

The Photochemistry of (Diene)(hydro)[tris(3,5-dimethylpyrazolyl)borato]rhodium Complexes

Preliminary Communication

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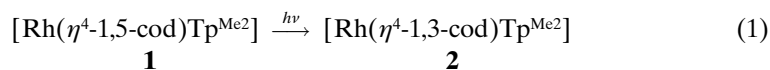
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The photochemical rearrangement of $[\text{Rh}(\eta^4\text{-}1,5\text{-cod})\text{Tp}^{\text{Me}_2}](\text{Tp}^{\text{Me}_2} = \text{hydrotris}(3,5\text{-dimethylpyrazolyl})\text{-borato}, 1,5\text{-cod} = \text{cycloocta-}1,5\text{-diene})$ to the new compound $[\text{Rh}(\eta^4\text{-}1,3\text{-cod})\text{Tp}^{\text{Me}_2}]$ (**2**) is described. The characterization of **2** was carried out using ^1H -, ^{13}C -, and ^{103}Rh -HMOC-NMR spectroscopy. Photolysis of **2** is a versatile entry point into the organometallic chemistry of the $\{\text{RhTp}^{\text{Me}_2}\}$ fragment as it can be used to produce *a*) hydrido-carbonyl ($[\text{Rh}(\text{CO})\text{H}_2\text{Tp}^{\text{Me}_2}]$), *b*) hydrido-phenyl-phosphite ($[\text{RhH}(\text{Ph})(\text{P}(\text{OMe})_3)\text{Tp}^{\text{Me}_2}]$), and *c*) ethoxide-hydrido-phosphite ($[\text{RhH}(\text{OEt})(\text{P}(\text{OMe})_3)\text{Tp}^{\text{Me}_2}]$) complexes.

Extensive photochemical studies have been carried out on alkene-transition-metal complexes [1–5]. These studies show that coordinated alkenes undergo a variety of photochemical reactions ranging from ligand substitution to isomerization and skeletal rearrangements. However, usually alkene complexes containing phosphines, π -cyclopentadienyls, and carbonyls as ancillary ligands have been investigated [1].

As there are structural and electronic relationships between complexes containing the η^5 -cyclopentadienyl anion (Cp) and those containing the hydrotris(pyrazolyl)borato anion [6], more recently the photochemical reactivity of complexes of the latter anion in general, and those of the type $[\text{M}(\text{L})_2\text{Tp}^{\text{Me}_2}]$ ($\text{Tp}^{\text{Me}_2} = \text{hydrotris}(3,5\text{-dimethylpyrazolyl})\text{-borato}$, $\text{M} = \text{Rh}$ and Ir , $\text{L} = \text{CO}$ in particular), have also been investigated [7–11]. Furthermore, it was recently shown that $[\text{IrH}_2(\eta^2\text{-coe})\text{Tp}^{\text{Me}_2}]$ ($\text{coe} = \text{cyclooctene}$) [4] and $[\text{Ir}(\eta^4\text{-}1,5\text{-cod})\text{Tp}^{\text{Me}_2}]$ ($1,5\text{-cod} = \text{cycloocta-}1,5\text{-diene}$) [5] photochemically activate C–H bonds as found for some π -cyclopentadienyl complexes of iridium [12][13].

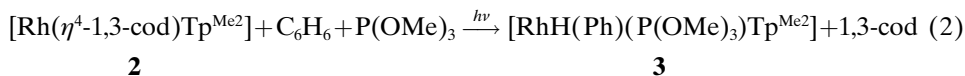
Electronic considerations and previous photochemical observations [4][5] have now led to the photochemical study of $[\text{Rh}(\eta^4\text{-}1,5\text{-cod})\text{Tp}^{\text{Me}_2}]$ (**1**) and the discovery of two new photoreactions. The first of them, occurring at **1**, is shown in *Eqn. 1*.



This reaction constitutes a high-yield photoisomerization of the alkene formally involving an intramolecular 1,3-H shift within the coordinated 1,5-cod, resulting in the

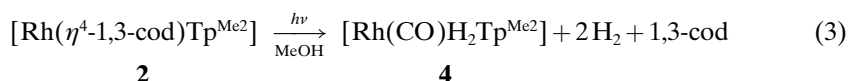
formation of coordinated 1,3-cod. Experimental evidence for this transformation is provided by ^1H -, ^{13}C -, $^{13}\text{C},^1\text{H}$ -HMQC- and $^{103}\text{Rh},^1\text{H}$ -HMQC-NMR spectroscopic studies. The new complex **2** is a very stable compound and a rare example of 1,3-cod bonded to a metal center [14–16].

The other type of photoreaction involves complex **2**. This, in the presence of $\text{P}(\text{OMe})_3$ in benzene, gives $[\text{RhH}(\text{Ph})(\text{P}(\text{OMe})_3)\text{Tp}^{\text{Me}2}]$ (**3**) (*Eqn. 2*)



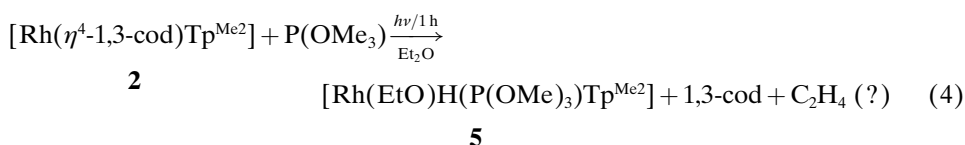
This reaction must occur in several stages. The first of them, most probably, is the photodissociation of 1,3-cod from **2** with formation of the coordinatively unsaturated fragment $\{\text{RhTp}^{\text{Me}2}\}$. The presence of 1 equiv. of free 1,3-cod in the distillate at the end of the reaction supports this hypothesis. This step is likely to be followed by the oxidative addition of a C–H bond of C_6H_6 to the above fragment with formation of $\{\text{RhH}(\text{Ph})\text{Tp}^{\text{Me}2}\}$, another coordinatively unsaturated species. Lastly, the latter is expected to react with $\text{P}(\text{OMe})_3$, forming $[\text{RhH}(\text{Ph})(\text{P}(\text{OMe})_3)\text{Tp}^{\text{Me}2}]$ (**3**).

Several related reactions have been carried out. Thus, irradiation of **2** in MeOH produces the carbonyl complex $[\text{Rh}(\text{CO})\text{H}_2\text{Tp}^{\text{Me}2}]$ (**4**) (*Eqn. 3*).



As the likely primary photoevent is the dissociation of 1,3-cod from **2**, the resulting transient $\{\text{RhTp}^{\text{Me}2}\}$ should cause the dehydrogenation of MeOH with formation of the carbonyl complex **4**. This reaction is analogous to that found for $[\text{Ir}(\eta^4\text{-1,5-cod})\text{Tp}^{\text{Me}2}]$ [5].

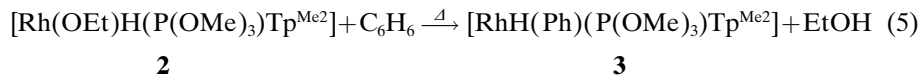
The photoreaction of $[\text{Rh}(\eta^4\text{-1,3-cod})\text{Tp}^{\text{Me}2}]$ (**2**) in Et_2O , in the presence of $\text{P}(\text{OMe})_3$, gives the new Rh^{III} complex $[\text{Rh}(\text{EtO})\text{H}(\text{P}(\text{OMe})_3)\text{Tp}^{\text{Me}2}]$ (**5**) (*Eqn. 4*). The formulation



of **5** is based on spectroscopic data and chemical reactivity. We propose the following sequence of reactions for the formation of **5**: *i*) initial photodissociation of 1,3-cod giving the primary photoproduct $\{\text{RhTp}^{\text{Me}2}\}$; *ii*) efficient interception of the transient 14- e^- species $\{\text{RhTp}^{\text{Me}2}\}$ by $\text{P}(\text{OMe})_3$ with formation of the intermediate $\{\text{Rh}(\text{P}(\text{OMe})_3)\text{Tp}^{\text{Me}2}\}$; *iii*) photoinduced oxidative addition of Et_2O by this intermediate, with formation of the transient $\{\text{Rh}(\text{Et})(\text{OEt})(\text{P}(\text{OMe})_3)\text{Tp}^{\text{Me}2}\}$; *iv*) loss of C_2H_4 from the latter and formation of product **5**.

The hydrido-ethoxy derivative **5** is quite reactive; in benzene solution, it thermally decomposes to give **3** as the final product (*Eqn. 5*), presumably through

the reductive elimination and extrusion of EtOH, followed by the oxidative addition of C₆H₆.



However, in addition to the oxidative addition reaction shown in *Eqn. 4*, after several hours of selective photolysis of complex **2**, a photostationary state is established between **5** and the new hydrido complex [RhH₂(P(OMe)₃Tp^{Me2})] (**6**) in a ratio of *ca.* 3:1.

The formation of **6** may be due to a secondary photochemistry of **5**, consistent with a reductive elimination of EtOH and its subsequent dehydrogenation to form the dihydrido complex **6** in analogy to the photochemical dehydrogenation of MeOH by [Ir(η⁴-1,5-cod)Tp^{Me2}] [5].

In summary, complex **1** shows a most interesting and varied photochemical behavior, which is being further investigated.

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Experimental Part

General. The photochemical experiments were carried out as described in [5]. The products were characterized by FT-IR and NMR spectroscopy, and elemental analysis. The NMR spectra were recorded in C₆D₆ soln. on a *Bruker AC 200* instrument and, in part, on a *Bruker AMX 500*, operating for ¹H at 200.13 (500.13), for ¹³C at 50.3 (125.6), and for ³¹P at 81.0 (202.4) MHz. The chemical shift scales are relative to internal TMS for ¹H, ¹³C, and CH₃NO₂ of ¹⁵N, and to external H₃PO₄ for ³¹P; the ¹⁰³Rh shifts are on the absolute scale $\Xi = 3.16$ MHz, whereas TMS resonates at exactly 100 MHz.

[Rh(η⁴-1,3-cod)Tp^{Me2}] (**2**). FT-IR (KBr): 2522 (B–H). ¹H-NMR (200 MHz, C₆D₆, 295 K): 5.62 (s, 3 H, H–C(4)); 5.12 (m, 2 CH); 4.20 (m, 2 CH); 2.27 (s, 9 H, Me–C(5)); 2.20 (s, 9 H, Me–C(3)); 1.73–1.37 (m, 4 CH₂). ¹³C-NMR (C₆D₆, 295 K): 151.2 (3 C, C(3)); 142.7 (3 C, C(5)); 107.7 (3 C, C(4)); 82.5 (*d*, *J*(Rh,C) = 6.1, 2 CH); 39.5 (*d*, *J*(Rh,C) = 18.3, 2 CH); 28.0, 25.5 (4 CH₂); 14.7 (3 C, Me–C(3)); 13.0 (3 C, Me–C(5)). ¹⁰³Rh, ¹H HMQC NMR (C₆D₆, 295 K): 1942. Anal. calc. for C₂₃H₃₄BN₆Rh: C 54.35, H 6.74, N 16.53; found: C 54.45, H 6.69, N 16.62.

[RhH(Ph)(P(OMe)₃Tp^{Me2})] (**3**). FT-IR (KBr): 2520 (B–H), 2100 (Rh–H). ¹H-NMR (200 MHz, C₆D₆, 295 K; primed atoms are those in *trans*-positions to P(OMe)₃, double primed atoms are those in *trans*-positions to the Ph group): 7.95 (H_o); 7.12 (H_m); 7.09 (H_o′); 6.99 (H_p); 6.85 (H_m); 5.89 (s, H–C(4)); 5.65 (s, H–C(4′′)); 5.49 (*J*(P,H) = 1.8, H–C(4′)); 3.14 (*d*, *J*(P,H) = 11.4, (P(OMe)₃)); 2.38 (Me–C(3)); 2.32 (Me–C(3′′)); 2.27 (Me–C(5′′)); 2.25 (Me–C(5)); 2.15 (s, Me–C(5′)); 1.77 (Me–C(3′)); –14.89 (*dd*, *J*(Rh,H) = 23.16, *J*(P,H) = 20.16, RhH). ¹³C-NMR (C₆D₆, 295 K): 151.8, 151.0, 150.9 (3 × 1 C, C(5)); 145.6 (C_o of Ph); 143.9, 143.6, 142.9 (3 × 1 C, C(5)); 140.3 (C_o of Ph); 126.2 (C_m of Ph); 125.4 (C_m of Ph); 121.8 (C_p of Ph); 107.2 (C(4)); 106.4 (C(4′)); 106.3 (C(4′′)); 51.4 (*d*, *J*(P,C) = 5.3, P(OMe)₃); 15.1 (Me–C(3′′)); 15.1 (Me–C(3′)); 14.8 (Me–C(3)); 13.0 (Me–C(5)); 12.9 (Me–C(5′)); 12.8 (Me–C(5′′)). ³¹P{¹H}-NMR (C₆D₆, 295 K): 137.6 (*d*, *J*(P,Rh) = 235; *dd* with off-resonance decoupling). ¹⁰³Rh, ¹H-HMQC-NMR (C₆D₆, 295 K): 1270. ¹⁵N, ¹H-HMQC-NMR (C₆D₆, 295 K): 127.5 (*J*(P,N) = 2, *J*(Rh,N) = 10). Anal. calc. for C₂₄H₃₇BN₆O₃PRh: C 47.86, H 6.19, N 13.95, found: C 47.91, H 6.08, N 14.05.

[RhH₂(CO)Tp^{Me2})] (**4**). FT-IR (KBr): 2518s, (B–H) 2035s, (Rh–H) 2010 (br., CO). ¹H-NMR (200 MHz, C₆D₆, 295 K; primed atoms are those in *trans*-positions to the CO ligand): 5.57 (s, 2 H, H–C(4)); 5.46 (s, H–C(4′)); 2.23 (s, Me–C(3′)); 2.21 (s, 6 Me–C(3)); 2.18 (s, Me–C(5′)); 2.07 (s, 6 H, Me–C(5)); –12.93 (*d*, *J*(Rh,H) = 18.8, RhH). ¹³C-NMR (C₆D₆, 295 K): 169.7 (*d*, *J*(Rh,C) = 31.74, CO); 150.3 (1 C, C(3′)); 149.8 (2 C, C(3)); 143.9 (1 C, C(5′)); 143.7 (2 C, C(5)); 105.7 (s, 2 C, C(4)); 105.6 (1 C, C(4′)); 16.6 (Me–C(3′)); 15.0

(2 C, Me–C(3)); 12.5 (Me–C(5)); 12.3 (2 C, Me–C(5)). Anal. calc. for $C_{16}H_{24}BN_6ORh$: C 44.68, H 5.62, N 19.55; found: C 44.74, H 5.60, N 19.54.

$[Rh(EtO)H(P(OMe)_3)Tp^{Me_2}]$ (**5**). 1H -NMR (200 MHz, C_6D_6 , 295 K): 5.81, 5.63, 5.59 (3s, 3 H, H–C(4)); 3.46 (*qd*, $J(H,H) = 7.08$, $J(Rh,H) = 1.4$, 2 H, CH_2 of EtO); 3.14 (*d*, $J(P,H) = 11.7$, 3 Me); 2.59, 2.57, 2.30, 2.24, 2.21, 2.14 (6s, 18 H, Me–C(3), Me–C(5)); 1.10 (*t*, $J(H,H) = 7.1$, 3 H, Me of EtO); –16.30 (*dd*, $J(P,H) = 21.8$, $J(Rh,H) = 23.7$, RhH). $^{31}P\{^1H\}$ -NMR (C_6D_6 , 295 K): 143.7 (*d*, $J(P,Rh) = 235$; *dd* with off-resonance decoupling). The ^{13}C -NMR spectrum of **5** has been frustrated due to a facile conversion in C_6D_6 to the species $[Rh(C_6D_5)(P(OMe)_3)Tp^{Me_2}]$ ((D₆)-**3**).

$[RhH_2(P(OMe)_3)Tp^{Me_2}]$ (**6**). 1H -NMR (200 MHz, C_6D_6 , 295 K): –15.97 (*dd*, $J(Rh,H) = 26.2$, $J(P,H) = 19.6$, RhH). $^{31}P\{^1H\}$ -NMR (C_6D_6 , 295 K): 153.2 (*d*, $J(P,Rh) = 228.0$); *dt* with off-resonance decoupling.

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