Inter- and Intramolecular Thermal Activation of Aliphatic C−H Bonds Mediated by Complexes Containing the Fragments [{$Cy_2P(CH_2)_nPCy_2$}M] (n = 1−4, M = Rh, Ru)

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Received December 4, 1996

Keywords: C−H activation / Homogeneous catalysis / Dehydrogenation / Phosphane complexes

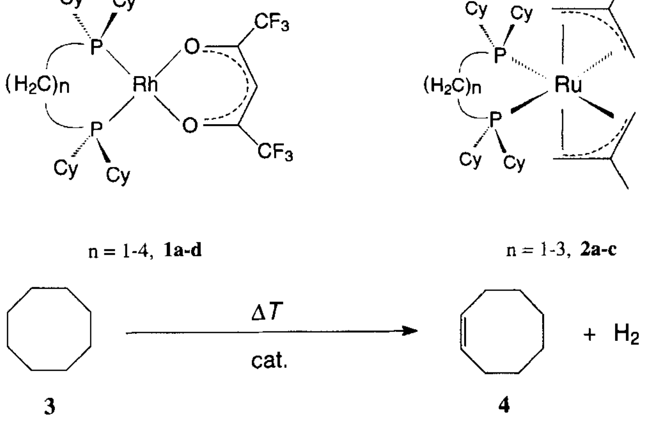
A well defined geometrical structure and a well established catalytic potential for a plethora of processes puts the chelate rings [{$R_2P(CH_2)_nPR_2$}M] (M = Rh, Ru) among the most interesting candidates for catalytic alkane functionalization in homogeneous solution. It is demonstrated that *intermolecular* thermal C−H activation (**3** → **4**) is possible with readily accessible complexes [{$Cy_2P(CH_2)_nPCy_2$}Rh(hfacac)] (n = 1−4, **1a**−**c**) and [{$Cy_2P(CH_2)_nPCy_2$}Ru(η^3-C_4H_7)$_2$] (n = 1−3, **2a**−**c**) containing such fragments. A maximum of 5 catalytic cycles was achieved with complex **2a**. In case of Ru complexes containing the same ligands with n = 3 and 4, *intramolecular* cleavage of three adjacent C− H bonds in one of the cyclohexyl substituents at phosphorus also occurs readily leading to formation of a new polydentate κ^2P,P′,η^3-allyl ligand.

The selective functionalization of alkanes is one of the major challenges in homogeneous catalysis[1,2,3]. In principle, catalytic cycles for such processes could be readily envisaged on basis of i) the formation of M−C and/or M−H bonds via C−H activation at a coordinatively unsaturated metal center, ii) functionalization via either of these reactive bonds, and iii) regeneration of the unsaturated metal species. Late transition metal complexes have been addressed as promising materials to provide approaches to this ambitious goal[1,2] and have been successfully applied in thermal dehydrogenation[4,5,6,7,8] and carbonylation/carboxylation processes[9]. Some remarkably efficient systems performing several hundred catalytic turnovers per hour have been reported for the dehydrogenation of cycloalkanes[4,5,7,8], but all these systems require the presence of a hydrogen acceptor. Direct catalytic dehydrogenation is far more difficult to achieve and turnover frequencies are at least two orders of magnitude smaller[5c,6]. The total number of turnovers in the absence of hydrogen acceptors is generally also low, as the process is severely limited by catalyst deactivation processes[5].

It appears quite surprising in this context that the potential of *cis*-chelate moieties [{$R_2P(CH_2)_nPR_2$}M] (M = Rh, Ru) for catalytic processes based upon C−H bond activation of alkanes has not yet been demonstrated[8b,c], although these fragments are involved in an overwhelming number of catalytic reactions based on the above sequence of events and starting from related E−H bonds (E = H, Si, sp^2- or sp-C)[10]. Furthermore, the intrinsic structural properties of the chelate rings as defined by the P−M−P angle, the size of R and the conformational flexibility can provide additional control over the reactivity of these systems[11].

We now report that neutral transition metal complexes [{$Cy_2P(CH_2)_nPCy_2$}Rh(hfacac)] (n = 1−4, hfacac = κ^2O,O'-hexafluoroacetylacetonate, **1a**−**d**) and [{$Cy_2P(CH_2)_nPCy_2$}Ru(2-Me-allyl)$_2$] (n = 1−3, 2-Me-allyl = η^3-C_4H_7, **2a**−**c**) containing the fragments [{$Cy_2P(CH_2)_n$-PCy_2}M] (M = Rh, Ru) and potentially thermolabile or chemically removable ligands are indeed suitable precursors for thermal intermolecular activation of C−H bonds in homogeneous solution. The dehydrogenation of cyclooctane (**3**) to cyclooctene (**4**) (Scheme 1) was used as a test reaction throughout this study[5d].

Scheme 1. Dehydrogenation of cyclooctane **3** to cyclooctene **4** as a test reaction for catalytic thermal C−H activation. Reaction conditions: **1a**−**d** or **2a**−**c**: 15.0−40.0 µmol, **3**: 5.0−8.0 ml, T_{bath} = 170 °C, t = 48 h



n = 1-4, **1a-d**

n = 1-3, **2a-c**

3

4

Our initial attempts focused on M = Rh, as complexes of group 9 metals are the most successful catalysts for dehydrogenation of **3** known to date[5,6,7,8]. Furthermore, complexes **1a–d** were recently introduced by us as the most active catalysts for CO_2 hydrogenation and as models to study structure/activity relationships in homogeneous catalysis[11]. They were now found to be able to activate the C–H bonds of **3** under refluxing conditions, but no catalytic process was achieved and the maximum turnover number for the formation of **4** was 0.6. The reaction mixtures were fully homogeneous at the beginning, but darkened quickly and considerable amounts of metallic rhodium separated during the course of reaction (amount/rate of decomposition: **1a** > **1b** ≈ **1c** > **1d**). Attempts to achieve catalytic turnover in the C–H activation with **1a** by addition of promoting agents that could be expected to remove the hfacac ligand under formation of 14e species P_2RhX (X = H, Cl, OC(O)R) were not successful. Generation of "$[\{Cy_2P(CH_2)_nPCy_2\}RhCl]$" ($n$ = 1,4) in situ from $[\{(\eta^2\text{-}C_8H_{14})_2Rh(\mu\text{-}Cl)\}_2]$ and the ligand[12] gave completely inactive catalysts.

In search for thermally more robust, but structurally similar fragments of type $[\{R_2P(CH_2)_nPR_2\}M]$ we turned to complexes **2a–c**[13]. Indeed, all complexes **2a–c** were found to catalytically dehydrogenate **3** in the *absence of a hydrogen acceptor* under gentle refluxing conditions and up to 5.2 turnovers for the formation of **4** were observed. Catalytic turnover could be achieved with complex **2c** even at temperatures as low as 120 °C (Table 1). It is noteworthy that only polyhydride complexes have so far been described to be catalytically active ruthenium compounds in thermal dehydrogenation of **3** and a large excess of an additional sacrificial hydrogen acceptor[14] was required for the formation of appreciable amounts of **4**[4]. The efficiency of complexes **2** for the dehydrogenation of **3** under evolution of H_2 in the absence of a hydrogen acceptor is comparable or even superior to the few known systems using other transition metal catalysts[5d,6].

Similarly to the situation with **1a**, no significant enhancement of the catalytic activity of **2c** could be achieved by addition of promoting reagents expected to result in formation of $[\{Cy_2P(CH_2)_3PCy_2\}RuX_2]$ (Table 1). A small improvement was observed upon addition of two equivalents of Et_3SiH. Again, completely inactive catalysts were formed with in situ systems based on $[\{(arene)(Cl)Ru(\mu\text{-}Cl)\}_2]$ precursors.

The following observations and additional experiments provide convincing evidence that dehydrogenation of **3** using **2a–c** is only catalyzed by molecular species in homogeneous solution[15]:

i) The solutions darkened during the course of the reaction, but only small amounts of metallic ruthenium precipitated even after prolonged heating.

ii) Optimum catalytic activity was observed in the early stages of reaction (Figure 1).

iii) Large amounts of metallic ruthenium were formed when the phosphine free complex $[(cod)Ru(2\text{-}Me\text{-}allyl)_2]$ was subjected to the reaction conditions, but dehydrogenation of **3** was very sluggish.

Table 1. Thermal catalytic dehydrogenation of cyclooctane **3** to cyclooctene **4** catalyzed by ruthenium complexes

Catalyst precursor	c(Ru) [mmol l^{-1}]	Additive	ton [a]
2a	6.52 / 5.50	---	5.2 / 4.6
2b	4.59 / 6.08	---	3.2 / 2.6
2c	5.67	---	2.4
2c [b]	7.02	---	1.3
2c	4.19	Hg [c]	2.5
2c	4.04	$CF_3SO_3SiMe_3$ [d]	2.0
2c	5.35	Et_3SiH [d]	3.4
2c	4.11	Me_3SiCl [d]	0.4
2c	4.24	CF_3CO_2H [d]	0.2
2c	6.19	H_2 [e]	1.6
5	5.01	---	0.5
6	5.42	---	1.2
$[(cod)Ru(2\text{-}Me\text{-}allyl)_2]$	12.8	---	0.5

[a] ton = turnover number = total amount of **4** formed per mol Ru as determined by GC; conditions as in scheme 1 unless otherwise stated. – [b] 120 °C. – [c] 20 mmol. – [d] 2 equiv./Ru. – [e] Stirred at room temperature under 5 atm of H_2 for 2 h prior to reaction.

iv) Addition of metallic mercury[16] did not effect catalytic dehydrogenation of **3** with **2c**.

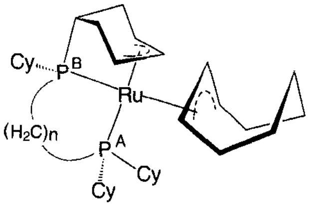
v) All metal containing species present in solution at the end of a reaction using **2c** were adsorbed on silica and investigated by high resolution TEM. Ruthenium was found to be homogeneously dispersed on the surface and no particles with diameters >5 Å could be detected.

Catalyst deactivation is a major problem in catalytic C–H activation processes and is usually responsible for turnover limitation. Product inhibition has been observed as a possible deactivation pathway for dehydrogenation of **3** using Rh catalysts[6,8], but appears unlikely to be of major importance for our ruthenium systems, as in situ catalysts formed from $[(cod)Ru(2\text{-}Me\text{-}allyl)_2]$ and the ligands gave results similar to the isolated complexes **2a–c**. Another common deactivation pathway is ligand degradation via P–C cleavage[5c], but we detected small amounts of benzene rather than cyclohexane in some reaction mixtures at the end of the catalytic runs.

In attempts to rationalise these findings, we found that the unusual bisallyl complex **5** was formed quantitatively from **2c** in the presence of one equivalent of 1,5-cyclooctadiene[17]. Complex **5** contains two different cyclic η^3-allyl groups, one of them being part of the new terdentate ligand $\kappa^2P,P'\text{-}Cy_2P(CH_2)_3PCy(3,4,5\text{-}\eta^3\text{-}C_6H_8)$ and was found to be considerably less efficient for the dehydrogenation of **3** than **2c** (Table 1).

The high specificity of the *intramolecular* C–H activation is quite remarkable in view of the substantial molecular reorganizations. The formation of **5** requires the cleavage of three adjacent C–H bonds in one of the cyclohexyl groups of the ligand[18] followed by hydride transfer to cod and subsequent rearrangement to give the η^3-cyclooctenyl ligand[19]. In case of the ligand $Cy_2P(CH_2)_4PCy_2$, intramolecular C–H activation is even more facile and only **6** could be obtained from the reaction with $[(cod)Ru(2\text{-}Me\text{-}allyl)_2]$

even under mild conditions. Again, **6** was a poor catalyst for the dehydrogenation of **3** (Table 1).



n = 3, **5**
n = 4, **6**

In conclusion, we have successfully demonstrated that the fragments $[\{Cy_2P(CH_2)_nPCy_2\}M]$ (M = Rh, Ru) are active in thermal C−H bond cleavage reactions under homogeneous conditions, whereby catalytic processes can be achieved in case of M = Ru. Intramolecular dehydrogenation of the phosphorus attached cyclohexyl groups to give an unusual terdentate κ^2P,P'-$Cy_2P(CH_2)_nPCy(3,4,5\text{-}\eta^3\text{-}C_6H_8)$ ligand is a facile process with n = 3 or 4 and may provide a possible catalyst deactivation pathway. Based on these findings, further studies to overcome these limitations and to achieve functionalization reactions other than dehydrogenation seem highly promising and are currently under investigation.

This work was supported by the *Max-Planck-Gesellschaft*, the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. Generous loans of precious metal compounds by *Degussa AG* and *Hoechst AG* are gratefully acknowledged. We thank the analytical departments of the *Max-Planck-Institut für Kohlenforschung* for their inevitable assistance. Special thanks are due to Prof. *P. W. Jolly* for communicating results prior to publication.

Experimental Section

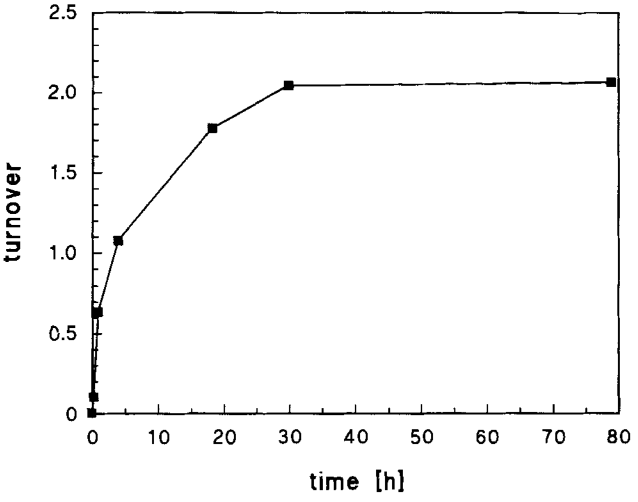
All manipulations were carried out under Argon atmosphere in flame dried glassware. Complexes **1a−d** were synthesized according to ref.[11]. Cyclooctane was purified by preparative GC and distilled from sodium. Its purity was verified to be greater than 99.99% by analytical GC prior to use.

2a−c: $[(cod)Ru(2\text{-}Me\text{-}allyl)_2]$ (437 mg) and the appropriate ligand (1.0 equiv.) were dissolved in n-hexane (40 ml) and kept at (70 ± 5)°C until quantitative conversion to **2a−c** was indicated by $^{31}P\{^1H\}$ NMR. Small colorless or pale yellow crystals were collected upon concentration of the solutions in 60−85% yield (not optimized). Satisfactory elemental analyses were obtained and the molecular ions were observed in EI-MS. $^{31}P\{^1H\}$ NMR ([D]$_6$benzene, 80.01 MHz, 300 K): **2a**: δ = 6.8 (s), **2b**: δ = 63.9 (s), **2c**: δ = 22.1 (s).

5: After **2c** was formed as described above, the mixture was heated under reflux for 25 h. The quantitative conversion of **2c** to **5** was followed by $^{31}P\{^1H\}$ NMR. Colorless crystalline **5** (255 mg, 35%) was obtained upon concentration. − M.p. 199−201°C (dec., DSC). − $^{31}P\{^1H\}$ NMR ([D]$_6$benzene, 80.01 MHz, 300 K): δ = 27.7 (d, P_A), 72.9 (d, P_B), $^2J(P,P)$ = 34 Hz. − $C_{35}H_{60}P_2Ru$ (643.88): calcd. C 65.29, H 9.39, P 9.62; found C 64.91, H 9.88, P 9.59.

6: $[(cod)Ru(2\text{-}Me\text{-}allyl)_2]$ (208 mg) was treated with $Cy_2P(CH_2)_4PCy_2$ (1.0 equiv.) as described for **2a−c**. Complex **6** (132 mg) could be isolated from the resulting mixture of compounds by fractional crystallisation in 32% yield. $^{31}P\{^1H\}$ NMR ([D]$_6$benzene, 80.01 MHz, 300 K): δ = 9.3 (d, P_A), 73.0 (d, P_B), $^2J(P,P)$ = 29 Hz.

Figure 1. Time dependence of the formation of cyclooctene **4** from thermal dehydrogenation of cyclooctane **3** using complex **2c** as a catalyst. − $c(\mathbf{2c})$ = 4.30 mmol l^{-1}, T_{bath} = 170°C



Catalytic Runs: The catalyst (ca. 15.0−40.0 µmol) was dissolved in 5.0−8.0 ml of **3** and the mixture was heated in an oil bath kept at 170°C for 48 h unless otherwise specified. Metal containing species were removed by trap-to-trap distillation or filtration over a plug of silica and the clear colorless solutions were analyzed by GC (60 m RTX-1; G/190, internal standard: cyclohexane in n-decane). Turnover numbers were shown to be reproducible within 10% deviation for selected examples.

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