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Photochemistry of rhodium(I) olefin complexes containing the (hydro)tris(pyrazolyl)borate ligand

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Abstract

The photoisomerisation (λ=400 nm) of [Tp^{Me2}Rh (η^4-1,5-COD)] (**1**), (Tp^{Me2}=hydrotris(3,5-dimethyl)pyrazolyl borate, 1,5-COD=1,5-cyclooctadiene) to [Tp^{Me2}Rh (η^4-1,3-COD)] (**2**) is reported. The photoreaction is an intramolecular (3,4) hydrogen shift of the coordinated 1,5-COD possibly involving an allylrhodium(III) intermediate. The selective photolysis of complex **2** with 336 nm light causes the dissociation of 1,3-COD forming the organometallic fragment {Tp^{Me2}Rh} (**A**) as its primary photoproduct. Fragment **A** is a versatile entry point in the photochemical preparation of new hydrido Rh(III) complexes. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Photolysis; Rh(III) complex; Absorption spectra

1. Introduction

Currently, there is a great flowering in the photochemistry of transition metal complexes with hydrotris(3,5-dimethyl)-pyrazolyl borate ligands [1–3]. Principally, this stems from the fact that the members of this class of compounds are useful in catalysing or assisting the activation of aromatic and saturated hydrocarbons following photolysis in room temperature solutions. These systems are especially significant since C–H bond activation occurs efficiently and with high thermodynamic selectivity [5].

In this paper, we report the results of our investigations into the solution photochemistry of the complex [Tp^{Me2}-Rh (η^4-1,5-COD)] (**1**) (Tp^{Me2}=hydrotris(3,5-dimethylpyrazolyl)borate, 1,5-COD=cyclooctadiene-1,5-diene) including an unprecedented example of synthesis of the isomer [Tp^{Me2}Rh (η^4-1,3-COD)] (**2**). Complex **2** is the first well defined compound in which the 1,3-COD is bonded to the {Tp^{Me2}Rh} fragment. The results revealed that the **1**→**2** isomerisation occurs very cleanly following photolysis in the visible region (λ=400 nm) and occurs with high conversion efficiencies in various solvents. Moreover, selective photolysis (λ=336 nm) of complex **2** in the presence of P(OMe)$_3$ leads to dissociation of 1,3-COD giving the unsaturated 14e metal fragment {Tp^{Me2}Rh} (**A**) as valuable synthon for the development of the C–H bond photoactivation of various organic substrates and for preparation of new hydride Rh(III) complexes.

2. Results and discussion

Photolysis of a de-aerated solutions of {Tp^{Me2}Rh (η^4-1,5-COD)} (**1**) in several solvents generates {Tp^{Me2}Rh (η^4-1,3-COD)} (**2**) as an isolable product readily characterised by elemental analysis, FT-IR, ^{1}H, ^{13}C and ^{103}Rh NMR spectroscopy.

^{1}H NMR spectra of 1 recorded from solutions kept in the dark at 293 K have established the absence of any thermal processes contributions during the course of these photochemical transformations.

Fig. 1 illustrates the UV–VIS absorption spectra recorded during the photolysis of **1** in benzene, including an isosbestic point at 362 nm. The lowest energy transition, centred at 400 nm, progressively decreases in intensity as the reaction proceeds. The band growing at 338 nm is due to the isomer species **2**. Consistent with its formulation, **2** exhibits ^{1}H NMR resonance at 1.73, 4.20, 5.12 ppm of 1,3-COD bonded to Rh as compared to that at 1.59, 2.13, 4.13 ppm for **1** where the olefin is the 1,5-COD, both in C$_6$D$_6$ at 295 K.

The changes in NMR spectra of the diene ligand on going from **1** to isomer **2** are quite striking. After 30 min of NMR tube photolysis (λ=400 nm), the resonance for the complex **2** had grown significantly in intensity and the resonance for the isomer **1** had decreased proportionally. After 1 h of photolysis, a complete conversion of **1** to **2** is observed.

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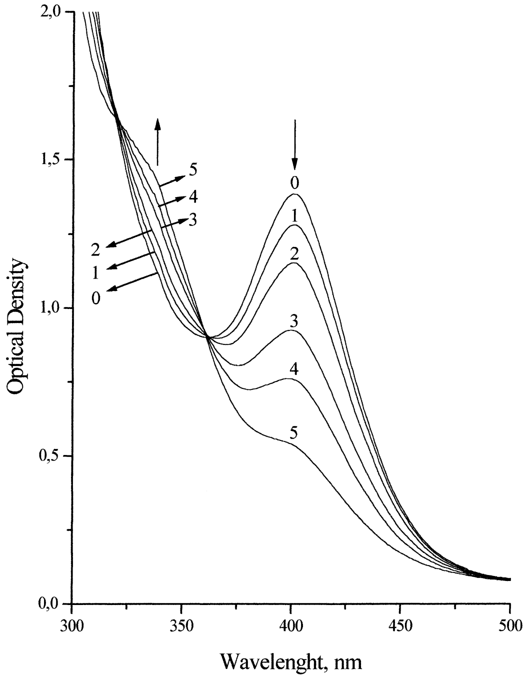
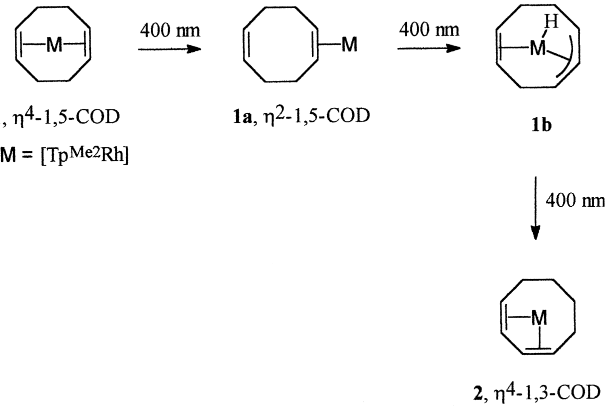


Fig. 1. Electronic absorption spectral changes which occur upon photolysis of a degassed solution of $[\mathrm{Tp^{Me2}Rh}(\eta^4\text{-}1,5\text{-COD})]$ (**1**) at 298 K with 400 nm light. Scans 1–2 after t=0 were taken at intervals of 2 min; scans 3–4 at intervals of 4 min; curve 5 corresponds to the electronic spectrum of the complex $[\mathrm{Tp^{Me2}Rh}(\eta^4\text{-}1,3\text{-COD})]$ (**2**).



Scheme 1. Proposed reaction mechanism for the photoisomerization of $[\mathrm{Tp^{Me2}Rh}(\eta^4\text{-}1,5\text{-COD})]$ (**1**) to $[\mathrm{Tp^{Me2}Rh}(\eta^4\text{-}1,3\text{-COD})]$ (**2**).

In the ^{1}H NMR spectrum of **1**, the ^{1}H of CH(COD) displays a multiplet at δ=4.13 ppm while the ^{1}H of CH_2(COD) shows two multiplets at δ=2.13 and 1.59 ppm. On going to **2**, the resonance of CH(COD) splits into two multiplets at δ=5.12 and 4.20 ppm while the resonance for CH_2(COD) undergoes a downfield shift to δ=1.73 and 1.37 ppm.

The splitting into two doublets of CH(COD) in the ^{13}C NMR spectrum as well the presence of two doublets for CH_2(COD) in complex **2** are also indicative of the 1–5 to 1–3 coordination change the olefin has undergone. Moreover, the values of the coupling constants may be considered in support of the formulation of complex **2** as the $[\mathrm{Tp^{Me2}Rh}$ $(\eta^4\text{-}1,3\text{-COD})]$ isomer.

To our knowledge, compound **2** is the first example of a complex containing the olefin 1,3-COD bonded to Rh centre. Any experiment carried out for a thermal synthesis of **2** starting directly from 1,3-COD invariably yields complex **1** with the bonded 1,5-COD.

The above results indicate that long wavelength (λ=400 nm) excitation of **1** results only in the formation of isomer **2**. The absorption centred at 401 nm is associated with an LF transition since its energy is independent of the solvent. Further, the absorption energy position is consistent with ligand field strengths of d^8 metals, as observed in analogous olefin complexes [4]. However, considerations derived from symmetry, the nature of the ligand, the central metal oxidation state and the relatively high intensity (ε=1186) of this transition indicate a contribution from a MLCT component [4,6]. On the basis of these considerations, a simple one-electron model predicts that LF excitation of **1** would result in photodissociation of one of the two Rh(I) coordinated carbon–carbon double bonds (Scheme 1) forming the coordinatively unsaturated complex **1a** with the olefin η^2-coordinated.

The coordinative unsaturation of Rh(I) in complex **1a** enhances the proclivity of this d^8 metal centre toward oxidative addition. It is, therefore, reasonable to suppose that in a subsequent photoreaction, an allylic C–H bond oxidatively adds to rhodium directly producing an allylrhodium hydride intermediate **1b** which yields the rhodium complex **2** by intramolecular hydrogen shift from the 5,6 position of the 1,5-COD to the 3,4 position of 1,3-cyclooctadiene. Experiments provided evidence for this assumption, since the photoisomerisation remains nearly unchanged upon variation of the solvent, as long as non coordinating solvents such as toluene, benzene and ether are used. Moreover, the proposal of participation of a hydrido-allyl intermediate in the photolysis of **1** is consistent with the mechanism proposed for the photoinduced hydrogen transfer from others olefins catalysed by Ir(I) complexes [2,6].

2.1. Photochemistry of [Tp^{Me2}Rh (1,3-COD)] **2**

An interesting new finding is that the 1,3-COD loss is effected upon short wavelength (λ=366 nm) excitation of **2** in benzene, giving the transient metal fragment $\{\mathrm{Tp^{Me2}Rh}\}$ **A** as its primary photoproduct. In the absence of added ligands, irradiation of **2** in benzene results in its slow decomposition. However, when photolysis of **2** is carried out in benzene containing 1 eq. of $P(OMe)_3$ the complex $[\mathrm{Tp^{Me2}RhH(C_6H_5)(P(OMe)_3)}]$ (**3**) is formed as the only photoproduct containing the $\{\mathrm{Tp^{Me2}Rh}\}$ fragment (Eq. (1)).

$$\underset{\mathbf{2}}{[\mathrm{Tp^{Me2}Rh(1,3\text{-}COD)}]} \xrightarrow[\text{1eq. P(OMe)}_3]{366\,\text{nm},\mathrm{C_6H_6}} \underset{\mathbf{3}}{[\mathrm{Tp^{Me2}Rh(H)(C_6H_5)(P(OMe)_3)}]} + 1.3\text{-COD} \qquad (1)$$

The dominant photochemistry of **2** is the dissociation of 1,3-COD. This reactivity is expected because excitation at the higher energy band (336 nm) is correlated with the MLCT transition that populates an olefin π^* orbital [2,4,5]. Typically, the energy carried by a 336 nm light beam is equivalent to 85 Kcal/mol. Then it is conceivable that after photoexcitation, the ligand 1,3-COD is totally dechelated to form the transient $\{Tp^{Me2}Rh\}$ (**A**) (Eq. (2)).

$$\underset{\mathbf{2}}{[Tp^{Me2}Rh(1,3-COD)]} \xrightarrow{h\nu} \underset{\mathbf{A}}{\{Tp^{Me2}Rh\}} + 1.3\text{-COD} \qquad (2)$$

The presence of 1 eq. of 1,3-COD in the distillate after photolysis, showed that photodissociation of 1,3-COD was quantitative, indicating that the formation of $[Tp^{Me2}Rh(H)(C_6H_5)(P(OMe)_3)]$ (**3**) proceed as shown in Eq. (3).

$$\underset{\mathbf{A}}{\{Tp^{Me2}Rh\}} + C_6H_6 \rightarrow \underset{\mathbf{B}}{\{Tp^{Me2}Rh(H)(C_6H_5)\}}$$
$$\xrightarrow{P(OMe)_3} \underset{\mathbf{3}}{[Tp^{Me2}Rh(H)(C_6H_5)(P(OMe)_3)]} \qquad (3)$$

The postulate that fragment $\{Tp^{Me2}Rh\}$ (**A**) is the primary photoproduct and the formation of **3** implies that **A** undergoes an oxidative addition of a C–H bond of C_6H_6, resulting in formation of the 16-electron, coordinatively unsaturated complex $\{Tp^{Me2}Rh(H)(C_6H_5)\}$ (**B**). $P(OMe)_3$ then react with the Rh(III) intermediate **B**, effecting an overall ligand saturation stabilising product **3**, as illustrated in Eq. (3).

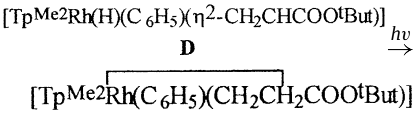
The role of the primary photoproduct **A** must be quite great, since photolysis of **2** leads to dehydrogenation of MeOH with formation of the hydridocarbonyl complex $\{Tp^{Me2}Rh\ H_2(CO)\}$ (**4**) (Eq. (4)) when the solvent is changed from C_6H_6 to CH_3OH.

$$\underset{\mathbf{2}}{[Tp^{Me2}Rh(1,3\text{-COD})]} \xrightarrow[CH_3OH]{h\nu} \underset{\mathbf{4}}{[Tp^{Me2}Rh(H)_2(CO)]}$$
$$+1.3\text{-COD} + H_2 \qquad (4)$$

The above results reported for the photochemistry of complex **2** can be used to demonstrate the synthetic utility of 1,3-COD dissociation in complex **2**. Indeed photolysis of **2** in benzene containing 2 eq. of ^{t}But-acrylate results in the formation of the product $[Tp^{Me2}Rh(C_6H_5)(CH_2CH_2CO_2{}^tBut)]$ (**5**). The reaction undoubtedly involves dissociative rupture of the two olefin bonds in **2**. The newly formed fragment **A** quickly reacts with a solvent molecule to form the unsaturated intermediate **B**. In this system, η^2-acrylate co-ordination can be achieved with formation of the Rh(III) complex **D** (Eq. (5)).

$$\begin{aligned}
&\underset{\mathbf{2}}{[Tp^{Me2}Rh(1,3\text{-COD})]} \xrightarrow[-1,3\text{-COD}]{h\nu, C_6H_6} \underset{\mathbf{B}}{\{Tp^{Me2}Rh(H)(C_6H_5)} \\
&\underset{\mathbf{B}}{\{Tp^{Me2}Rh(H)C_6H_5)\}} \xrightarrow{CH_2CHCOO^tBut} \underset{\mathbf{D}}{\{Tp^{Me2}Rh(H)(C_6H_5)(\eta^2\text{-}CH_2CHCOO^tBut)\}}
\end{aligned} \qquad (5)$$

Under continuos photolysis, the metal centre in **D**, now schielded by the complexed acrylate, can only undergo an insertion of ^{t}Bu-acrylate in the Rh–H bond of **D** to form the product **5** (Eq. (6)).



$$\underset{\mathbf{D}}{[Tp^{Me2}Rh(H)(C_6H_5)(\eta^2\text{-}CH_2CHCOO^tBut)]} \xrightarrow{h\nu} \underset{\mathbf{5}}{[Tp^{Me2}Rh(C_6H_5)(CH_2CH_2COO^tBut)]} \qquad (6)$$

^1H and ^{13}C NMR spectroscopy studies and FT-IR data allowed a full structural assignment for complex **5**. The ^1H and ^{13}C NMR spectra indicate that photolysis has inserted *t*-butyl-acrylate into the Rh–H bond of **5** to form a (^{t}Butoxycarbonyl)ethyl moiety, serving as a five-membered C,O chelating ligand similar in fashion to (alkoxycarbonyl)vinyl moieties [7,8]. In **5**, the absence of any signals due to Rh–H as observed in **3** and the signals of Rh–CH_2 and Rh–CH_2CH_2 support the photoinsertion of the olefin in the Rh–H bond. It is noteworthy that the photoinduced insertion of the ^{t}Bu-acrylate in the Rh–H bond of a complex such as **D** appears to be unprecedented and opens the way for the development of organometallic photocatalysis of the $\{Tp^{Me2}Rh\}$ fragment.

3. Experimental details

3.1. *Spectra*

All UV–VIS absorption spectra were obtained using a JASCO UVIDEC-650 double beam spectrometer. The infrared spectra were recorded on a Bruker IFS 88 FT-IR Spectrometer. All NMR data were acquired using a Bruker AC200 and Bruker AMX500 spectrometers operating, respectively, at 200.13 (500.13) for ^1H and 50.2 (125.6) for ^{13}C.

3.2. *General data*

All preparations and photochemical experiments were carried out under an atmosphere of dry Argon using standard Schlenk techniques. The solvents were dried by refluxing them over sodium/benzophenone and were distilled under argon prior to use. The deuterated solvents C_6D_6 and CD_2Cl_2 were obtained from Fluka and dried over molecular sieves (3 Å).

Elemental analysis was performed by the Microanalytical Laboratory of the Department of Chemistry, University of Ferrara. The *t*-Butyl-acrylate (from Fluka) was degassed under argon prior to use.

The starting material $[Tp^{Me2}Rh\ (1,5\text{-COD})]$ 1 was prepared as described elsewhere [9]. The analytical and spectroscopic data for **1** are:

Anal. Found Calc. (Mis.) ($C_{23}H_{34}BN_6Rh$; M=508.28): C 54.35 (53.97); H 6.74 (6.75); N 16.53 (16.60). FT-IR (KBr): 2464 (B–H). UV–VIS in C_6H_6: λ max (nm)=401 (1816). ^{1}H NMR (200 MHz, $CDCl_3$) ppm: 5.81 (s, 3H, H-4); 4.44 (s, 1H, B–H); 4.13 (m, 4H, CH(COD)); 2.34, 2.13 (s, 2×9H, CH_3-3, CH_3-5); 2.13 (m, 4H, CH_2(COD)); 1.59 (m, 4H, CH_2(COD)). ^{13}C NMR (200 MHz, C_6D_6) ppm: 150.6 (s, 3C, C-3); 143.6 (s, 3C, C-5); 106.7 (s, 3C, C-4); 75.2 (d, 4C, CH(COD), J(Rh,C)=12.4 Hz); 26.2 (s, 4C, CH_2(COD)); 14.9 (s, 3C, CH_3-3); 12.9 s, 3C, CH_3-5). ^{103}Rh-^{1}H NMR HMQC (250 MHz, C_6D_6) ppm: 1107.

3.3. Photochemical procedures

UV-photolysis was performed with light from a 500 W Oriel Hg lamp housing the apparatus set on an optical rail. Monochromatic light was obtained using an Applied Photophysics f/3.4 monochromator or with bandpass interference filters form Oriel corp.

3.4. Photochemical preparation of [Tp^{Me2}Rh (1,3-COD)] **2**

A solution of **1** (25 mg, 0.049 mmol) in benzene (4 ml) was degassed by three freeze-pump throw cycles on a high vacuum line. The solution was transferred through a cannula to a quartz couvette sealed with a septum cap. The solution was irradiated with λ=400 nm at 20°C. The progress of photoreaction was followed by monitoring the ^{1}H NMR spectra of the solution (see below). Irradiation was stopped after 120 min. The spectra showed the total conversion of **1** to **2**. Removal of the solvent under vacuum and recrystallisation of the residue from CH_3CN/CH_2Cl_2 (1:1) at −20°C gave pure **2** in 98% isolated yield. Its ^{1}H NMR spectrum showed resonance of free 1,3-COD in the distillate. Larger amounts of **3a** were obtained by repeating the above photoreaction 10 times.

Anal. Found Calc. (Mis.) ($C_{23}H_{34}BN_6Rh$; M=508.28): C 54.35 (54.45), H 6.74 (6.69), N 16.53 (16.62). FT-IR (KBr, cm^{-1}): 2522 (B–H). UV–VIS in C_6H_6: λ max (nm)=338 (3000), 400 (1100). ^{1}H NMR (200 MHz, C_6D_6) ppm: 5.62 (s, 3H, H-4); 5.12 (m, 2H, CH(COD)); 4.20 (m, 2H, CH(COD)); 2.27 (s, 9H, CH_3-5); 2.20 (s, 9H, CH_3-3); 1.73–1.37 (m, 8 H, CH_2(COD)). ^{13}C NMR (200 MHz, C_6D_6) ppm: 151.2 (s, 3C, C-3); 142.7 (s, 3C, C-5); 107.7 (s, 3C, C-4); 82.5 (d, 2C, CH(COD), J(Rh,C)=6.12 Hz); 39.5 (d, 2C, CH(COD), J(Rh,C)=18.3 Hz); 28.0, 25.5 (s, 4C, CH_2(COD)); 14.7 (s, 3C, CH_3-3); 13.0 (s, 3C, CH_3-5). ^{103}Rh-^{1}H NMR HMQC (250 MHz, C_6D_6) ppm: 1942.

3.5. Photochemical experiments in the NMR tube

A typical analytical photolysis was carried out as follows: an NMR tube with a vacuum line adapter was charged with 10 mg of **1** in C_6D_6 (0.5 ml). After the tube was capped, it was immersed in a water-filled quartz dewar in front of the focused photolysis beam. In some cases, the reaction was monitored periodically by examining the recognisable groups of signals in the NMR spectrum of complexes **1** and **2**. In other cases, the analysis was performed after 2 h of photolysis. After irradiation, the reaction mixture was taken back into the vacuum line to remove the solvent. The residue was taken up in benzene-d$_6$ and added to a new NMR tube to record the NMR spectra.

3.6. Photochemical preparation of [Tp^{Me2}Rh H(C_6H_5)(P(OMe)$_3$)] **3**

A solution of **2** (25 mg, 0.049 mmol) in benzene (4 ml) containing P(OMe)$_3$ (4.5 μl, 0.038 mmol) was degassed and irradiated at λ=336 nm for 120 min. Removal of the solvent under vacuum yielded a residue which was recrystallised from methanol and dried under vacuum (yield 80%). The ^{1}H NMR spectrum of the distillate showed only the presence of free 1,3-COD. Larger amount of **3** were obtained by repeating the above photochemical preparation 10 times.

Anal. Found Calc. (Mis.) ($C_{24}H_{37}BN_6O_3PRh$; M= 601.25): C 47.86 (47.91), H 6.19 (6.08), N 13.95 (14.05). FT-IR (KBr, cm^{-1}): 2520 ν(B–H); 2100 ν(Rh–H). ^{1}H NMR (200 MHz, C_6D_6) ppm: 7.95–6.8 (m, Ph); 5.89 (s, 1H, H-4); 5.65 (s, 1H, H-4″); 5.49 (d, 1H, H-4′, J(P,H)=1.8 Hz); 3.14 (d, CH_3-(P(OMe)$_3$), J(P,H)=11.4 Hz); 2.38 (s, 3H, CH_3-3); 2.32 (s, 3H, CH_3-3″); 2.27 (s, 3H, CH_3-5″); 2.25 (s, 3H, CH_3-5); 2.15 (s, 3H, CH_3-5′); 1.77 (m, 3H, CH_3-3′); −14.89 (dd, 1H, Rh–H, J(Rh,H)=23.16 Hz, J(P,H)=20.16 Hz). ^{13}C NMR (200 MHz, C_6D_6) ppm: 151.8 (s, 1C, C-3); 151.0 (s, 1C, C-3); 150.91 (1C, C-3); 145.6 (s, 1C, Ph); 143.93 (s, 1C, C-5); 143.56 (s, 1C, C-5); 142.91 (s, 1C, C-5); 140.32 (s, 1C, Ph); 126.14 (s, 1C, Ph); 125.29 (s, 1C, Ph); 121.80 (s, 1C, Ph); 107.21 (s, 1C, C-4); 106.36 (s, 1C, C-4′); 106.31 (s, 1C, C-4″); 51.44 (d, 3C, CH_3(P(OMe)$_3$), J(P,C)=5.3 Hz); 15.10 (s, 1C, CH_3-3″); 15.07 (s, 1C, CH_3-3′); 14.83 (s, 1C, CH_3-3); 13.01 (s, 1C, CH_3-5); 12.94 (s, 1C, CH_3-5′); 12.77 (s, 1C, CH_3-5″). ^{13}P{^{1}H} NMR (200 MHz, C_6D_6) ppm: 137.16 (d, J(Rh,P)=235.59 Hz); (dd, in off-resonance).

3.7. Photochemical preparation of [Tp^{Me2}Rh H_2(CO)] **4**

A solution of **2** (25 mg, 0.049 mmol) in methanol (4 ml) was degassed and irradiated as described for the preparation of **3**. Removal of the solvent under vacuum yielded a residue which was washed 3 times with cold methanol and dried under vacuum (yield 72%). The ^{1}H NMR spectrum of the distillate showed only the presence of free 1,3-COD. Larger amounts of **4** were obtained by repeating the above photochemical preparation eight times.

Anal. Found Calc. (Mis.) ($C_{16}H_{24}N_6BRhO$; M=432.6): C, 44.68 (44.74), H, 5.62 (5.60), N, 19.55 (19.54). FT-IR (KBr, cm^{-1}): ν(B–H) 2518 s; ν(Rh–H) 2035 s, ν(CO)=2010 b. ^{1}H NMR (200 MHz, C_6D_6) ppm: 5.57 (s, 2H, H-4); 5.46 (s, 1H, H-4′); 2.23 (s, 3H, CH_3-3′); 2.21 (s, 6H, CH_3-3);

2.18 (s, 3H, CH_3-5′); 2.07 (s, 6H, CH_3-5); −12.93 (d, 2H, *J*(Rh,H)=18.81 Hz, Rh–H). ^{13}C NMR (200 MHz, C_6D_6) ppm: 169.7 (d, 1C, *J*(Rh,C)=31.74 Hz, CO); 150.3 (s, 1C, C-3); 149.8 (s, 2C, C-3); 143.9 (s, 1C, C-5); 143.7 (s, 2C, C-5); 105.7 (s, 2C, C-4); 105.6 (s, 1C, C-4); 16.6 (s, 1C, CH_3-3); 15.0 (s, 2C, CH_3-3); 12.5 (s, 1C, CH_3-5); 12.3 (s, 2C, CH_3-5).

3.8. Photochemical preparation of [$Tp^{Me2}Rh(C_6H_5)(CH_2CH_2COO^tBu)$] **5**

A solution of **2** (10 mg, 0.019 mmol) in benzene (4 ml) containing *t*-Butyl-acrylate (3.5 μl, 0.024 mmol) was degassed and irradiated as described for the preparation of **3**. Removal of the solvent under vacuum yielded a residue which was recrystallised from CH_3OH and dried under vacuum.

The ^{1}H NMR spectrum of the distillate showed only the presence of free 1,3-COD. Larger amounts of **5** were obtained by repeating the above photochemical preparation 10 times.

Anal. Found Calc. (Mis.) ($C_{28}H_{40}BN_6O_2Rh$; *M*=740.15): C 45.39 (45.19), H 5.40 (5.22), N 11.34 (11.27). FT-IR (KBr, cm^{-1}): 2508 ν(B–H); 1610 ν(CO). ^{1}H NMR (200 MHz, C_6D_6) ppm: 7.5–6.7 (m, 5H); 5.78, 5.76, 5.48 (3s, 3×1H, H-4); 2.81 (m, 2H, $CH_2(Rh\mathit{CH}_2)$); 2.30, 2.29, 2.19, 2.17, 1.80, 1.79 (6s, 6×3H, CH_3-3,5); 1.29 (m, 2H, $CH_2(RhCH_2CH_2)$); 1.05 (s, 3×3H, CH_3 *t*-Bu). ^{13}C NMR (200 MHz, C_6D_6) ppm: 193 (d, 1C, CO, *J*(Rh,C)=25.18 Hz); 153.28, 149.95, 148.17 (3s, 3×1C, C-5); 143.93, 143.25, 142.30 (3s, 3×1C, C-3); 141.5, 133.8, 126.3, 126, 121.7 (5s, 5×CH, Ph); 108.54, 107.13, 106.47 (3s, 3×1C, C-4); 30.18 (s, 1C, $CH_2(RhCH_2CH_2)$); 27.6 (s, 3C, CH_3 *t*-Bu); 15.23, 13.80, 13.47, 13.36, 12.82, 12.27 (6s, 6×1C, CH_3-3,5); 2.10 (d, 1C, $CH_2(RhCH_2)$, *J*(Rh,C)=25.18 Hz).

Acknowledgements

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