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

Preliminary Communication

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The photochemical rearrangement of $[Rh(\eta^4\text{-}1,5\text{-cod})Tp^{Me2}]$($Tp^{Me2}$ = hydrotris(3,5-dimethylpyrazolyl)borato, 1,5-cod = cycloocta-1,5-diene) to the new compound $[Rh(\eta^4\text{-}1,3\text{-cod})Tp^{Me2}]$ (**2**) is described. The characterization of **2** was carried out using ^1H-, ^{13}C-, and ^{103}Rh-HMQC-NMR spectroscopy. Photolysis of **2** is a versatile entry point into the organometallic chemistry of the $\{RhTp^{Me2}\}$ fragment as it can be used to produce *a*) hydrido-carbonyl ($[Rh(CO)H_2Tp^{Me2}]$), *b*) hydrido-phenyl-phosphite ($[RhH(Ph)(P(OMe)_3)Tp^{Me2}]$), and *c*) ethoxide-hydrido-phosphite ($[RhH(OEt)(P(OMe)_3)Tp^{Me2}]$) 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 $[M(L)_2Tp^{Me2}]$ (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borato, M = Rh and Ir, L = CO in particular), have also been investigated [7–11]. Furthermore, it was recently shown that $[IrH_2(\eta^2\text{-coe})Tp^{Me2}]$ (coe = cyclooctene) [4] and $[Ir(\eta^4\text{-}1,5\text{-cod})Tp^{Me2}]$ (1,5-cod = cycloocta-1,5-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 $[Rh(\eta^4\text{-}1,5\text{-cod})Tp^{Me2}]$ (**1**) and the discovery of two new photoreactions. The first of them, occurring at **1**, is shown in *Eqn. 1*.

$$\underset{\mathbf{1}}{[Rh(\eta^4\text{-}1,5\text{-cod})Tp^{Me2}]} \xrightarrow{h\nu} \underset{\mathbf{2}}{[Rh(\eta^4\text{-}1,3\text{-cod})Tp^{Me2}]} \qquad (1)$$

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 ^{1}H-, ^{13}C-, $^{13}C,^{1}H$-HMQC- and $^{103}Rh,^{1}H$-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 $P(OMe)_3$ in benzene, gives $[RhH(Ph)(P(OMe)_3)Tp^{Me2}]$ (**3**) (*Eqn. 2*)

$$\underset{\mathbf{2}}{[Rh(\eta^4\text{-1,3-cod})Tp^{Me2}]} + C_6H_6 + P(OMe)_3 \xrightarrow{h\nu} \underset{\mathbf{3}}{[RhH(Ph)(P(OMe)_3)Tp^{Me2}]} + \text{1,3-cod} \quad (2)$$

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 $\{RhTp^{Me2}\}$. 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 $\{RhH(Ph)Tp^{Me2}\}$, another coordinatively unsaturated species. Lastly, the latter is expected to react with $P(OMe)_3$, forming $[RhH(Ph)(P(OMe)_3)Tp^{Me2}]$ (**3**).

Several related reactions have been carried out. Thus, irradiation of **2** in MeOH produces the carbonyl complex $[Rh(CO)H_2Tp^{Me2}]$ (**4**) (*Eqn. 3*).

$$\underset{\mathbf{2}}{[Rh(\eta^4\text{-1,3-cod})Tp^{Me2}]} \xrightarrow[\text{MeOH}]{h\nu} \underset{\mathbf{4}}{[Rh(CO)H_2Tp^{Me2}]} + 2\,H_2 + \text{1,3-cod} \quad (3)$$

As the likely primary photoevent is the dissociation of 1,3-cod from **2**, the resulting transient $\{RhTp^{Me2}\}$ should cause the dehydrogenation of MeOH with formation of the carbonyl complex **4**. This reaction is analogous to that found for $[Ir(\eta^4\text{-1,5-cod})Tp^{Me2}]$ [5].

The photoreaction of $[Rh(\eta^4\text{-1,3-cod})Tp^{Me2}]$ (**2**) in Et_2O, in the presence of $P(OMe)_3$, gives the new Rh^{III} complex $[Rh(EtO)H(P(OMe)_3)Tp^{Me2}]$ (**5**) (*Eqn. 4*). The formulation

$$\underset{\mathbf{2}}{[Rh(\eta^4\text{-1,3-cod})Tp^{Me2}]} + P(OMe_3) \xrightarrow[Et_2O]{h\nu/1\,h} \underset{\mathbf{5}}{[Rh(EtO)H(P(OMe)_3)Tp^{Me2}]} + \text{1,3-cod} + C_2H_4\ (?) \quad (4)$$

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 $\{RhTp^{Me2}\}$; *ii*) efficient interception of the transient 14-e^- species $\{RhTp^{Me2}\}$ by $P(OMe)_3$ with formation of the intermediate $\{Rh(P(OMe)_3)Tp^{Me2}\}$; *iii*) photoinduced oxidative addition of Et_2O by this intermediate, with formation of the transient $\{Rh(Et)(OEt)(P(OMe)_3)Tp^{Me2}\}$; *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 C_6H_6.

$$\underset{\mathbf{2}}{[\mathrm{Rh(OEt)H(P(OMe)_3)Tp^{Me2}}]} + \mathrm{C_6H_6} \xrightarrow{\Delta} \underset{\mathbf{3}}{[\mathrm{RhH(Ph)(P(OMe)_3)Tp^{Me2}}]} + \mathrm{EtOH} \quad (5)$$

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 $[RhH_2(P(OMe)_3Tp^{Me2}]$ (**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 $[Ir(\eta^4\text{-}1,5\text{-cod})Tp^{Me2}]$ [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 C_6D_6 soln. on a *Bruker AC 200* instrument and, in part, on a *Bruker AMX 500*, operating for ^1H at 200.13 (500.13), for ^{13}C at 50.3 (125.6), and for ^{31}P at 81.0 (202.4) MHz. The chemical shift scales are relative to internal TMS for ^1H, ^{13}C, and CH_3NO_2 of ^{15}N, and to external H_3PO_4 for ^{31}P; the ^{103}Rh shifts are on the absolute scale $\Xi = 3.16$ MHz, whereas TMS resonates at exactly 100 MHz.

$[Rh(\eta^4\text{-}1,3\text{-cod})Tp^{Me2}]$ (**2**). FT-IR (KBr): 2522 (B–H). ^1H-NMR (200 MHz, C_6D_6, 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 CH_2). ^{13}C-NMR (C_6D_6, 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 CH_2); 14.7 (3 C, *Me*–C(3)); 13.0 (3 C, *Me*–C(5)). $^{103}Rh,^1H$ HMQC NMR (C_6D_6, 295 K): 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.

$[RhH(Ph)(P(OMe)_3)Tp^{Me2}]$ (**3**). FT-IR (KBr): 2520 (B–H), 2100 (Rh–H). ^1H-NMR (200 MHz, C_6D_6, 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). ^{13}C-NMR (C_6D_6, 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″)). $^{31}P\{^1H\}$-NMR (C_6D_6, 295 K): 137.6 (*d*, *J*(P,Rh) = 235; *dd* with off-resonance decoupling). $^{103}Rh,^1H$-HMQC-NMR (C_6D_6, 295 K): 1270. $^{15}N,^1H$-HMQC-NMR (C_6D_6, 295 K): 127.5 (*J*(P,N) = 2, *J*(Rh,N) = 10). Anal. calc. for $C_{24}H_{37}BN_6O_3PRh$: C 47.86, H 6.19, N 13.95, found: C 47.91, H 6.08, N 14.05.

$[RhH_2(CO)Tp^{Me2}]$ (**4**). FT-IR (KBr): 2518*s*, (B–H) 2035*s*, (Rh–H) 2010 (br., CO). ^1H-NMR (200 MHz, C_6D_6, 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). ^{13}C-NMR (C_6D_6, 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^{Me2}] (**5**). ^{1}H-NMR (200 MHz, C_6D_6, 295 K): 5.81, 5.63, 5.59 (3*s*, 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 (6*s*, 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{^{1}H}-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 [RhD(C_6D_5)(P(OMe)$_3$)Tp^{Me2}] ((D_6)-**3**).

[RhH$_2$(P(OMe)$_3$)Tp^{Me2}] (**6**). ^{1}H-NMR (200 MHz, C_6D_6, 295 K): –15.97 (*dd*, *J*(Rh,H) = 26.2, *J*(P,H) = 19.6, RhH). ^{31}P{^{1}H}-NMR (C_6D_6, 295 K): 153.2 (*d*, *J*(P,Rh) = 228.0); *dt* with off-resonance decoupling.

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