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Synthesis, characterization and reactivity of [Rh(bpy)(C_2H_4)Cl]. A study on the reaction with C_1 molecules (CH_2O, CO_2) and $NaBPh_4$

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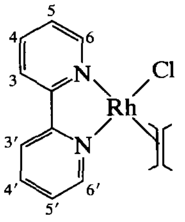
Abstract

The synthesis, spectroscopic characterization and reactivity of [Rh(bpy)(C_2H_4)Cl] (**1**) (bpy = 2,2′-bipyridine) are reported. Compound **1** reacts with CH_2O to afford the known carbonyl complex [Rh(bpy)(CO)Cl] (**3**). The reaction with CO_2 leads to ethylene carboxylation and gives a propionic acid derivative. The reaction of [Rh(bpy)(C_2H_4)Cl] with $NaBPh_4$ affords the new complex [(bpy)Rh(η^6-$PhBPh_3$)] (**2**), a unique example of η^6-coordinated tetraphenylborate to the "(bpy)Rh" moiety.

1. Introduction

The study of transition metal complexes with 2,2′-bipyridine (bpy) and related ligands has received considerable attention as these systems are catalysts in several chemical [1] and electrochemical [2] reactions. More recently, they have been shown to exhibit peculiar photochemical and photophysical properties [3]. Numerous examples of complexes containing the "(bpy)$_n$Rh" (n = 1, 2, 3) moiety have been described, but only a rather limited number of them are Rh^I systems. Moreover, most of the "(bpy)$_n$Rh^I" complexes investigated are ionic compounds of formula [Rh(bpy)L_2]X (L = CO [4–7]; L_2 = 1,5-cyclooctadiene [5,6,8,9], cyclooctatetraene [5], norbornadiene [6,9–15], 1,5-hexadiene [16], or bpy [17]), [Rh(bpy)LL′]X (L = CO; L′ = phosphane [5]), [Rh(bpy)L_3]X (L = CO [6]), [Rh(bpy)LL'_2]X (L = CO, L′ = phosphane [5,18,19]; L = phosphane, L'_2 = cyclooctadiene [5]), [Rh$(bpy)_2$L]X (L = tetracyanoethylene [6]). Indeed, examples of neutral complexes are very rare [6,7,15,17]. Recently, Krause and co-workers [15] reported the X-ray structure of the pentacoordinate species [Rh(bpy)(nbd)Cl] (nbd = norbornadiene). To the best of our knowledge, the only examples of four-coordinate neutral Rh(bpy) compounds are carbonyl complexes of formula [Rh(bpy)(CO)X] (X = Cl, Br, or I) [6,7,17]. Complexes of formula [Rh(bpy)(L)X], where L is an olefin or phosphane, have not been described to date. In this paper we report the synthesis and characterization of [Rh(bpy)(C_2H_4)Cl] (**1**) and describe its reactivity towards C_1 molecules such as CH_2O and CO_2. The synthesis and properties of [(bpy)Rh(η^6-$PhBPh_3$)] (**2**), a unique example of tetraphenylborate η^6-coordinated to the "(bpy)Rh" unit, are also reported.



(**1**)

2. Results and discussion

2.1. *Synthesis and spectroscopic characterization of Rh(bpy)(C_2H_4)Cl*

The reaction of [{Rh(C_2H_4)$_2$Cl}$_2$] with bpy (Rh/bpy molar ratio = 1) (eqn. (1)) affords [Rh(bpy)(C_2H_4)Cl],

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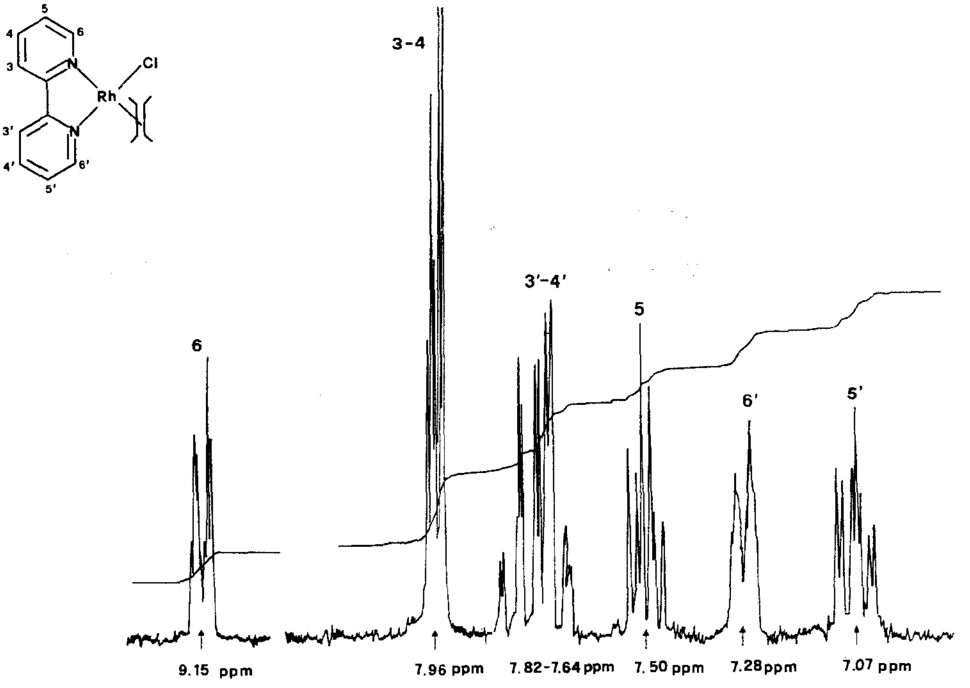

Fig. 1. ^{1}H NMR spectrum (CD_2Cl_2, 293 K) of [Rh(bpy)(C_2H_4)Cl] (1) in the low field region.

a deep purple microcrystalline solid that can be isolated pure if work is carried out under an inert gas.

$$[\{Rh(C_2H_4)_2Cl\}_2] + 2bpy \longrightarrow 2[Rh(bpy)(C_2H_4)Cl] + 2C_2H_4 \quad (1)$$

(1)

The IR spectrum in Nujol shows typical absorptions at 1600, 754 and 719 cm^{-1} due to the bpy and one band at 1220 cm^{-1} assigned to coordinated ethylene. The Rh–Cl stretch is found at 316 cm^{-1}.

The UV-VIS spectrum (in CH_2Cl_2) shows bands at 548 ($\epsilon = 1.40 \times 10^3$ M^{-1} cm^{-1}), 368 ($\epsilon = 2.80 \times 10^3$ M^{-1} cm^{-1}) and 308 nm ($\epsilon = 7.61 \times 10^3$ M^{-1} cm^{-1}), assigned to d(metal) → π*(ligand) transitions. The emission spectrum measured at 77 K does not give any indication of luminescent behaviour.

In the ^{1}H NMR spectrum (CD_2Cl_2, 293 K) of **1** a broadened singlet at 3.56 ppm suggests that the coordinated ethylene molecule rotates fast on the ^{1}H NMR time scale [20]. The ^{1}H spectrum of **1** in the low-field region is shown in Fig. 1. Double-resonance experi-

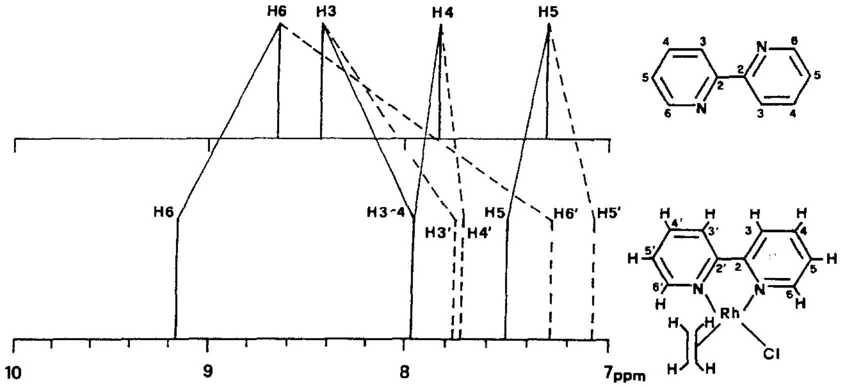

Fig. 2. ^{1}H chemical shifts (CD_2Cl_2) of the bpy protons in free 2,2'-bipyridine (top) (from [23b]; in free bpy the two rings are equivalent) and [Rh(bpy)(C_2H_4)Cl] (1) (bottom) (this work).

TABLE 1. Chemical shifts [δ (ppm), CD_2Cl_2, 293 K] of the tetraphenylborate protons in some Rh(η^6-PhBPh$_3$) complexes

Complex	$H_{o,\eta^6\text{-}(Ph)_n}$	$H_{m,\eta^6\text{-}(Ph)_n}$	$H_{p,\eta^6\text{-}(Ph)_n}$	H_{o,BPh_m}	H_{m,BPh_m}	H_{p,BPh_m}
[(bpy)Rh(η^6-PhBPh$_3$)] [a]	5.96	5.59	[b]	[b]	[b]	[b]
[(diphos)Rh(η^6-PhBPh$_3$)] [c]	6.23	5.47	6.31	7.09	6.89	6.86
[(C_2H_4)$_2$Rh(η^6-PhBPh$_3$)] [d]	6.44	6.07	6.98	7.32	7.14	7.02
[{(C_2H_4)$_2$Rh(η^6-Ph)}$_2$BPh$_2$]O$_3$SCF$_3$ [d]	6.52	6.36	7.26	7.40	7.24	7.13
[{(C_2H_4)$_2$Rh(η^6-Ph)}$_3$BPh](O$_3$SCF$_3$)$_2$ [d]	6.69	6.56	7.39	7.69	7.40	7.34

[a] This work. [b] $H_{p,\eta^6\text{-Ph}}$, H_{o,BPh_3}, H_{m,BPh_3} and H_{p,BPh_3} give overlapping signals in the 6.7–7.0 ppm region. [c] Ref. [25]. [d] Ref. [26].

ments [21*] have shown that the signals of the bpy are grouped in two sets (A and A′) of four, each set containing the proton resonances of only one of the bpy rings. Indeed, the two rings of the bpy in **1** are not equivalent, as a result of the different natures of the *trans* ligands. Set A, a doublet of quartets at 9.15 ppm (H6), the multiplet at 7.50 ppm (H5), and the signals near 7.96 ppm, is due to the almost isochronous H3 and H4 protons. The bpy protons at the five- and six-positions of the second ring (H5′ and H6′, set A′) resonate at 7.07 and 7.28 ppm, respectively, whereas the H3′ and H4′ protons give the overlapping multiplets in the 7.64–7.82 ppm region.

Coordination of bpy in the absence of both π-back-donation from the metal and additional factors due to ancillary ligands, should build a positive charge at the various C-atoms of the chelating ligand. This should be particularly important at the positions closest to the metal, and lead to general downfield shifts of the proton resonances of coordinated bpy with respect to those of the free base [22]. The downfield shift at the 3-position should be enhanced owing to the conformational change undergone by the bpy upon chelation [23]. In Fig. 2 the ^{1}H chemical shifts of free bpy are compared with those of bpy in **1**. Upon coordination, the proton resonances of one of the rings of the heterocycle are all shifted upfield (set A′) with respect to those of free bpy. In contrast, the resonances of the second ring (set A), appear at lower fields than set A′ ($\delta_{H_n} > \delta_{H_{n'}}$, $n = n' = 3$–6), and are, in general, observed at lower field than the resonances of the free bpy. The resonances of protons H3 and H3′ undergo large upfield shifts. Metal-bpy back π-bonding thus plays an important role. The poorer σ-donor properties and higher π-acidity of ethylene with respect to chloride reflect the bonding of bpy to Rh, so that the ring *trans* to Cl experiences a higher back-donation from the metal d-orbitals than the ring *trans* to ethylene, that competes for the d_π electron of the metal. Therefore, we assign the A′ resonances to the ring *trans* to chloride and the A signals to the protons of the ring *trans* to ethylene.

It is worth noting that upon coordination of bpy, the protons at H6 and H6′ undergo a remarkable shift in opposite directions. This apparently surprising behaviour may be the outcome of supplementary effects caused by the closeness of these protons to the ancillary ligands: the diamagnetic anisotropy of the coordinated ethylene molecule can account for the very large upfield shift of the proton H6′, while deshielding by the non-bonding electrons of the Cl ligand can contribute to the downfield shift of the H6 proton.

2.2. Reaction of [Rh(bpy)(C$_2$H$_4$)Cl] with sodium tetraphenylborate

The chlorine atom of [Rh(bpy)(C$_2$H$_4$)Cl] can be easily removed by reaction of **1** with Cl-extracting reagents such as silver triflate [24] or sodium tetraphenylborate. In this paper, we report in detail results concerning the reactivity of **1** towards NaBPh$_4$.

We have found that [Rh(bpy)(C$_2$H$_4$)Cl] reacts smoothly with NaBPh$_4$ in toluene (eqn. (2)) to afford the green complex [(bpy)Rh(η^6-PhBPh$_3$)] (**2**) that is quite stable in dry air.

$$\underset{(1)}{[Rh(bpy)(C_2H_4)Cl]} + NaBPh_4 \longrightarrow \underset{(2)}{[(bpy)Rh(\eta^6\text{-}PhBPh_3)]} + NaCl + C_2H_4 \quad (2)$$

The ^{1}H NMR ($CDCl_3$) spectrum of **2** shows a triplet at 5.63 ppm (t, 2H, $H_{meta,\eta^6\text{-Ph}}$) and a doublet at 6.10 (d, 2H, $H_{ortho,\eta^6\text{-Ph}}$), confirming that the tetraphenylborate anion is η^6-coordinated to rhodium [25–27]. The resonance due to $H_{para,\eta^6\text{-Ph}}$ is masked by the BPh$_3$ group signals that appear in the range 6.7–7.0 ppm: these signals rightly integrate for 16 protons. These features are consistent with those of other Rh(η^6-PhBPh$_3$) complexes we have prepared (Table 1) [25,26].

The two rings of the bpy are now equivalent in the ^{1}H spectrum; however, we believe that this is the result of the fast rotation (on the NMR time scale) of Rh-bpy fragment around the Rh–(η^6-Ph) bond vector rather

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* Reference number with asterisk indicates a note in the list of references.

than of a symmetric rigid conformation of **2** that confers equivalence on the two rings of the bpy. The first-order structure of the η^6-Ph proton resonances substantiates this point of view. It is worth noting that a similar internal motion has been documented by us for some other Rh(η^6-PhBPh$_3$) complexes [25,26].

To the best of our knowledge, **2** represents the second example of a Rh(η^6-PhBPh$_3$) complex with a *N*-donor chelating ligand, and it has been obtained by a new synthetic route. Mestroni and co-workers [16] reported [(phen)Rh(η^6-PhBPh$_3$)] (phen = 1,10-phenantroline) from hydrogenation of [(phen)Rh(1,5-hexadiene)]BPh$_4$. It is of interest that the reaction of [(nbd)RhL$_2$]Cl (L or L$_2$ denotes a mono- or bi-dentate *N*-donor, respectively) with NaBPh$_4$ does not give complexes of formula [L$_2$Rh(η^6-PhBPh$_3$)] but, depending on L, leads to the formation of [(nbd)Rh(η^6-PhBPh$_3$)] or ionic complexes [(nbd)RhL$_2$]BPh$_4$ [12].

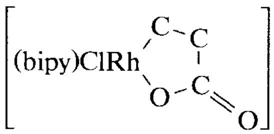
2.3. Reactivity of [Rh(bpy)(C_2H_4)Cl] towards paraformaldehyde and carbon dioxide

[Rh(bpy)(C_2H_4)Cl] reacts rapidly with formaldehyde at room temperature in THF to afford the deep purple-red complex [Rh(bpy)(CO)Cl] (**3**) [6,7,17]. The gas over the reaction mixture contains dihydrogen, ethylene and a little ethane. We have not observed formaldehyde-ethylene coupling products; moreover, neither methanol nor methylformate was detected in the reaction mixture. These findings show that the reaction of **1** with CH_2O results in the dehydrogenation of the aldehyde to give dihydrogen and bound CO. An analogous behaviour has been observed by us and others using Rh^I [25] or Ni^0 [28] systems. Roper and co-workers [29] have shown that H_2 and bound CO can be the products of thermal decomposition of M-(η^2-CH_2O) metal complexes (M = Os) via a hydride-formyl intermediate; however, these species were not observed in the present work, although inferred by us in analogous Rh systems [25].

[Rh(bpy)(CO)Cl] has been characterized by IR and ^{1}H NMR spectroscopy. The IR spectrum (Nujol) of **3** shows a very strong band at 1958 cm^{-1} due to ν(CO) and absorptions at 1600m, 760 and 720 cm^{-1} assigned to the bpy. The ^{1}H NMR (CD_2Cl_2, 293 K) spectrum of **3** confirms that the two rings of the bpy are not equivalent, as two sets of resonances (B and B′) are observed. The protons at H3, H3′, H4, and H4′ give complicated overlapping signals in the range 7.90–8.12 ppm and integrate for four protons. Other signals are observed at 9.40 ppm (d, *J*(H6–H5) = 5.2 Hz, H6), 8.81 ppm [dm (two ill-resolved multiplets), *J*(H6′–H5′) = 6.3 Hz, H6′], 7.62 ppm (m, H5) and 7.30 ppm (m, H5′). We assign the protons H3–H6 to the ring *cis* to Cl, the modest downfield shift of these protons with respect to the corresponding ones in **1** being related to the replacement of C_2H_4 by CO as *trans*-ligand. Consequently, the signals H3′–H6′ are due to the protons of the second ring. It is worth noting that the proton at the 6′-position resonates at a much lower field than the H6′-proton of **1**.

Our interest in both carbon dioxide activation by transition metal complexes and metal-assisted carboxylation of organic substrates via CO_2 utilization [30] led us to study the reactivity of **1** towards the heterocumulene.

At room temperature in THF, [Rh(bpy)(C_2H_4)Cl] reacts very slowly (> 9 days) with carbon dioxide (*P* = 0.1 MPa) to give a brown solid that precipitates from the reaction solution. The IR spectrum of this solid has bands in the 1650–1500 cm^{-1} range. These absorptions are not due to coordinated CO_2 [31] or carbonate coming from the "dismutation" of the heterocumulene [32], as no CO_2 evolution is observed upon treatment of the compound with iodine or dilute acids and GC analysis of the gas phase in equilibrium with the solution does not reveal CO. These data suggest the formation of carboxylated species of type A [33*] found on the metal [34]. However, we note that bands due to coordinated ethylene are no longer found in the spectrum of the isolated product, suggesting carboxylation reaction of the ethylene. This is supported by the fact that the ^{13}C-APT spectrum of the product (in DMSO-d_6) obtained from the reaction of **1** with labelled $^{13}CO_2$ shows a signal at 174.01 ppm, in the range typical of carboxylate groups [34a,c,e] and attributable to a carbon atom not bound to hydrogen atoms. Furthermore, signals assignable to a methylene carbon directly bound to Rh (doublet, *J*C–Rh = 20 Hz [35]) and to a CH_2 group adjacent to the carboxylic function are observed at 18.4 [36] and 29 ppm [37], respectively.



(A)

The stoichiometric carboxylation of olefines with CO_2 to give carboxylate metallacycles or dicarboxylates or acrylate has been accomplished using Ni^0 [33d], Ti^{II} [38], Fe^0 [39], and Mo^0 [34a], but no example has been reported involving Rh. Lapidus and co-workers [40] claimed the Rh-promoted catalytic formation of propionic acid and ethylpropionate from ethylene and CO_2 under severe conditions, but it may not be that of the carboxylic function arising from carbon dioxide [41]. Our data seem to confirm the ability of Rh^I systems to promote the carboxylation of ethylene to propionic acid using carbon dioxide. We found similar behaviour in the Rh-catalyzed electrochemical carboxylation reaction of ethylene under CO_2 to afford propionic acid [42].

3. Experimental details

Unless otherwise stated, all reactions and manipulations were conducted under dinitrogen by using vacuum-line techniques. All solvents were dried as described in the literature and stored under dinitrogen. $[\{Rh(C_2H_4)_2Cl\}_2]$, $NaBPh_4$ and 2,2′-bipyridine were Aldrich products. Paraformaldehyde was purchased by Farmitalia Carlo Erba. CO_2 (99.99% pure) and $^{13}CO_2$ (99% ^{13}C) were from SIO SpA and CIL, respectively.

Infrared and UV-VIS spectra were obtained with a Perkin Elmer 883 spectrophotometer and a Cary 219 Varian instrument, respectively. NMR spectra were run on a Varian XL-200 spectrometer (at 200 MHz for ^1H and 50.3 MHz for ^{13}C). Chemical shifts are reported in ppm *vs.* TMS. GC analyses of reaction solutions were performed with a DANI HR 3800 gas-chromatograph equipped with a Carbopack C 0.1% or SE-30 column (2 m × 0.32 mm) and a HP 5890 gas-chromatograph (capillary column: 30 m SE-30, 0.25 mm i.d.; 0.25 μm film thickness) linked to a HP 5970 selective mass detector. GC analyses of the gas phase were carried out with a DANI 86.10 gas-chromatograph equipped with a TCD 866 detector using a Carbosieve S II column.

3.1. Synthesis of [Rh(bpy)(C_2H_4)Cl (1)]

Bpy (0.3652 g, 2.34 mmol) in toluene (10 ml) was added to a filtered solution of $[\{Rh(C_2H_4)_2Cl\}_2]$ [43*] (0.5041 g, 1.30 mmol) in toluene (80 ml) and the reaction mixture was stirred for 2 h at 293 K. The purple solid precipitated was isolated by filtration, washed with toluene, and dried *in vacuo* (0.6945 g, 92%).

^1H NMR (CD_2Cl_2, 293 K): δ 3.56 (s, 4H, ethylene protons); 7.07 (m, 1H, H5′); 7.28 (dm, 1H, H6′); 7.50 (m, 1H, H5); 7.64–7.82 (multiplets, 2H, H3′ and H4′); 7.96 (multiplets, 2H, H3 and H4); 9.15 (dm, 1H, J(H6–H5) = 5.60 Hz, J(H6–Rh) = 1.27 Hz, H6). UV-Vis (CH_2Cl_2) λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 548 (1.40×10^3), 368 (2.80×10^3), 308 (7.61×10^3). ^{13}C NMR (CD_2Cl_2, 293 K) δ: 151.32, 148.51, 139.37, 134.06, 126.84, 126.32, 122.63, 121.19 [44*]. IR (Nujol mull, CsI) ν 1600, 1220, 754, 719, 316 cm^{-1}. Anal. Found: C, 44.64; H, 3.69; N, 8.47; Cl, 11.02. $C_{12}H_{12}ClN_2Rh$ calcd.: C, 44.68; H, 3.75; N, 8.68; Cl, 10.99%.

3.2. Synthesis of [(bpy)Rh(η^6-PhBPh$_3$)] (2)

$NaBPh_4$ (0.4005 g, 1.17 mmol) in deaerated absolute ethanol (5 ml) was added to [Rh(bpy)(C_2H_4)Cl] prepared *in situ* from $[\{Rh(C_2H_4)_2Cl\}_2]$ (0.252 g, 1.30 mmol) and bpy (0.1830 g, 1.17 mmol) as described above [toluene (40 ml)]. The reaction mixture was stirred overnight at 295 K. The deep green precipitate was isolated by filtration, washed with distilled water, absolute ethanol, toluene, pentane, and dried *in vacuo* (0.450 g, 67%).

^1H NMR ($CDCl_3$, 293 K) δ: 5.63 (t, 2H, $J(H_{meta}-H_{ortho}) = J(H_{meta}-H_{para}) = 6.2$ Hz, H(*meta*,η^6-Ph)); 6.10 (d, 2H, H(*ortho*,η^6-Ph)); 6.7–7.0 (m, 16H, $-BPh_3$ protons and H(*para*,η^6-Ph)); 7.3–7.7 (m, 4H, H4 and H5); 7.92 (d, 2H, J(H3–H4) = 8.19 Hz, H3); 8.05 (d, 2H, J(H6–H5) = 5.78 Hz, H6). IR (Nujol mull, KBr): ν 1600, 770–700 cm^{-1}. Anal. Found: C, 70.50; H, 4.80; N, 4.81. $C_{34}H_{28}BN_2Rh$ calcd.: C, 70.61; H, 4.88; N, 4.84%.

3.3. Reaction of [Rh(bpy)(C_2H_4)Cl] with paraformaldehyde

Monomeric CH_2O, obtained by thermal depolymerization of an excess of paraformaldehyde (0.556 mg, 18.5 mmol) previously dried over P_2O_5, was bubbled into a THF (80 ml) solution of [Rh(bpy)(C_2H_4)Cl] (0.3090 g, 0.958 mmol) at room temperature (293 K). The reaction solution turned to red and after stirring for about 1 h at room temperature, was filtered. Pentane was added to the motherliquor and cooled to 253 K. The red precipitate of **3** was filtered, washed with pentane and dried *in vacuo* (0.247 g, 80%).

^1H NMR (CD_2Cl_2, 293 K): δ 7.30 (m, 1H, H5′); 7.62 (m, 1H, H5); 7.90–8.12 (m, 4H, H3, H3′, H4, H4′); 8.81 (d, 1H, 6.3 Hz, H6′); 9.40 (d, 1H, 5.2 Hz, H6). IR (Nujol mull, KBr): ν 1958, 1600, 760 and 720 cm^{-1}. Anal. Found: C, 41.22; H, 2.76; N, 8.49; Cl, 10.29. $C_{11}H_8Cl\ N_2ORh$ calcd.: C, 40.96; H, 2.50; N, 8.68; Cl, 10.99%.

3.4. Reaction of [Rh(bpy)(C_2H_4)Cl] with carbon dioxide

A THF (30 ml) solution of [Rh(bpy)(C_2H_4)Cl] (0.2000 g, 0.636 mmol) was stirred at 293 K under carbon dioxide (0.1 MPa) for 9d. The brown precipitate was filtered, washed with pentane and dried *in vacuo* (0.150 g). It was probably $[(bpy)ClRh\{\overline{CH_2CH_2C(O)O}\}]$ [34]. ^{13}C NMR (DMSO-d_6, 293 K): δ 174.01. IR (Nujol mull, KBr) ν 1650–1500 cm^{-1}. Anal. Found: C, 39.65; H, 3.87; N, 6.84; Cl, 9.59. $C_{13}H_{12}CL\ N_2ORh$ calcd.: C, 42.59; H, 3.30; N, 7.63; Cl, 9.67%.

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