<http://www.diva-portal.org>

This is the published version of a paper published in *Dalton Transactions*.

Citation for the original published paper (version of record):

Stewart, B., Nyhlén, J., Martin-Matute, B., Bäckvall, J-E., Privalov, T. (2013)

A computational study of the CO dissociation in cyclopentadienyl ruthenium complexes relevant to the racemization of alcohols.

Dalton Transactions, 42(4): 927-934

<https://doi.org/10.1039/c2dt31919e>

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

Reproduced from *Dalton Transactions*, 2013, 42 (4), 927-934 with permission of The Royal Society of Chemistry.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:su:diva-87154>

A computational study of the CO dissociation in cyclopentadienyl ruthenium complexes relevant to the racemization of alcohols†‡

Cite this: *Dalton Trans.*, 2013, **42**, 927

Beverly Stewart,§ Jonas Nyhlen, Belén Martín-Matute, Jan-E. Bäckvall and Timofei Privalov*

The formation of an active 16-electron ruthenium *sec*-alkoxide complex *via* loss of the CO ligand is an important step in the mechanism of the racemization of *sec*-alcohols by $(\eta^5\text{-Ph}_5\text{C}_5)\text{Ru}(\text{CO})_2\text{X}$ ruthenium complexes with X = Cl and O^tBu. Here we show with accurate DFT calculations the potential energy profile of the CO dissociation pathway for a series of relevant $(\eta^5\text{-Ph}_5\text{C}_5)\text{Ru}(\text{CO})_2\text{X}$ complexes, where X = Cl, O^tBu, H and COO^tBu. We have found that the CO dissociation energy increases in the following order: O^tBu (lowest), Cl, COO^tBu and H (highest). Using the distance between ruthenium and C_{CO}, $r = \text{Ru}-\text{C}_{\text{CO}}$, as a constraint, and by optimizing all other degrees of freedom for a range of Ru–CO distances, we obtained relative energies, $\Delta E(r)$ and geometries of a sufficient number of transient structures with the elongated Ru–CO bond up to $r = 3.4 \text{ \AA}$. Our calculations provide a quantitative understanding of the CO ligand dissociation in $(\eta^5\text{-Ph}_5\text{C}_5)\text{Ru}(\text{CO})_2\text{Cl}$ and $(\eta^5\text{-Ph}_5\text{C}_5)\text{Ru}(\text{CO})_2(\text{O}^t\text{Bu})$ complexes, which is relevant to the mechanism of their catalytic activity in the racemization of alcohols. We recently reported that exchange of the CO ligand by isotopically labeled ¹³CO in the Ru–O^tBu complex occurs twenty times faster than that in the Ru–Cl complex. This corresponds to a difference of 1.8 kcal mol^{−1} in the CO dissociation energy (at room temperature). This is in very good agreement with the calculated difference between the two potential energy curves for Ru–O^tBu and Ru–Cl complexes, which is about 1.8–2 kcal mol^{−1} around the corresponding transition states of the CO dissociation. The calculated difference in the total energy for CO dissociation in $(\eta^5\text{-Ph}_5\text{C}_5)\text{Ru}(\text{CO})_2\text{X}$ complexes is related to the stabilization provided by the X group in the final 16-electron complexes, which are formed *via* product-like transition states. In addition to the calculated transition states of CO dissociation in Ru–O^tBu and Ru–Cl complexes, the calculated transient structures with the elongated Ru–CO bond provide insight into how the geometry of the ruthenium complex with a potent heteroatom donor group (X) gradually changes when one of the COs is dissociating.

Received 5th July 2012,
Accepted 17th September 2012

DOI: 10.1039/c2dt31919e

www.rsc.org/dalton

Introduction

Dynamic kinetic resolution (DKR) by combining an enzyme with a racemization catalyst is a powerful method for the synthesis of enantiomerically pure compounds in high yields.^{1,2} We have successfully applied this methodology to a large variety of *sec*-alcohols by using a lipase as the resolving catalyst

and $(\eta^5\text{-Ph}_5\text{C}_5)\text{Ru}(\text{CO})_2\text{Cl}$ (**1**) as the racemization catalyst.³ Complex **1** allows for a fast reaction at room temperature. Mechanistic investigations of the mode of action of ruthenium complexes, in particular catalyst **1**,⁴ have recently attracted considerable attention.⁵

The mechanism of racemization of *sec*-alcohols by **1** is quite complex and consists of several key steps (Scheme 1).^{4,6} Activation by ^tBuOK produces complex **3** (see ref. 3a and 2b) with ruthenium-coordinated *tert*-butoxide *via* assistance of coordinated CO (an acyl intermediate **2** in Scheme 1).^{4b,c} Subsequently, an alcohol–alkoxide exchange rapidly generates an 18-electron ruthenium *sec*-alkoxide complex **4**.^{4b} For reasons already discussed in the literature,⁶ the reaction proceeds *via* an inner-sphere mechanism without involvement of ruthenium hydride $(\eta^5\text{-Ph}_5\text{C}_5)\text{Ru}(\text{CO})_2\text{H}$ (**6**, Scheme 1).^{3b} The actual racemization step is the β -hydride elimination, **4** → **5** in

Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91 Stockholm, Sweden. E-mail: priti@organ.su.se

†Dedicated to Professor David Cole-Hamilton on the occasion of his retirement and for his outstanding contribution to transition metal catalysis.

‡Electronic supplementary information (ESI) available. See DOI: 10.1039/c2dt31919e

§Departamento de Quimica, Universidade de Coimbra, Coimbra, Portugal 3004-535.

Scheme 1 Mechanistic outline for racemization of *sec*-alcohols by ruthenium catalyst **1**. CO stretching frequencies, ν_{CO} , of selected complexes in toluene are according to *in situ* IR (for **1**, **3** and **4** see ref. 4a; for **7** see ref. 6; complex **6** – present work). Complex **7** was observed to form irreversibly from **3** in the presence of added carbon monoxide.⁶

Scheme 1, which requires creation of a free coordination site on ruthenium in the 18-electron complex **4**.⁴ According to our recent density functional theory (DFT) calculations, the formation of an active 16-electron complex **4'** *via* loss of the CO ligand, **4** $\rightarrow$ **4'** in Scheme 1, is overall a more favorable pathway in comparison with an alternative $\eta^5 \rightarrow \eta^3$ ring slip route.^{4b}

Direct support of our prediction that CO dissociation is a key step in the racemization of alcohols by catalyst **1**^{4b} was provided by a ^{13}C CO exchange study of **1** and **3** using ^{13}C NMR spectroscopy, which showed that fast exchange of carbon monoxide occurs with **3**.⁶ The corresponding exchange of carbon monoxide with **1** was ≈ 20 times slower.⁶ Complex **7** was observed to form irreversibly from **3** in the presence of added carbon monoxide (see details in ref. 6) inhibiting the racemization (complex **7** is not active as a racemization catalyst for *sec*-alcohols). The $^{12}\text{CO}/^{13}\text{CO}$ exchange indicates that dissociation of CO from ruthenium complexes **1** and **3** occurs followed by addition of the isotopically labeled ^{13}CO . An alternative concerted exchange pathway (*vide infra*) is unfavored due to the fact that **1** and **3** are 18-electron complexes. It is also worth mentioning (a) the recently reported coordination of an olefin to ruthenium during the racemization which strongly suggests the creation of a vacant site on ruthenium during racemization,⁷ and (b) the use of well defined 16-electron N-heterocyclic carbene (NHC) and phosphine-containing ruthenium(II) complexes by Nolan and co-workers as effective racemization catalysts of aromatic and aliphatic *sec*-alcohols.^{8,9}

Two synergistic components of the metal–CO bonding are (a) the so-called σ donation of the lone pair of CO and (b) the so-called π -backbonding, which is an interaction of a filled metal d-orbital with the unoccupied π^* orbital of CO.^{10,11} A red shift of the CO stretching frequency of complex **3** (ν_{CO} in Scheme 1 measured by *in situ* IR) compared to that of complex **1** suggests that the ruthenium–CO bond is stronger in complex **3** than in complex **1**, however, the CO exchange experiment shows that the CO exchange is considerably faster for complex **3** in comparison to complex **1**.

The line of our quantum-chemical inquiry is therefore (a) comparative analysis of the CO dissociation process in ($\eta^5\text{-Ph}_5\text{C}_5$)Ru(CO)₂X ruthenium complexes; (b) calculations directly relevant to a measurably faster CO dissociation (faster ^{13}C CO exchange) for complex **3** in comparison with complex **1**; (c) the mechanism of the irreversible formation of complex **7** at a higher CO concentration in the CO-exchange experiments. All computational details and miscellaneous data are included in the ESI.[†]¹²

Results and discussion

1. Calculated and measured vibrational frequencies of 18-electron ruthenium complexes

In the ($\eta^5\text{-Ph}_5\text{C}_5$)Ru(CO)₂X complexes from Scheme 1, where X = Cl, O^{*t*}Bu, OC(H)CH₃Ph and H, as well as in complexes **2**

Table 1 Experimental and calculated vibrational frequencies (vibr. freq.) for the selected complexes from Scheme 1 (in cm^{-1})

Complex	Vibr. freq. (cm^{-1})		Shift of vibr. freq. compared to free CO (cm^{-1})	
	Calculated	<i>In situ</i> IR	Calculated ^a	<i>In situ</i> IR ^b
1	2117.15	2049	−90.07	−94
	2077.75	2001	−129.47	−142
2	2101.28	1933	−196.94	−210
	2094.01	2021	−113.21	−122
3	2043.76	1964	−163.46	−179
	2105.51	2037	−101.71	−106
7	2059.14	1983	−148.08	−160
	2091.51	2025	−115.71	−118
4	2043.88	1971	−163.34	−172
	2100.27	2023	−106.95	−120
6	2053.43	1963	−153.79	−180

^a Shift of vibr. freq. with respect to calculated value of free CO (2207.22 cm^{-1}). ^b Shift of vibr. freq. with respect to experimental value of free CO (2143 cm^{-1}).

and 7, the strength of the Ru–CO bond(s) should relate to the electron donating abilities of the ligands on ruthenium. The CO stretching frequencies are often regarded as a probe for the electronic state of the metal and the electron-donating ability of the metal-coordinating groups.¹⁰ The vibrational frequencies from *in situ* IR measurements and calculations are given in Table 1. The relationship between the absolute values, as well as the shifts with respect to free CO, of calculated and measured vibrational frequencies is close to linear (see Table 1 and Fig. S1†) for all complexes shown in Scheme 1.

From the comparison of theory with experiment, it appears that the calculations adequately describe the coordination environment of the ruthenium center and the donor strength of various ligands in the aforementioned complexes. We have also checked that there is no meaningful difference between the calculated and the X-ray structures of the 18-electron ($\eta^5\text{-Ph}_5\text{C}_5$)Ru(CO)₂X complexes with X = H, Cl and I from ref. 3b, see Fig. S2.† With that in mind, we proceeded to calculate CO-dissociation energies (pathway) using the fully optimized 18-electron complexes 1, 3 and 6, as well as complex 7 as the starting point.

2. The potential energy profile of the CO-dissociation

Because we aim to investigate the electronic structure and geometry of a series of ruthenium complexes as each of these “evolves” along a plausible CO-dissociation pathway, we can at first limit ourselves to the potential energy profile of the CO dissociation in the condensed phase (toluene). To get an idea about the key differences in the electronic and structural properties that affect the CO dissociation in complexes 1, 3, 6 and 7, a suitable choice of a reaction coordinate is the distance between ruthenium and C_{CO}, $r = \text{Ru}-\text{C}_{\text{CO}}$ as shown in Fig. 1. The difference between the combined potential energies of the 16-electron ruthenium complex plus free CO and the potential energy of the corresponding 18-electron complex, $\Delta E^{\text{dis}} = \{E(16e) + E(\text{CO})\} - E(18e)$, using only fully optimized structures

Fig. 1 Calculated potential energy profiles for the CO-dissociation from the 18-electron complexes 1, 3, 6, and 7. The change of the potential energy versus r , $\Delta E(r)$, is in kcal mol^{-1} . The distance between ruthenium and C_{CO}, $r = \text{Ru}-\text{C}_{\text{CO}}$, is in Å. The potential energy dissociation limit, ΔE^{dis} , is shown to the right in the diagram (in kcal mol^{-1}).

will be referred to simply as the dissociation limit. From the fully optimized structures of 18-electron complexes 1, 3, 6 and 7, by optimizing all degrees of freedom except the Ru–C_{CO} bond length (r), which was fixed at a number of values, we obtained relative energies, $\Delta E(r)$, and geometries of a sufficient number of transient structures with the elongated Ru–CO bond up to $r = 3.4$ Å. The latter r value corresponds to an elongation of about 1.5 Å of the Ru–C_{CO} bond compared to the 18-electron complexes ($\eta^5\text{-Ph}_5\text{C}_5$)Ru(CO)₂X (Fig. 1). The calculated transient structures were subjected to the electronic-structure analysis and visualization of the selected molecular orbitals (MOs).

Naturally, the potential energy change differs from the Gibbs free energy change upon CO dissociation mainly because of a fairly large entropy change. However, the resulting thermochemical corrections to ΔE^{dis} at 298.15 K are fairly similar for complexes 1, 3, 6 and 7 – being on average ≈ -14.65 kcal mol^{-1} (see also Table S1 in ESI†). Hence, comparison of the potential energy profiles of CO dissociation, $\Delta E(r)$ in Fig. 1, is valid (*vide infra* for the discussion of the Gibbs free energy profiles).

For the ruthenium–hydride complex 6, $\Delta E(r)$ monotonously increases with the increase of r toward the dissociation limit, complex 6', which is at 46 kcal mol^{-1} with respect to the 18-electron complex 6 at the equilibrium (Fig. 1).¹³ In the 16-electron ruthenium–hydride complex 6', the relative arrangement of the ruthenium–hydride and ruthenium–CO bonds is not much different from that in the 18-electron ruthenium–hydride complex (*vide infra*). At $r = 3.2$ Å, $\Delta E^{\text{dis}} - \Delta E(r)$ is about 7 kcal mol^{-1} . Complex 7 shows similar behavior as that of hydride 6 with a monotonous increase of $\Delta E(r)$ all the way to the dissociation limit at 35.4 kcal mol^{-1} . For the ruthenium–chloride complex 1, the slope of $\Delta E(r)$ versus r is noticeably less steep with $\Delta E(r)$ approaching the dissociation limit already for $r \geq 3.2$ Å (Fig. 1). At $r = 3.2$ Å, $\Delta E^{\text{dis}} - \Delta E(r)$ is only about 2 kcal mol^{-1} for complex 1. Finally complex 3 shows a slope of $\Delta E(r)$ quite similar to that of complex 1 but with overall lower energy of CO dissociation (*vide infra*).

Fig. 2 (a) An illustration of the structure of the 18-electron complex with planes which are perpendicular to the Cp-ligand and drawn through the Ru–CO and Ru–Cl bonds. (b) An illustration of key changes in Ru–Cl bonding with one of CO dissociating.

Fig. 3 The plots of the angle θ (°) from Fig. 2a versus the Ru...CO distance r (Å).

3. Key structural changes in ruthenium complexes on CO dissociation

The reason for the large difference in rate between the ruthenium hydride and ruthenium chloride in CO dissociation is apparent from the potential energy profile in Fig. 1 and is reflected by how the geometry at the ruthenium atom changes on CO dissociation. It is instructive to consider the angle θ between the two planes drawn through the Ru–CO and Ru–Cl bonds as shown in Fig. 2a perpendicular to the plane of the carbon atoms of the Cp ligand. In the ruthenium chloride complex, θ is 65.7° in the 18-electron complex. As CO is dissociating, the Ru–Cl complex gradually changes from the starting material-like geometry towards the product-like geometry. The angle θ remains almost unchanged until the Ru...CO distance is about 2.3 Å (Fig. 3); this is about 0.4 Å of an elongation of the Ru–CO bond. With a further increase of the Ru...CO distance, at $r > 2.3$ Å, θ gradually decreases toward its value in the 16-electron ruthenium–chloride complex, which is about 10°. The Ru–O^tBu complex shows a similar change of θ as that of the Ru–Cl complex. The angle θ changes from about 58° in the 18-electron complex to 4.5° in the 16-electron complex. In contrast to the changes in θ for the Ru–Cl and Ru–O^tBu complexes, the Ru–H complex mostly retains the starting material-like geometry; θ remains about 70° in the ruthenium–hydride complexes all the way through the CO-dissociation process ($\theta =$

70.7° and 68.2° in the 18- and 16-electron ruthenium–hydride complexes, respectively).

As CO dissociates, one of the d orbitals of ruthenium eventually becomes empty, making possible a better donation from a heteroatom donor through the d–p orbital interaction which stabilizes the complex as a whole. The required orbital overlap between the p donor orbital of the heteroatom and the d orbital, which at some point becomes empty due to the dissociation of one of the Ru–CO bonds, promotes a rearrangement of the atoms coordinated to the ruthenium, as schematically shown in Fig. 2b. This interaction, and the rearrangement at the ruthenium, should proceed well with halogen and alkoxy ligands but not in the ruthenium hydride complex (see Fig. 3). This explains the large difference in the total energy of the dissociation of the CO ligand in hydride 6 *versus* chloride 1 and alkoxide 3, which is 20.5 and 27 kcal mol^{−1}, respectively.

Both Ru–Cl and Ru–O^tBu complexes exhibit similar rearrangement at the ruthenium with the dissociation of CO (see Fig. 4, as well as $\theta(r)$ for the ruthenium–chloride and the ruthenium–O^tBu complexes in Fig. 3). However, the dissociation of CO in Ru–Cl and Ru–O^tBu complexes has similarities, but also differences. As mentioned previously ¹³CO incorporation into the ruthenium–O^tBu complex was found to occur twenty times faster than that for the ruthenium chloride complex. This rate difference corresponds to an energy difference of 1.78 kcal mol^{−1} in the CO-dissociation energy between these two complexes. According to our calculations shown in Fig. 1, $\Delta E(r)$ is consistently smaller for ruthenium–O^tBu in comparison with that of ruthenium–chloride from $r = 2.46$ Å onwards. The difference between the two potential energy curves is about 1.8 kcal mol^{−1} at the point where Ru...CO $\approx$ 2.8 Å. This Ru...CO distance is close to the Ru...CO distance in the transition state (≈ 2.7 Å) of the CO dissociation from our earlier study.^{4b} The difference in the energy of the dissociation of the CO ligand for the Ru–Cl *versus* the Ru–O^tBu complexes is about 6.5 kcal mol^{−1} (Fig. 1), and is attributed to the better donor properties of O^tBu *versus* Cl.

The potential energy curves of the partial optimizations with the Ru...C(CO) constraint (Fig. 1) exhibit a consistently smooth advancing toward the dissociation limit.¹⁴ We regard this as an indication that calculations retain sufficient accuracy in the region of large Ru...C(CO) elongations and also that the transition state search in such an area is perhaps meaningful for additional qualitative insight into the CO dissociation. With that in mind, we have calculated the transition states of the CO dissociation in Ru–Cl and Ru–O^tBu complexes. Energetically and structurally, both transition states are located rather close to the dissociation limit of the potential energy curves of CO dissociation. Both transition states have the product like geometries with the elongated Ru...C(CO) in the range 2.8 Å–2.9 Å (see geometrical details in Fig. S4 in ESI†).¹⁵ In each of the two transition states, the correct normal vibrational mode, $\nu_o \approx -151$ cm^{−1} for X = Cl and $\nu_o \approx -168$ cm^{−1} for X = O^tBu in (η^5 -Ph₅C₅)Ru(CO)₂X ruthenium complexes, corresponds to the clearly dissociative movement of CO relative to ruthenium. The transition state energy of the dissociation of the CO ligand for

Fig. 4 Structural details of the selected 18- and 16-electron complexes with the view from the top with respect to $(\eta^5\text{-Ph}_5\text{C}_5)\text{Ru}$. All distances are in Å.

the Ru-Cl complex is about 3 kcal mol⁻¹ higher than that for the Ru-O^tBu complex.

Favoring the 16-electron product and the free CO, the entropy change upon CO dissociation is the main contributor to the thermochemical correction of the potential energy change. At 298.15 K and based on 18-electron starting and 16-electron product complexes, the thermochemical corrections are -14.59 kcal mol⁻¹ and -14.48 kcal mol⁻¹ for complexes **1** and **3**, respectively; the Gibbs free energy changes upon CO dissociation are plotted in Fig. S5.†

The possible push-pull effect between the π -donating X-group, *i.e.* halogen and alkoxy, and the π^* of CO is small; in

the 16-electron complexes there is no considerable change (elongation) of the CO bond length compared to that in the corresponding 18-electron complexes (Fig. 4). A contraction of the Ru-C_{CP} bonds, *i.e.* overall “tightening” of the Ru-Cp binding, could be seen in all 16-electron complexes compared to the corresponding 18-electron complexes. However, at an early stage of CO dissociation a stabilization of the bonding between ruthenium and the π -donating X group contributes to the lowering of the $\Delta E(r)$ profile while the shortening of the Ru-C_{CP} bonds is insignificantly small. This effect makes Ru-X complexes with a substantially different X-group, *i.e.* **6**, **7** and **3** together with **1**, show a different slope of the $\Delta E(r)$ profile (Fig. 1). At the same time, X = O^tBu and Cl have a similar effect on the initial part of the $\Delta E(r)$ profile (Fig. 1).

While exploring the potential energy of the CO-dissociation, $\Delta E(r)$, for the ruthenium-O^tBu complex in the region of large Ru...CO distance, we have noticed that $\Delta E(r)$ first reaches its apex, 20.11 kcal mol⁻¹, at $r = 2.94$ Å, and then decreases with the increase of r . Inspection of the transient structures along the potential energy profile of Ru-Cl at $r \approx 3.8$ Å, see Fig. 1, leads us to suspect that non-covalent interactions between the dissociating CO molecule and C-H groups of O^tBu and Ph groups occur and that a stable but weakly bound complex could exist. We have indeed found such a complex in which the CO molecule has a number of close contacts with hydrogen atoms of the C-H groups of O^tBu, see the fully optimized structure in Fig. S6.†

4. The mechanism of CO incorporation into the Ru-O^tBu complex

In the experimental ¹³CO exchange studies of Ru-O^tBu complex **3**, complex **7** was isolated as a side product, and based on experimental results it was suggested that complex **7** is responsible for the inhibition of the alcohol racemisation, at a higher concentration of CO. According to our calculations, addition of CO to complex **3** to give **7** is highly exothermic: $E(7) - \{E(3) + E(\text{CO})\} = -34.5$ kcal mol⁻¹ (Scheme 2). This calculated high stability of **7** is in agreement with the experimental finding that the reaction **3** → **7** is irreversible. Based on the calculated energies (Scheme 2), it is sensible that addition of carbon monoxide shifts the equilibrium towards complex **7** thus inhibiting the formation of the 16-electron complex **3'**.

Calculation of the potential energy profile of the CO-dissociation (Fig. 1) reveals that the CO dissociation from complex **7** requires considerably more energy than the CO dissociation from complex **3**. An increase of the Ru-CO distance beyond a certain point, *ca.* 2.8 Å, allows the acyl group to readjust so that both carbon and oxygen atoms eventually coordinate to ruthenium. The adjustment of the acyl-ruthenium coordination does help to stabilize the potential energy of transient structures but less efficiently in comparison to the effect of the readjustment of the donor-heteroatom coordination to ruthenium in complexes **1** and **3**. The optimized structure of the analog of **7** with the completely dissociated CO, complex **7'**, is shown in Fig. 4. Since it has an almost η^2 -acyl ligand, **7'** is a pseudo-hexacoordinated ruthenium complex just about

Scheme 2 Mechanistic outline for the CO exchange for complex **3** with the calculated relative energies of stationary intermediates and transition states in square brackets.

Fig. 5 The side-view of the intermediates **3** (**3'**) and **7** (**7'**), as well as the transition states **TS1** and **TS2** from Scheme 2. All distances are in Å.

1 kcal mol⁻¹ higher in energy than complex **3**. The transition state, **TS1**, which “connects” complexes **3** and **7'** has been located and is shown in Fig. 5. The structure of **TS1** and the normal vibrational mode, $\nu_o = -189$ cm⁻¹, is consistent with an attack of the O'Bu group on CO at the ruthenium center (migratory insertion). We have checked that **TS1** relaxes towards complex **7'**.

Comparing calculated structures of complexes **3** and **7'**, it appears that ruthenium is the least accessible for an addition of CO in complex **3** in a direct one-step pathway **3** → **7**.

Nevertheless, such a pathway has been investigated and we have located a plausible transition state, **TS2**, in which an attack of the O'Bu group on CO at the ruthenium center (migratory insertion) combines with the coordination of an additional CO to the ruthenium center. In **TS2** (Fig. 5), the C–O distance is shorter than that in **TS1** indicating that O'Bu has to migrate further towards CO in order to allow for the ruthenium–CO bond formation as pointed out above. The normal vibrational mode, $\nu_o = -72$ cm⁻¹, describes both the movement of CO towards ruthenium and an attack of O'Bu on CO at the ruthenium center.

With respect to **3**, $\Delta E^\ddagger(\text{TS2})$ is 16.1 kcal mol⁻¹ while $\Delta E^\ddagger(\text{TS1})$ is 9.5 kcal mol⁻¹, the total thermochemical corrections to $\Delta E^\ddagger(\text{TS1})$ and $\Delta E^\ddagger(\text{TS2})$ are -1.4 kcal mol⁻¹ and 11.3 kcal mol⁻¹, respectively. Although already quite high at the potential energy level, **TS2** becomes even higher by taking into account the entropy change in the process. Thus, the two-step **3** → **7** pathway, **3** → **7'** via **TS1** followed by **7'** + CO → **7**,¹⁶ is favorable both at the potential energy and the Gibbs free energy levels. The overall change of the Gibbs free energy, $\Delta G(\mathbf{3} \rightarrow \mathbf{7}) = -19.72$ kcal mol⁻¹, is less dramatic than $\Delta E(\mathbf{3} \rightarrow \mathbf{7})$ primarily due to the change of the entropy in this transformation.

Conclusions

The formation of an active 16-electron ruthenium complex via loss of the CO ligand is an important step in the mechanism of the racemization of *sec*-alcohols by ruthenium catalyst **1**. Accurate DFT calculations provide the potential energy profile of the CO-dissociation pathway for a series of $(\eta^5\text{-Ph}_5\text{C}_5)\text{Ru}(\text{CO})_2\text{X}$ complexes, where X = Cl, O'Bu, and H and an acyl group (complex **7**). The potential energy change (barrier) for the CO-dissociation increases in the following order: O'Bu- (lowest), Cl-, acyl- and H-groups. In order to better understand the process of the dissociation of CO in Ru–Cl and Ru–O'Bu complexes, a sufficient number of transient structures with the elongated Ru–CO bond were calculated. Relevant transition states were calculated and found to have product-like

geometries with Ru...C(CO) distances in the range of 2.8 Å–2.9 Å. The calculated difference between the energy changes upon CO dissociation in Ru–O^tBu and Ru–Cl complexes is in the range of 2–3 kcal mol^{−1}. This is in accordance with the experimental value of 1.8 kcal mol^{−1} (the rate of ¹³CO/¹²CO exchange for the Ru butoxide was 20 times faster than that for Ru chloride). According to our calculations, the difference in the total energy of the dissociation of the CO ligand in (η⁵-Ph₅C₅)Ru(CO)₂X complexes is primarily attributed to the donor properties of the X-group with regard to the 16-electron product ruthenium complex.

Experimental section

Experimental

Complex **6** was synthesized according to a published procedure (see ref. 3b). *In situ* IR measurements of hydride **6** were performed using a ReactIR iC10 (Mettler Toledo). Thus, **6** (ca. 20 mg) was dissolved in toluene (3 mL) in a two-necked flask. The flask was connected to the SiComp probe of the IR reactor. The spectrum was recorded and the data were processed with the iC IR software. The IR analysis showed two bands at 1963 and 2023 cm^{−1} for the CO groups of **6**.

Theoretical

Computational details,¹² supplementary for vibr. freq. calculations, structural comparison of the 18-electron ruthenium complexes, supplementary for the calculated potential energy profiles, molecular orbital analysis and selected XYZ data.

Acknowledgements

The Berzelius Center EXSELENT, the Knut and Alice Wallenberg foundation and Swedish Research Council are gratefully acknowledged for financial support.

References

- (a) F. F. Huerta, A. B. E. Minidis and J.-E. Bäckvall, *Chem. Soc. Rev.*, 2001, **30**, 321; (b) M. Ito, A. Osaku, S. Kitahara, M. Hirakawa and T. Ikariya, *Tetrahedron Lett.*, 2003, **44**, 7521; (c) O. Pàmies and J.-E. Bäckvall, *Chem.–Eur. J.*, 2001, **7**, 5052; (d) O. Pàmies and J.-E. Bäckvall, *Chem. Rev.*, 2003, **103**, 3247; (e) Y. Ahn, S.-B. Ko, M.-J. Kim and J. Park, *Coord. Chem. Rev.*, 2008, **252**, 647.
- For recent reviews, see: (a) B. Martín-Matute and J.-E. Bäckvall, *Curr. Opin. Chem.*, 2007, **11**, 226; (b) J. H. Lee, K. Han, M.-J. Kim and J. Park, *Eur. J. Org. Chem.*, 2010, 999; (c) A. Parvulescu, J. Janssens, J. Vanderleyden and D. De Vos, *Top. Catal.*, 2010, **53**, 931; (d) N. Turner, *Curr. Opin. Chem. Biol.*, 2010, **14**, 115–121; Y. Kim, J. Park and M.-J. Kim, *ChemCatChem*, 2011, **3**, 271–277; (e) H. Pellissier, *Tetrahedron*, 2011, **67**, 3769; (f) M. C. Warner, C. P. Casey and J.-E. Bäckvall, *Top. Organomet. Chem.*, 2011, **37**, 85–125; (g) R. Marcos and B. Martín-Matute, *Isr. J. Chem.*, 2012, **52**, 639.
- (a) B. Martín-Matute, M. Edin, K. Bogár and J.-E. Bäckvall, *Angew. Chem., Int. Ed.*, 2004, **43**, 6535; (b) B. Martín-Matute, M. Edin, K. Bogár, B. Kaynak and J.-E. Bäckvall, *J. Am. Chem. Soc.*, 2005, **127**, 8817; (c) A. Träff, K. Bogár, M. Warner and J.-E. Bäckvall, *Org. Lett.*, 2008, **10**, 4807.
- (a) B. Martín-Matute, J. B. Åberg, M. Edin and J.-E. Bäckvall, *Chem.–Eur. J.*, 2007, **13**, 6063; (b) J. Nyhlén, T. Privalov and J.-E. Bäckvall, *Chem.–Eur. J.*, 2009, **15**, 5220; (c) J. B. Åberg, J. Nyhlén, B. Martín-Matute, T. Privalov and J.-E. Bäckvall, *J. Am. Chem. Soc.*, 2009, **131**, 9500; (d) O. Verho, E. V. Johnston, E. Karlsson and J.-E. Bäckvall, *Chem.–Eur. J.*, 2011, **17**, 11216; (e) C. Hedberg, K. Källström, P. I. Arvidsson, P. Brandt and P. G. Andersson, *J. Am. Chem. Soc.*, 2005, **127**, 15083.
- (a) J. S. M. Samec, J.-E. Bäckvall, P. G. Andersson and P. Brandt, *Chem. Soc. Rev.*, 2006, **35**, 237; (b) B. L. Conley, M. K. Pennington-Boggio, E. Boz and T. J. Williams, *Chem. Rev.*, 2010, **110**, 2294; (c) C. P. Casey, S. W. Singer, D. R. Powell, R. K. Hayashi and M. Kavana, *J. Am. Chem. Soc.*, 2001, **123**, 1090; (d) C. P. Casey and J. B. Johnson, *J. Org. Chem.*, 2003, **68**, 1998; (e) C. P. Casey, T. B. Clark and I. A. Guzei, *J. Am. Chem. Soc.*, 2007, **129**, 11821; (f) H. Guan, M. Iimura, M. P. Magee, J. R. Norton and G. Zhu, *J. Am. Chem. Soc.*, 2005, **127**, 7805; (g) J. B. Åberg and J.-E. Bäckvall, *Chem.–Eur. J.*, 2008, **14**, 9169; (h) R. J. Hamilton and S. H. Bergens, *J. Am. Chem. Soc.*, 2008, **130**, 11979; (i) A. Comas-Vives, G. Ujaque and A. Lledós, *Organometallics*, 2007, **26**, 4135; (j) A. Comas-Vives, G. Ujaque and A. Lledós, *Organometallics*, 2008, **27**, 4854; (k) T. Privalov, J. S. M. Samec and J.-E. Bäckvall, *Organometallics*, 2007, **26**, 2840.
- M. C. Warner, O. Verho and J.-E. Bäckvall, *J. Am. Chem. Soc.*, 2011, **133**, 2820.
- J. B. Åberg, M. C. Warner and J.-E. Bäckvall, *J. Am. Chem. Soc.*, 2009, **131**, 13622.
- (a) J. Bosson and S. P. Nolan, *J. Org. Chem.*, 2010, **75**, 2039; (b) J. Bosson, A. Poater, L. Cavallo and S. P. Nolan, *J. Am. Chem. Soc.*, 2010, **132**, 13146.
- Dissociation of a CO molecule has previously been observed for the Shvo catalyst when the reaction was run in room fluorescent light (ref. 5c),⁹ however, the dissociation slowed down considerably when the reaction was run in the dark. The potential energy barrier for CO dissociation from the Shvo catalyst was calculated to be ≈51 kcal mol^{−1} in the gas phase, which was reduced to ≈39 kcal mol^{−1} by the entropic effect (ref. 5i).
- (a) G. Frenking and N. Fröhlich, *Chem. Rev.*, 2000, **100**, 717; (b) J. T. Poulton, M. P. Sigalas, K. Folting, W. E. Streib, O. Eisenstein and K. G. Caulton, *Inorg. Chem.*, 1994, **33**, 1476; (c) A. W. Ehlers and G. Frenking, *Organometallics*, 1995, **14**, 423; (d) J. Li, G. Schreckenbach and T. Ziegler, *J. Am. Chem. Soc.*, 1995, **117**, 486.
- K. G. Caulton, *New J. Chem.*, 1994, **18**, 25.

- 12 Computational details in short: All calculations of the potential energy profile of the CO-dissociation in all ruthenium complexes have been carried out with the M06-2X density functional, see [Y. Zhao, D. G. Truhlar, *J. Chem. Phys.*, 2006, **125**, 194101] and additional references in ESI,[†] using the lacvp** basis set (see references in ESI,[†]) as implemented in the Jaguar computational package [v. 7.7, Schrodinger, LLC, New York, NY, 2010]; the molecular orbital visualization has been performed with Gaussian 03 [M. J. Frisch *et al.*, see full reference in ESI,[†]] and GaussView.
- 13 For clarity, the range of the Ru...CO distance from the equilibrium till 2.5 Å is shown magnified in Fig. S3.[†]
- 14 The potential energy calculations with the B3LYP density functional (Fig. S3B in ESI,[†]) did not show meaningful differences from the results obtained with the M06-2X density functional using the same basis set; see also Fig. S2.[†] for the structural comparison of the calculated and X-ray structures of some relevant 18-electron Ru-complexes.
- 15 The calculation of the transition states of CO dissociation is technically challenging mostly because of the behavior (the profile) of the potential energy change *versus* the Ru...C(CO) distance – the energy of the complex going up till full dissociation. The vibrational frequency analysis fully validated the calculated transition states. However, considering the shape of the potential energy change *versus* the Ru...C(CO) distance, we regard these transition states as a qualitative rather than a quantitative result.
- 16 For the CO addition step $7' + \text{CO} \rightarrow 7$, the transition state has been calculated (Fig. S4a[†]). The potential energy barrier is about 4 kcal mol⁻¹ with respect to complex 3 in Scheme 2. According to the principle of microscopic reversibility, the same transition state describes CO dissociation from complex 7.