \text{ Å}$ $\gamma = 90^\circ$
V [Å ³]	687.89(15)	849.58(9)	1297.3(4)
Z	1	1	2
D _{calcd.} [g cm ⁻³]	1.720	1.557	1.880
μ [mm ⁻¹]	1.250	1.021	1.339
F(000)	362	410	732
Goodness-of-fit on F2	1.054	1.026	1.082
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0300, wR2 = 0.0586	R1 = 0.0386, wR2 = 0.0541	R1 = 0.0315, wR2 = 0.0609
R indices (all data)	R1 = 0.0378, wR2 = 0.0655	R1 = 0.0553, wR2 = 0.0647	R1 = 0.0435, wR2 = 0.0674
Extinction coefficient	n/a	n/a	n/a

FIGURE 3: Synthesis of compounds 1-4.

Selected data are summarized in Table 2. Finally, the structure of 1-2 and 4 was corroborated by X-ray diffraction analysis.

2.3. X-Ray Structural Analysis of Complexes 1-2 and 4. The adducts of rhodium acetate, containing a nitrogen donor ligand as pyridine, picoline, and aniline derivatives, were reported earlier [23, 66, 67]. Complexes 1-2 crystallized in a space group P-1, while complex 4 crystallized in a P 21/c one. The 1-2 and 4 binuclear core showed a Rh-Rh bond distance in an expected range of 2.3925(6), 2.3886(5), and 2.3860(6) Å, respectively (see Figures 5(a)-7(a) and Table 3) [68-70]. These facts show that the oxygen donor atom has slightly compressed the Rh-Rh bond distance in 0.065 Å, which is 0.025 Å less than in the Rh-N core. Furthermore, a strong π - π stacking interaction was found in compound

4 with a distance of 3.403 Å among the coumarin rings (Figure 7(b)) [71-75]. It is possible that the natural bulkiness of either methyl or isopropyl groups in the complexes 1-2 was clearly enough to affect the unit cell packing with a concurrent missing of the π - π stacking interaction. Thus, a near interaction was found between the aryl groups at 7.793 and 7.972 Å, Figures 6(b) and 7(b), respectively. Finally, the NH₂Ar ligand adopted a transoid geometry arrangement around the Rh-Rh core.

2.4. ESI-MS, MS/MS, and Cyclic Voltammetry (CV) of Compound 1. Recently, ESI-MS and MS/MS spectrometry have shown their relevance in understanding the stability, reactivity, and selective bond activation of different [Rh₂(OAc)₄(L)₂] transition metal complexes [76-80]. The ESI-MS(+) spectrum of compound 1 shows the expected signal at m/z 713.0798, which was attributed to the protonated molecule; the same spectrum contains a fragment ion at m/z 577.9757, formed by the loss of one aniline group suggesting a formation of [Rh₂(OAc)₄(L)]⁺ molecular ion. The MS/MS fragmentation pattern of the two above ions is presented in Figure 8. As can be observed, these same fragments are present in both MS/MS spectra; all of them are assigned to the loss of one or more acetate groups.

Figure 9 shows cyclic voltammograms of a solution of compound 1 in dimethylsulfoxide (DMSO) and LiCl as supporting electrolyte; tests were carried out at a scan rate of 10-100 mV/s. Both curves show obvious electrochemical response over the glass carbon electrode. Also it is possible to distinguish some anodic signal at -0.08V and the rest of line is the same. Anodic signals were assigned, respectively, according to their donor and acceptor groups; and the cathodic process is attributed to a reduction process. Thus,

FIGURE 4: Sequence of the plausible formation of intermediate complexes $1'-4'$.

FIGURE 5: (a) ORTEP perspective of compound **1**. Selected bond distances (Å) and angles (°). Rh(1)-Rh(1) 2.3925(6), C(1)-N(1) 1.431(4), O(1)-Rh(1) 2.031(2), O(2)-Rh(1) 2.0333(18), O(3)-Rh(1) 2.0450(19), O(4)-Rh(1) 2.0506(18), Rh(1)-O(3) 2.0450(19), Rh(1)-O(4) 2.0506(18), Rh(1)-N(1) 2.316(2); C(10)-O(1)-Rh(1) 119.29(18), C(12)-O(2)-Rh(1) 118.62(17), O(1)-Rh(1)-O(2) 90.01(8), O(1)-Rh(1)-N(1) 88.87(8), O(2)-Rh(1)-N(1) 85.02(8). (b) Unit cell of compound **1** (hydrogen atoms where omitted by clarity).

at a scan rate of 10 to 100 mV/s, the values of $E_{p,a}$ and $E_{p,c}$ linearly increase with v and $v^{1/2}$, respectively, in good according with analogous species [81–83].

2.5. Computational Analysis of the Preference of Ligation in Rhodium (II) Paddlewheel Complexes. As we mentioned above, Gois et al. reported the synthesis of the binuclear NHC complex with the formula $[\text{Rh}_2(\text{OAc})_4(\text{NHC})]$, which is an excellent catalytic precursor into the aldehyde arylation reaction [49]. However, under our experimental conditions, the isolation of complexes of the type $[\text{Rh}_2(\text{OAc})_4(\text{L})]$ ($1'-4'$) did not take place. Instead, the quantitative formation of $[\text{Rh}_2(\text{OAc})_4(\text{L})_2]$ (**1–4**) complexes is observed (Figure 4). At this point, we faced the following question: what is the driven force that allows us to obtain only species **1–4**? In order to answer this, we carried out theoretical calculations at the DFT-M06-L level for obtaining reaction energies and comparing them with the other reported complexes (gas-phase geometry optimizations were done at the M06-L/(6-311G,LANL08) level. Solvent effects were added later using standard parameters for toluene. See Supporting Information

for further details on the computational methodology used in this work). Therefore, we have analyzed both cases: (i) having one and (ii) two auxiliary ligands linked to the $[\text{Rh}_2(\text{OAc})_4]$ core.

Our results are summarized in Table 4. All of the insertion reactions that lead to the formation of monocoordinate complexes $1'-4'$ are highly exothermic, following the next sequence: NH_2Dip ($2'$) > NH_2Mes ($1'$) > NH_2Couma ($3'$) > Coumarin ($4'$) with the reaction energies of -27.4 , -25.7 , -25.6 and $-17.7 \text{ kcal}\cdot\text{mol}^{-1}$, respectively. Furthermore, the second insertion reaction that produces complexes **1–4** is still exothermically favored, following the same sequence as the previous one (-22.5 , -21.1 , -18.1 , and $-12.2 \text{ kcal}\cdot\text{mol}^{-1}$, resp.). Our calculations agree with the experimental results. So, the binuclear complex **I** has a high affinity for binding to two auxiliary ligands. In the case of Gibbs free energy values (ΔG_R^0), we can observe that complex $1'$ is a species also favored by entropic effects. All these thermodynamic data suggest that it is possible to incorporate one ligand, but under such conditions, stopping the reaction is not possible (to only obtain $1'-4'$). Moreover, in order to shed more

FIGURE 6: (a) ORTEP perspective of compound 2. Selected bond distances (Å) and angles (°). Rh(1)-Rh(1) 2.3886(5), O(1)-Rh(1) 2.034(2), O(2)-Rh(1) 2.038(2), O(3)-Rh(1) 2.037(2), O(4)-Rh(1) 2.041(2), Rh(1)-O(2) 2.038(2), Rh(1)-N(1) 2.309(3); C(13)-O(1)-Rh(1) 118.5(2), C(15)-O(3)-Rh(1) 118.2(2), O(1)-Rh(1)-O(3) 90.19(8), O(1)-Rh(1)-O(4) 89.94(9), O(3)-Rh(1)-O(4) 176.42(9), O(1)-Rh(1)-N(1) 87.52(9), O(3)-Rh(1)-N(1) 87.88(9), O(4)-Rh(1)-N(1) 95.71(9). (b) *Unit cell* of compound 2 (hydrogen atoms where omitted by clarity).

FIGURE 7: (a) ORTEP perspective of compound 4. Selected bond distances (Å) and angles (°). Rh(1)-Rh(1) 2.386(6), C(1)-O(1) 1.384(4); C(9)-O(2) 1.225(4); C(9)-O(1) 1.371(3); C(12)-O(4) 1.264(4); O(2)-Rh(1) 2.318(2); O(3)-Rh(1) 2.032(2); O(4)-Rh(1) 2.027(2); O(5)-Rh(1) 2.032(2); O(6)-Rh(1) 2.037(2); C(9)-O(2)-Rh(1) 132.6(2), C(10)-O(3)-Rh(1) 118.56(19), C(12)-O(4)-Rh(1) 118.92(19), O(4)-Rh(1)-O(5) 90.74(9), O(3)-Rh(1)-O(5) 176.45(8), O(3)-Rh(1)-O(6) 90.22(9), O(5)-Rh(1)-O(2) 89.86(8). (b) *Unit cell* of compound 4 (hydrogen atoms where omitted by clarity).

FIGURE 8: Proposed structures suggested for molecular ions observed by ESI-MS and tandem MS/MS.

light into the formation of complexes **1–4**, we have used an energy decomposition analysis [84, 85] for the reaction energy ($\Delta E_{R \times n}$) according to the following equation:

$$\Delta E_{R \times n} = E_{\text{Bond}} + E_{\text{Def}}. \quad (1)$$

Thus $\Delta E_{R \times n}$ is the energy difference between relaxed fragments and the total complex. This energy can be decomposed into E_{Bond} (the same energy difference but for the non-optimized geometry of the fragments) and E_{Def} (the energy necessary to deform the original geometry of the reactants when isolated to the geometry they adopt in the product).

This way, we can compare the strength of the $L \rightarrow M$ bond. In all cases, the addition of a first ligand L is energetically more favored than the addition of the second one to the binuclear Rh complex. However, by analyzing E_{Def} , we can see that, for ligands NH_2Dip and NH_2Mes , the deformation is larger when the first ligand is inserted. Now, by considering the addition of a second ligand, the $[\text{Rh}_2(\text{OAc})_4(L)]$ and L fragments are slightly deformed for **1** and **2** (-0.3 and $0.2 \text{ kcal}\cdot\text{mol}^{-1}$, resp.), whereas for $\text{NH}_2\text{coumarin}$, **3**, a similar energy is required for incorporating either the first or the second ligand. When $L = \text{coumarin}$, Gibbs free energy values are larger when adding the second ligand than when adding the first one, where the coumarin ligand is the only one that binds to a rhodium through an oxygen atom. So probably in the competition between the coumarin oxygen and oxygens from acetate groups lies the fact that this ligand is less favored, because of a π -conflict, for being bound to the binuclear Rh(II) complex. Moreover, we have also calculated the binuclear NHC complexes with the formula $[\text{Rh}_2(\text{OAc})_4(L)]$ ($L = \text{IDip}$, **V**; $L = \text{SIDip}$, **Va**) and $[\text{Rh}_2(\text{OAc})_4(L)_2]$ ($L = \text{IDip}$, **V'**; $L = \text{SIDip}$, **Va'**) (for comparison with that reported by Gois et al. [49] see Table S1 in Supplementary Material available online at <https://doi.org/10.1155/2017/5435436>). We presume that similar conclusions would be drawn for analogous complexes. These reactions are noticeably more exothermic (by almost the double of energy) than those reported herein. Although the value of the reaction energy of the first ligation

TABLE 4: Reaction energies and energy decomposition ($\text{kcal}\cdot\text{mol}^{-1}$), calculated at the M06-L/(6-311G, LANL08) level, for the complexes $[\text{Rh}_2(\text{OAc})_4(L)]$, **1'–4'**, and $[\text{Rh}_2(\text{OAc})_4(L)_2]$, **1–4** according to the following reactions: $\text{Rh}_2(\text{OAc})_4 + L \rightarrow [\text{Rh}_2(\text{OAc})_4(L)]$, $[\text{Rh}_2(\text{OAc})_4(L)] + L \rightarrow [\text{Rh}_2(\text{OAc})_4(L)_2]$.

Complex	ΔH_R^0	ΔG_R^0	$E_{R \times n}$	E_{Bond}	E_{Def}
1'	−25.7	−9.9	−23.4	−29.2	5.8
1	−21.1	−12.7	−16.5	−16.2	−0.3
2'	−27.4	−11.1	−24.2	−30.9	6.7
2	−22.5	−10.2	−16.6	−16.8	0.2
3'	−25.6	−10.6	−22.8	−25.9	3.1
3	−18.1	−5.3	−12.2	−14.7	2.5
4'	−17.7	−5.4	−16.2	−17.7	1.5
4	−12.2	2.2	−6.9	−10.2	3.3

FIGURE 9: Cyclic voltammograms of a solution of compound **1** under condition: $1 \times 10^{-3} \text{ M}$ (in dmso), at different scan rate (from 10 to 100 mV/s), using LiCl as supporting electrolyte. The working electrode was glassy carbon, Ag/AgCl as reference, and Pt as the counter electrode.

is almost twice that for the second ligation, the reaction should be continued until the addition of the second ligand NHC. The calculated energy reaction to form complex **V** is $-53.6 \text{ kcal}\cdot\text{mol}^{-1}$ whereas the energy reaction for the second ligand addition in **Va** is $-31.5 \text{ kcal}\cdot\text{mol}^{-1}$. We believe that the use of conventional heating or microwaves is the difference between obtaining binuclear complexes with one ligand and the reaction going further until the incorporation of the second ligand.

3. Conclusions

In summary, we report herein the synthesis and characterization of four paddlewheel rhodium complexes, **1–4**,

assisted by microwave irradiation under laboratory atmosphere in quantitative yields. An X-ray diffraction study shows a slight interaction between amine (NH_2Ar) and carbonyl (coumarin) ligands inside the Rh-Rh bond core. Additionally, a well-defined π - π stacking interaction is found in **4**. However, the natural bulkiness of the NH_2Ar auxiliary ligands avoids this interaction in species **1-2**. The ESI-MS spectrum shows that **1** can form mono-, di-, and triprotonated ionic species, **1a-b**. Later, a tandem MS study was carried out on the **1a** ion, which showed the formation of at least two molecular ions attributed to **1a**- H^+ and **1a**'-H. The attempts to obtain the hydroamination products of the reaction of PA and the corresponding aromatic amines catalysed by **1** were unfruitful under our established conditions. Finally, a DFT study reveals that the formation of **1-4** is thermodynamically favoured with respect to a tentative isolation of the monosubstituted products **1'-4'** because of the use of mw conditions.

4. Experimental

4.1. General: Materials and Methods. $[\text{Rh}_2(\text{OAc})_4]$ was purchased from Chemical Pressure Co. and used as received. Coumarin, phenylacetylene, and the corresponding amines were acquired from Sigma-Aldrich. All other chemicals, filter aids, and chromatographic materials were reagent grade and were used as received. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were measured on a 400 MHz Bruker Advance III or 500 MHz Bruker Ultra-Shield instrument (See Supporting Information). A model maXis impact ESI-QTOFMS equipped with Data Analyzer 4.1 (Bruker Daltonics) was used to resolution mass spectra by direct infusion ($3\ \mu\text{L}/\text{min}$). ESI was operated in positive mode with ion spray voltage 4500 V, drying gas 4 L/min, drying temperature 180°C , and nebulizing gas pressure 0.5 bar (nitrogen). Spectra were acquired in the m/z range 80–1500. Elemental analysis occurred with a Varian Micro Cube instrument from Elementary. IR spectra were acquired in a Bruker Tensor 27 spectrophotometer (KBr pellet, 99% of purity). Melting points were undertaken in a Fisher-Johns apparatus. CEM microwave reactor was used for the synthesis of rhodium complexes. UV-Visible spectra were acquired in Shimadzu UV-2401PC model spectrophotometer. CV experiments were carried out using a galvanostat potentiostat BioLogic 250, model: VSP s/n: 1355, power: 110–240 Vac 50/60 Hz, Fuses: 5 A, Pmax: 300 W. X-ray data were obtained on an Oxford Diffraction Gemini A diffractometer with a CCD area detector, and the CrysAlisPro and CrysAlis RED software packages were used for data collection and data integration [86, 87]; collected data were corrected for absorbance by using analytical numeric absorption correction using a multifaceted crystal model based on expressions upon the Laue symmetry using equivalent reflections [87]. The structures were solved using SHELXS-9721 and refined by full-matrix least-squares on F2 with SHELXL-97.22 Weighted R factors, R_w , and all goodness-of-fit indicators, S , were based on F2. The observed criterion of ($F2 > 2\sigma F2$) was used only for calculating the R factors. All nonhydrogen

atoms were refined with anisotropic thermal parameters in the final cycles of refinement. Hydrogen atoms were placed in idealized positions, with C-H distances of 0.93 and 0.98 Å for aromatic and saturated carbon atoms, respectively. The isotropic thermal parameters of the hydrogen atoms were assigned the values of $U_{\text{iso}} = 1.2$ times the thermal parameters of the parent nonhydrogen atom. A summary of crystallographic data is presented in Table 3.

4.2. Synthetic Procedures

General Method. A mw tube was charged with a mixture of $[\text{Rh}_2(\text{OAc})_4]$ (0.1 g, 0.22 mmol), toluene (2 mL), and the corresponding ligands (0.45 mmol). The mixture was irradiated under mw at 110°C , 150 W and 0.5 h.

Complex 1. Anal. Cal. for $\text{C}_{26}\text{H}_{38}\text{N}_2\text{O}_8\text{Rh}_2$ (M_w 712.4 g mol $^{-1}$) C, 43.83; H, 5.38; N, 3.93. Found: C, 43.3; H, 5.3; N, 3.8. M.p. 301°C . IR (KBr pellet, cm^{-1}): 3372, 3308 (N-H , H_2NAr), 3018 (CH , Ar), 1594 (C-O , OAc). UV/Vis (λ nm, ϵ $\text{M}^{-1}\text{cm}^{-1}$): 283 (36786). ^1H NMR (500 MHz, CDCl_3 , 25°C): 6.87 (s, 2H, CH_m), 5.42 (b.s., 2H, NH_2), 2.37 (s, 6H, CH_3 , Ar_o), 2.24 (s, 3H, CH_3 , Ar_p), 1.63 (OCH_3) ppm. ^{13}C NMR (125 MHz, CDCl_3 , 25°C): 190.9 (C=O), 138.6 ($\text{C}_{\text{Ar-NH}_2}$), 130.0 (C_q), 129.0 (CH , Ar_m), 125.4 (C_q), 20.6 (CH_3 , Ar_p), 17.6 (CH_3 , Ar_o), 23.7 (OCH_3) ppm. ESI-MS (+, m/z): 713.0798.

Complex 2. Anal. Cal. For $\text{C}_{32}\text{H}_{50}\text{N}_2\text{O}_8\text{Rh}_2$ (M_w 796.56 g mol $^{-1}$): C, 48.25; H, 6.33; N, 3.52. Found: C, 48.1, H, 6.3, N, 3.7. M.p. 304°C . IR (KBr pellet, cm^{-1}): 3402, 3334 ($\text{H}_2\text{N-Ar}$). UV/Vis (λ nm, ϵ $\text{M}^{-1}\text{cm}^{-1}$): 274 (20331). ^1H NMR (500 MHz, CDCl_3 , 25°C): 7.17 (d, 2H, CH , $^3J_{\text{H-H}} = 7.1$ Hz); 7.05 (t, 1H, CH , $^3J_{\text{H-H}} = 7.0$ Hz); 5.90 (b.s., 2H, NH_2); 3.48 (sept, 2H, $\text{CH}(\text{CH}_3)_2$, $^3J_{\text{H-H}} = 3.4$ Hz); 1.80 (OCH_3); 1.31 (d, 12H, CH_3 , $^3J_{\text{H-H}} = 3.4$ Hz). ^{13}C NMR (125 MHz, CDCl_3 , 25°C): 190.6 (C=O); 138.2 ($\text{C}_{\text{Ar-NH}_2}$); 136.6 ($\text{C}_{\text{Ar-iPr}}$); 126.0 (CH_m); 121.7 (CH_p); 27.0 ($\text{CH}(\text{CH}_3)_2$); 23.2 ($\text{CH}(\text{CH}_3)_2$); 23.6 (OCH_3).

Complex 3. Anal. Calc. for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_{12}\text{Rh}_2$ (M_w 764.3 g mol $^{-1}$) C, 40.86; H, 3.43; N, 3.67. Found: C, 40.7; H, 3.5; N, 3.6. M.p. 307°C . IR (KBr pellet, cm^{-1}): 3346, 3275 ($\text{H}_2\text{N-Ar}$). UV/Vis (λ nm, ϵ $\text{M}^{-1}\text{cm}^{-1}$): 298 (36785). ^1H NMR (500 MHz, CD_3CN , 25°C): 7.69 (d, 1H, CH_b , $^3J_{\text{H-H}} = 7.6$ Hz); 7.08 (d, 1H, CH_f , $^3J_{\text{H-H}} = 7.0$ Hz); 6.88 (m, 1H, CH_e , $^3J_{\text{H-H}} = 6.8$ Hz) 6.77 (d, H, CH_c , $^3J_{\text{H-H}} = 6.7$ Hz); 6.29 (d, H, CH_a , $^3J_{\text{H-H}} = 6.2$ Hz); 4.27 (b.s., 2H, NH_2); 1.76 (OCH_3). ^{13}C NMR (125 MHz, CD_3CN , 25°C): 208.7 (O-C=O); 192.1 (C=O); 147.5 (C_q , CAr); 145.8 (C_q - NH_2); 141.7 (C_b , CH); 122.3 (C_f , CH); 120.0 (C_q , CAr); 116.6 (C_c , CH); 116.5 (C_a , CH); 23.5 (OCH_3).

Complex 4. Anal. Cal. For $\text{C}_{26}\text{H}_{24}\text{O}_{12}\text{Rh}_2$ (M_w 734.27 g mol $^{-1}$). C, 42.53; H, 3.29. Found: C, 42.5; H, 3.2. M.p. 300°C . IR (KBr pellet, cm^{-1}): 1669, 1590 (C=O). UV/Vis (λ nm, ϵ $\text{M}^{-1}\text{cm}^{-1}$): 370 (119602). ^1H NMR (500 MHz, CD_3CN , 25°C): 7.86 (d, 1H, CH_b , $^3J_{\text{H-H}} = 7.87$ Hz); 7.61 (d, 1H, CH_c , Ar , $^3J_{\text{H-H}} = 7.61$ Hz); 7.34 (t, 1H, CH_e , Ar , $^3J_{\text{H-H}} = 7.32$ Hz);

7.32 (m, H, CH_e, ³J_{H-H} = 6.88 Hz); 6.39 (d, 1H, CH_a, ³J_{H-H} = 6.39 Hz); 1.79 (OCH₃). ¹³C NMR (125 MHz, CD₃CN, 25°C): 205.5 (O-C=O); 190.6 (C=O); 153.0 (C_q); 149.0 (C_b, CH); 137.1 (C_f, CH); 133.5 (C_e, CH); 129.8 (C_c, CH); 129.6 (C_d, CH); 126.4 (C_q); 121.7 (Ca, CH); 21.6 (OCH₃).

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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