Generation of [Tp*Rh(η^4-1,3-COD)] (Tp* = hydridotris (3,5-dimethyl)pyrazolylborate, 1,3-COD = cyclooctadiene) and its potential in C–H bond activation

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Dedicated to Prof. Renato Ugo on the occasion of his 65th birthday

Abstract

Photolysis of [Tp*Rh(η^4-1,5-COD)] $\underline{1}$ (Tp* = hydridotris(3,5-dimethylpyrazolyl)borate, 1,5-COD = cyclooctadiene) in benzene at 400 nm gives a quantitative yield of the new compound [Tp*Rh(η^4-1,3-COD)] $\underline{2}$. Selected photolysis of $\underline{2}$ at 336 nm can be used to produce (a) hydrido-phenyl-phosphite [Tp*Rh(H)(C$_6$H$_5$)P(OMe)$_3$], (b) hydrido-carbonyl [Tp*Rh(H)$_2$(CO)], (c) chelate [Tp*Rh(C$_6$H$_5$)(CH$_2$CH$_2$COO^{t}Bu] when the photoreactions were made in the presence of P(OMe)$_3$, CH$_3$OH and ^{t}Bu-acrylate, respectively. These results are interpreted in terms of oxidative addition reactions by the reactive intermediates photogenerated in the Rh system $\underline{2}$.
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1. Introduction

The problem of activating C–H bonds of alkanes and alkenes via soluble organometallic complexes is a topic of fundamental scientific interest. In the chemical technology, understanding C–H activation should help to develop methods for converting hydrocarbons into functionalized compounds more easily utilized in chemical transformations.

Starting from organometallic compounds, alkane C–H bond activation was pioneered by Janowicz and Bergman [1,2] and Hoyano and Graham [3,4] whose groups used permethylcyclopentadienyl iridium com-

plexes. Several discoveries of new-low valent metal complexes containing C$_5$Me$_5$, PR$_3$ or CO ligands that could also activate the C–H bonds of hydrocarbons rapidly followed [5,6]. Similar results, but at a lower temperature, were obtained with permethyl-cyclopentadienyl [C$_5$Me$_5$Rh(PMe$_3$)(H$_2$)] [3,4] and [C$_5$Me$_5$Re(PMe$_3$)$_2$] [7] complexes.

The general approach to C–H bond activation involves oxidative addition processes with coordinatively unsaturated transition metal species containing good electron donors (hydride, C$_5$Me$_5$, P(alkyl)$_3$). These species could be generated either thermally or photochemically via reactions that may involve excited-state chemistry or oxidative addition of a nucleophilic nature.

More recently, hydridotris(pyrazolyl)borate (Tp^R, substituted Tp derivatives) complexes of Ir and Rh,

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analogs of $[(C_5Me_5)Ir(CO)_2]$ and $[(C_5Me_5)Rh(CO)_2]$ have been shown to undergo an efficient photochemical reaction in hydrocarbon solvents (benzene, cyclohexane) to give adducts, $[Tp^R M(H)(R)(CO)]$ (M = Ir, Rh) [8]. The hydridotris(pyrazolyl)borate anions Tp^R are tridentate ligands particularly interesting because of their great structurally versatility and stability to form complexes with metal centers having open shell electron configuaration [9]. In addition these ligands allow the preparation of very stable alkene complexes of Ir(I) and Rh(I) [10]. A plausible pathway for these C–H bond activation reactions is the photoinduced loss of one CO ligand to generate a coordinatively unsaturated $[Tp^R M(CO)]$ intermediate which then undergoes oxidative addition of a C–H bond of the solvent [11]. Insights into the individual steps in the metal mediated C–H activation reactions of alkane and arene bonds using alkane $[Tp^{Me_2}Rh(L)(R)(H)]$ (L = $CNCH_2CMe_3$) complexes have been obtained from kinetic modeling of deuterium labeling experiments [12].

Wishing to extend the chemistry of Rh(I)pyrazolylborate complexes, we have sought to examine potential C–H bond activation of $[Tp^*Rh(\eta^4\text{-}1,5\text{-}COD)]$ $\underline{1}$ (Tp^* = hydridotris(3,5-dimethylpyrazolyl)borate, COD = 1,5-cyclooctadiene). Photolysis of this compound might generate organometallic fragments capable of oxidative addition reactions. One additional feature of complex $\underline{1}$ to be considered is the possible η^3 to η^2-Tp^* hapticity conversion during photolysis. The presence of a pendant pyrazolyl group of a η^2-coordinated Tp^* ligand introduce the potential for intercepting coordinatively unsaturated species generated in the photoreactions.

Herein we report (i) that a high yield of the novel $[Tp^*Rh(\eta^4\text{-}1,3\text{-}COD)]$ $\underline{2}$ may be obtained by photoisomerization ($\lambda = 400$ nm) of $\underline{1}$, (ii) that selected photolysis ($\lambda = 336$ nm) of $\underline{2}$ induces the dissociation of 1,3-COD with formation of very reactive $\{Tp^*Rh(I)\}$ metal fragment, (iii) that this Rh(I) species has potential for C–H bond activation since rapid oxidative addition of organic substrates occurs with formation of Rh(III) complexes.

2. Experimental

All procedures were carried out in Schlenk-type glassware interfaced to a high-vacuum line. Solvents were dried and distilled under argon before use by employing the following drying agents: dry Mg turnings and I_2 for CH_3OH and CD_3OD (Fluka); CaH_2 for CH_2Cl_2 (Fluka); sodium/benzophenone ketyl for C_6H_6 and C_6D_6. The complex $[Tp^*Rh(\eta^4\text{-}1,5\text{-}COD)]$ $\underline{1}$ was prepared as described in [13].

[1]H, ^{13}C spectra were recorded on either Bruker AC 200 or Bruker AMX 500 operating at 200.13 (500.13), 50.32 (125.7) MHz, respectively; [103]Rh–^{1}H NMR HMQC and ^{31}P{^{1}H} NMR spectra were recorded, respectively, on Bruker AMX 500 (15.9 MHz) and Bruker AC 200 (81.01 MHz). ^{1}H NMR spectra were referenced to the protio impurity in the solvent: C_6D_6 (δ 7.15 ppm). ^{31}P{^{1}H} NMR spectra were referenced to 85% H_3PO_4 (0.00 ppm); the [103]Rh shifts were on the absolute scale $\Xi = 3.16$ MHz, whereas TMS resonates exactly 100 MHz. The infrared spectra were recorded on a Bruker IFS 88 FT-IR spectrometer. MS were recorded on a Varian mat CH7 instrument. The photochemical reactions were performed with the output of a 500 W Oriel Hg lamp fitted with an IR blocking filter and a water filter to remove excess heat. Monochromatic light was obtained with an Applied Photophysics f/3.4 monochromator or with bandpass interference filters.

2.1. Synthesis of $[Tp^*Rh(\eta^4\text{-}1,3\text{-}COD)]$ $\underline{2}$

This complex was prepared by photolysis ($\lambda = 400$ nm) at $20\,°C$ of $\underline{1}$ (25 mg, 0049 mmol) in benzene (4 ml) in a quartz cuvette sealed with a septum cup. After irradiation (120 min) the solvent was removed under a vacuum. Recrystallization of the residue from CH_3CN/CH_2Cl_2 (1:1) at $-20\,°C$ gave a 98% yield of pure $\underline{2}$. ^{1}H NMR spectrum of the distillate showed the presence of 1,3-COD.

^{1}H NMR (C_6D_6): δ 5.61 (s, 3H, CH_{pz}); 5.10 (m, 2H, CH–COD); 4.20 (m, 2H, CH–COD); 2.27, 2.20 (s, 9H each, Me_{pz}); 1.73 (m, 2H, CH_2–COD); 1.50 (m, 2H, CH_2–COD); 1.37 (m, 4H, CH_2–COD). ^{13}C {^{1}H} NMR (C_6D_6): δ 151.2 ($C_{pz}(3)$); 142.7 ($C_{pz}(5)$); 107.7 ($C_{pz}(4)$); 82.5 (d, RhCH–COD, $^1J_{(C–Rh)} = 6.1$ Hz,); 39.5 (d, RhCH–COD, $^1J_{(C–Rh)} = 18.3$ Hz); 28.0, 25.5 (CH_2–COD); 14.7, 13.0 (Me_{pz}). [103]Rh–^{1}H–HMQC NMR (C_6D_6): δ 1942.

Anal. Calc. for $C_{23}H_{34}BN_6Rh$: C 54.35, H 6.74, N 16.53. Found: C 54.45, H 6.69, N 16.62.

FT-IR (KBr, cm^{-1}): 2522 (B-H). UV-Vis in C$_6$H$_6$: λ_{max} (nm) = 338 (ε = 3000), 400 (ε = 1100).

2.2. Synthesis of [Tp*Rh(H)(C$_6$H$_5$)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 recrystallized from methanol and dried under vacuum (yield 80%). The ^{1}H NMR spectrum of the distillate showed the presence of free 1,3-COD.

^{1}H NMR (C$_6$D$_6$): δ 7.96 (H$_o$); 7.12 (H$_m$); 7.09 (H$_o$); 6.99 (H$_p$); 6.85 (H$_m$); 5.89; 5.65 (s, 1H each, CH$_{pz}$); 5.50 (d, 1H, CH$_{pz}$, $^4J_{(H–Rh)} \approx$ 1.8 Hz); 3.16 (d, 9H, CH$_3$–(P(OMe)$_3$), $^3J_{(H–P)}$ = 11.4 Hz); 2.39; 2.32; 2.27; 2.26; 2.15; 1.77 (s, 3H each, 6Me$_{pz}$); −14.89 (dd, 1H, Rh–H, $^1J_{(H–Rh)}$ = 23.16 Hz, $^2J_{(H–P)}$ = 20.16 Hz). ^{13}C {^{1}H} NMR (C$_6$D$_6$): δ 151.8, 151.0, 150.9 (C$_{pz}$(3)) 150.7 (C$_{ar}$, $^1J_{C–Rh}$ = 29.7 Hz, $^2J_{(C–P)}$ = 14.5 Hz); 145.6 (C$_o$ of ar); 143.9, 143.0, 142.9 (C$_{pz}$(5)); 140.3 (C$_o$ of ar); 126.2 (C$_m$ of ar); 125.4 (C$_m$ of ar); 121.8 (C$_p$ of ar); 107.2; 106.4; 106.3 (C$_{pz}$(4)); 51.4 (d, CH$_3$(P(OMe)$_3$), $^2J_{(C–P)}$ = 5.5 Hz); 15.1; 15.0; 14.8; 13.0; 12.9; 12.8 (Me$_{pz}$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 137.6 (d, $^1J_{(P–Rh)}$ = 235.6 Hz). ^{103}Rh–^{1}H–HMQC NMR (C$_6$D$_6$): δ 1270.

Anal. Calc. for C$_{24}$H$_{37}$BN$_6$O$_3$PRh: C 47.86, H 6.19, N 13.95. Found: C 47.91, H 6.08, N 14.05.

FT-IR (KBr, cm^{-1}): 2520 (B-H); 2100 (Rh–H).

2.3. Synthesis of [Tp*Rh(H)$_2$(CO)] 4

A solution of 2 (25 mg, 0.049 mmol) in benzene (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 three times with cold methanol and dried under vacuum (yield 72%). The ^{1}H NMR spectrum of the distillate showed the presence of free 1,3-COD.

^{1}H NMR (C$_6$D$_6$): δ 5.57 (s, 2H, CH$_{pz}$); 5.47 (s, H, CH$_{pz}$); 2.23 (s, 3H, Me$_{pz}$); 2.21 (s, 6H, 2Me$_{pz}$); 2.18 (s, 6H, 2Me$_{pz}$); 2.08 (s, 3H, Me$_{pz}$); −12.93 (d, 2H, Rh–H, $_1J_{(H–Rh)}$ = 18.8 Hz). ^{13}C {^{1}H} NMR (C$_6$D$_6$): δ 169.7 (d, CO, $J_{(C–Rh)}$ = 31.7 Hz); 150.3; 149.8 (C$_{pz}$(3)); 143.9, 143.7 (C$_{pz}$(5)); 105.7, 105.6 (C$_{pz}$(4)); 16.6; 15.0; 12.5; 12.3 (Me$_{pz}$).

Anal. Calc. for C$_{16}$H$_{24}$N$_6$BRhO: C 44.68, H, 5.62, N 19.55. Found: C 44.74, H 5.60, N 19.55.

FT-IR (KBr, cm^{-1}): 2518 s (B-H); 2035 s (Rh–H), 2010 b (CO).

2.4. Synthesis of [Tp*Rh(C$_6$H$_5$)(CH$_2$CH$_2$COO^{t}Bu)] 9

A solution of 2 (10 mg, 0.0019 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 4. Removal of the solvent under vacuum yielded a residue which was recrystallized from CH$_3$OH and dried under vacuum (yield 72%). The ^{1}H NMR spectrum of the distillate showed only the presence of free 1,3-COD.

^{1}H NMR (C$_6$D$_6$): δ 7.5–6.7 (m, 5H, C$_6$H$_5$); 5.78, 5.76, 5.48 (s, 1H each, CH$_{pz}$); 3.0–3.35 (m, 2H, CH$_2$–CO); 2.81 (m, 2H, Rh–CH$_2$); 2.30, 2.29, 2.19, 2.18, 1.80, 1.79 (s, 3H each, Me$_{pz}$); 1.06 (s, 9H, ^{t}Bu). ^{13}C {^{1}H} NMR (C$_6$D$_6$): δ 193.0 (d, CO–Rh, $J_{(C–Rh)}$ = 3.7 Hz); 157.4 (d, C$_{ar}$–Rh, ^1J = 30 Hz);153.4, 150.2, 148.1, 144.1, 143.2, 142.3 (C$_{qpz}$); 141.5, 133.5, 128.3, 126.3, 121.7 (CH$_{ar}$); 108.5, 107.1, 106.5 (C$_{pz}$ (4)); 85.0 (C$_q$ ^{t}Bu) 40.0 (CH$_2$–CO); 27.7 (^{t}Bu); 15.2, 13.8, 13.5, 13.4, 12.8, 12.3 (Me$_{pz}$); 1.9 (d, Rh–CH$_2$, $^1J_{(C–Rh)}$ = 25 Hz).

Anal. Calc. for C$_{28}$H$_{40}$BN$_6$O$_2$Rh: C 44.39, H, 5.40, N 11.34. Found. C 44.19, H 5.22, N 11.27.
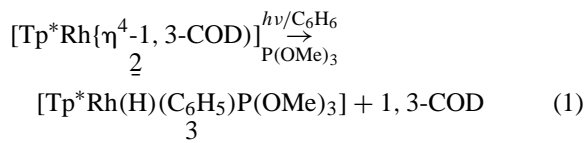
FT-IR (KBr, cm^{-1}): 2508 (B-H); 1610 (CO).

3. Results and discussion

Photolysis (λ = 400 nm) of a deaerated solution of [Tp*Rh(η^4-1,5-COD)] 1 in benzene provides the new complex [Tp*Rh(η^4-1,3-COD)] 2 in high yield. Complex 2 was characterized by ^{1}H, ^{13}C, ^{103}Rh, ^{1}H–HMQC spectroscopic studies which showed a diagnostic signal of 1,3-COD bonded to the {Tp*Rh(I)} fragment.[1] The magnetic equivalence of the three Tp* ligands indicated by ^{1}H and ^{13}C NMR spectra of the complex 2 is likely due to a dynamic process of interconversion between the η^3 and η^2-Tp*coordination forms. Under anaerobic conditions 2 is indefinitely

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[1] This and the other postulated intermediates, whose formation was deduced from the nature of the final products, have been enclosed in "curly bracket", i.e {..}.
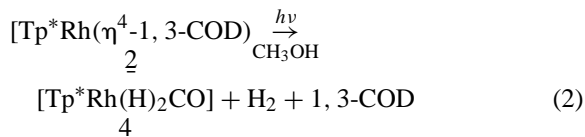
stable and a rare example of 1,3-COD bonded to a metal center [14]. Even though there is a structurally characterized 1,3-COD complex of Rh, $[(\eta^5C_5Ph_5)Rh(\eta^4\text{-}1,3\text{-COD})]$ [15], this compound was not synthesized via photoinduced intramolecular 1,3-H shift within the coordinated 1,5-COD. Selected photolysis ($\lambda = 336$ nm) of **2** in benzene containing $P(OMe)_3$ results in the clean displacement of 1,3-COD and the formation of $[Tp^*Rh(H)(C_6H_5)P(OMe)_3]$ **3**. Excitation of **2** with 336 nm light is correlated with a MLCT transition [16,17] that populates an olefin π^* orbital. Therefore, it is conceivable that photolysis reduces the 1,3-COD hapticity from η^4 to η^2 causing the dissociation of 1,3-COD as primary photoevent. After the 1,3-COD dissociation from the metal center, the solvent moved to occupy the empty site on Rh and formed the transient complex $\{Tp^*Rh(C_6H_6)\}$ as observed in the flash photolysis studies of $[Tp^*Rh(CO)_2]$ [11]. Arene complexes are increasingly implicated as significant intermediates in C–H bond activation [11,16,17], and the observation of free 1,3-COD after photolysis of **2** imply the formation in situ of the transient species $\{Tp^*Rh\}$ which rapidly form the solvent complex $\{Tp^*Rh(C_6H_6)\}$. The coordinative and electronic unsaturation of the solvate species, allows the C–H oxidative addition of C_6H_6 to occur with the formation of $\{Tp^*Rh(H)(C_6H_5)\}$. Lastly, the latter react with $P(OMe)_3$ forming the final product $[Tp^*Rh(H)(C_6H_5)P(OMe)_3]$ **3**. Thus the role of $P(OMe)_3$ is to act as a Lewis base and form a coordinatively saturated metal center, a necessary requirement for the photochemical stability of the final product **3**.

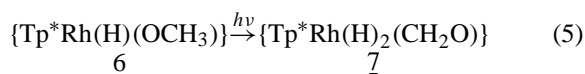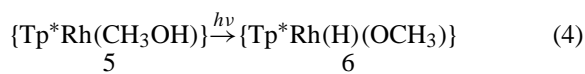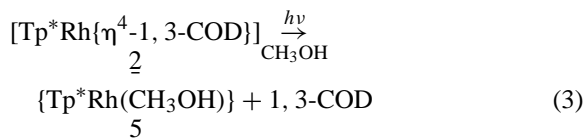Accordingly, the overall course of the photoreaction of **2** in benzene can be written as shown in Eq. (1).

$$[Tp^*Rh\{\eta^4\text{-}1,3\text{-COD})] \underset{\underset{2}{}}{\overset{h\nu/C_6H_6}{\underset{P(OMe)_3}{\rightarrow}}}$$
$$[Tp^*Rh(H)(C_6H_5)P(OMe)_3] + 1,3\text{-COD} \qquad (1)$$
$$\underset{3}{}$$

Support for this analysis of the photoreaction pathway is obtained considering (a) the absence of any thermal reaction of **2** with $P(OMe)_3$ and (b) that GC/MS studies of the distillate of the reaction mixture at the end of photolysis show the presence of 1 eq. of free 1,3-COD.
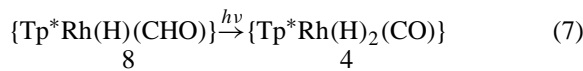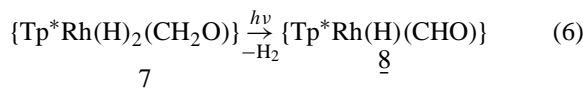
The synthetic utility of the photolysis of **2** can be demonstrated by the observed dehydrogenation of CH_3OH with the formation of the hydrido-carbonyl complex $[Tp^*Rh(H)_2(CO)]$ **4** when the solvent is changed from C_6H_6 to CH_3OH (Eq. (2)).

$$[Tp^*Rh(\eta^4\text{-}1,3\text{-COD}) \underset{\underset{2}{}}{\overset{h\nu}{\underset{CH_3OH}{\rightarrow}}}$$
$$[Tp^*Rh(H)_2CO] + H_2 + 1,3\text{-COD} \qquad (2)$$
$$\underset{4}{}$$

A GC/MS study of the distillate of the reaction mixture after photolysis shows the presence of H_2 and 1,3-COD.
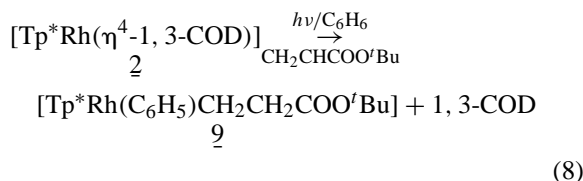
Of particular relevance to the reaction illustrated in Eq. (2) are previously studies reported by several groups [17,18] which have shown that transition metal compounds react with CH_3OH to give CH_2O which then act as a source of CO. Thus we can combine the results of this study with earlier results to assemble a comprehensive reaction mechanism for the C–H activation reaction by $[Tp^*Rh(1,3\text{-COD})]$ in CH_3OH as in Eqs. (3)–(7). It is proposed that, after photoinduced dissociation of 1,3-COD, CH_3OH occupies the vacant site on the metal with the formation of the solvent complex $\{Tp^*Rh(CH_3OH)\}$ **5**. It is likely that oxidative addition of an O–H bond of CH_3OH, postulated as the next step, will occur at the short-lived photo excited **5**. The product of this reaction should be the monohydrido-alkoxo complex $\{Tp^*Rh(H)(OCH_3)\}$ **6** whose coordinative unsaturation will induce a β-H abstraction reaction from the OCH_3 group giving the Rh(III) dihydrido species $\{Tp^*Rh(H)_2(CH_2O)\}$ **7** which contains coordinated CH_2O. The species **7** then undergo β-H transfer and elimination of H_2 with the formation of $\{Tp^*Rh(H)(CHO)\}$ **8**. Intramolecular rearrangement of **8** would then yield the corresponding hydride $[Tp^*Rh(H)_2(CO)]$ **4** as final product.

$$[Tp^*Rh\{\eta^4\text{-}1,3\text{-COD}\}] \underset{\underset{2}{}}{\overset{h\nu}{\underset{CH_3OH}{\rightarrow}}}$$
$$\{Tp^*Rh(CH_3OH)\} + 1,3\text{-COD} \qquad (3)$$
$$\underset{5}{}$$

$$\{Tp^*Rh(CH_3OH)\} \overset{h\nu}{\rightarrow} \{Tp^*Rh(H)(OCH_3)\} \qquad (4)$$
$$\underset{5}{} \qquad\qquad\qquad \underset{6}{}$$

$$\{Tp^*Rh(H)(OCH_3)\} \overset{h\nu}{\rightarrow} \{Tp^*Rh(H)_2(CH_2O)\} \qquad (5)$$
$$\underset{6}{} \qquad\qquad\qquad\qquad \underset{7}{}$$

$${Tp^*Rh(H)_2(CH_2O)} \xrightarrow[-H_2]{h\nu} {Tp^*Rh(H)(CHO)} \qquad (6)$$
$$\underline{7} \qquad\qquad\qquad \underline{8}$$

$${Tp^*Rh(H)(CHO)} \xrightarrow{h\nu} {Tp^*Rh(H)_2(CO)} \qquad (7)$$
$$\underline{8} \qquad\qquad\qquad \underline{4}$$

The mechanism for the photogeneration of $\underline{4}$ as in Eqs. (3)–(7) is also consistent with experimental results since $\underline{4}$ is isolated as the only Rh product and 1,3-COD and H_2 are detected in the distillate after photolysis of $\underline{2}$.

Having reasonable confidence that photolysis of $\underline{2}$ generates useful ${Tp^*Rh}$ intermediates, we decided to examine its photochemical behavior in the presence of ^tBu-acrylate. Thus photolysis of $\underline{2}$ in benzene in the presence of 2 eq. of ^tBu-acrylate results in the formation of the chelate product $[Tp^*Rh(C_6H_5)(CH_2CH_2COO^tBu)]$ $\underline{9}$ and loss of 1,3-COD (Eq. (8)).

$$[Tp^*Rh(\eta^4\text{-}1, 3\text{-COD})] \xrightarrow[CH_2CHCOO^tBu]{h\nu/C_6H_6}$$
$$\underline{2}$$
$$[Tp^*Rh(C_6H_5)CH_2CH_2COO^tBu] + 1, 3\text{-COD}$$
$$\underline{9}$$
$$(8)$$

The reaction sequence of this process is also consistent with the experimental procedure for preparing $\underline{3}$. Thus, after the photodissociation of 1,3-COD, the oxidative addition product ${Tp^*Rh(H)(C_6H_5)}$ is formed. This intermediate is expected to interact with ^tBu-acrylate giving ${Tp^*Rh(H)(C_6H_5)(\eta^2\text{-}^tBu\text{-acrylate})}$. This species under continuous photolysis, can only undergo an insertion reaction of ^tBu-acrylate in the Rh–H bond to form the chelate $\underline{9}$. Support for the formation of $\underline{9}$ comes from elemental analysis as well as ^1H, ^{13}C NMR studies and FT-IR data. While the presence of C_6H_5 signals is consistent with oxidative addition of C_6H_6, the absence of any signal of Rh–H as well as the presence of Rh–CH_2 and Rh–CH_2CH_2 resonances support the photoinsertion of ^tBu-acrylate in the Rh–H bond of the species ${Tp^*Rh(H)(C_6H_5)(\eta^2\text{-}^tBu\text{-acrylate})}$. FT-IR data indicate that the carbonyl oxygen of the acrylate group is coordinated to the Rh center $\underline{9}$. It is noteworthy that the photoinduced insertion of ^tBu-acrylate in the Rh–H bond of a complex as ${Tp^*Rh(H)(C_6H_5)(\eta^2\text{-}^tBu\text{-acrylate})}$ appears to be unprecedented.

Together the above results illustrated that the complex $[Tp^*Rh(\eta^4\text{-}1,3\text{-COD})]$ $\underline{2}$ is both conveniently accessible by photoisomerization of $[Tp^*Rh(\eta^4\text{-}1,5\text{-COD})]$ $\underline{1}$ and highly versatile in C–H bond activation processes.

4. Conclusions

We have prepared the new compound $[Tp^*Rh(\eta^4\text{-}1,3\text{-COD})]$ $\underline{2}$ by photoinduced intramolecular rearrangement of $[Tp^*Rh(\eta^4\text{-}1,5\text{-COD})]$ $\underline{1}$. ^1H and ^{13}C NMR spectroscopy of the new compound proved helpful in establishing that the cyclooctadiene ligand is bonded in a 1,3-fashion to Rhodium. Selective photolysis of the complex $[Tp^*Rh(\eta^4\text{-}1,3\text{-COD})]$ $\underline{2}$ is a versatile entry point into the organometallic chemistry of ${Tp^*Rh}$ fragment as it can be used to produce, by oxidative addition reaction (a) hydrido-phenyl-phosphite $[Tp^*Rh(H)(C_6H_5)P(OMe)_3]$ $\underline{3}$, (b) hydrido-carbonyl $[Tp^*Rh(H)_2(CO)]$ $\underline{4}$, (c) the chelate $[Tp^*Rh(C_6H_5)(CH_2CH_2COO^tBu)]$ $\underline{9}$ when the photoreactions were made in the presence of $P(OMe)_3$, CH_3OH, and ^tBu-acrylate, respectively. We are presently studying the potential of the $[Tp^*Rh(\eta^4\text{-}1,3\text{-COD})]$ $\underline{2}$ and similar complexes with various substituents at the pyrazolyl ring, in C–H bond activation of alkanes, at room temperature and pressure.

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