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Protonation of π-alkene–rhodium(I) complexes leads to σ-alkyl–rhodium(III)—an NMR study

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Abstract

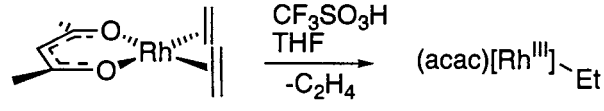
The reaction of Rh(β-diketonato)(alkene)$_2$ complexes with CF_3SO_3H in THF gives Rh(β-diketonato)(alkyl) species when the alkene is ethylene, *cis*-butene or 5-methylene-cycloheptene whereas 1,5-cyclooctadiene complexes are unreactive. The reaction was followed by means of NMR-spectroscopy at low temperature and the products were characterized in solution by 2D-NMR techniques. Three possible reaction mechanisms are discussed: ligand assisted proton transfer, hydride transfer and direct protonation of the alkene. The Rh(III)ethyl species are stable against degradation by β-hydride elimination. However, Rh(III)(β-diketonato)(*n*-butyl) complexes lose butene rapidly when ethylene is added and Rh(β-diketonato)(ethyl) complexes are formed. A mechanism preventing the formation of higher oligomers is proposed, where β-hydride elimination is followed by rapid alkene exchange and hydride re-insertion.

1. Introduction

Protonation is often a convenient method of preparing transition metal hydrides [1,2]. However, it happens that the proton appears somewhere else, for example as a CH_3 hydrogen, and the initial protonated (hydride) complex is not observed.

Such protonation may generate the active complex in a catalytic cycle. A classical example is the oxidative addition of HCl to Rh(acac)(ethylene)$_2$ **1** or Rh_2Cl_2(ethylene)$_4$ [3]. This generates a Rh-ethyl complex that catalyses the dimerization of ethylene [4]. More recently, studies of the protonation of Rh(Cp)(ethylene)$_2$, Co(Cp)(ethylene)$_2$ and related complexes have produced new insights into the mechanisms of migratory insertion of alkenes into a hydride–metal or a σ-alkyl–metal bond, as well as new catalytic processes [5–7].

Here we present a study of the protonation of Rh(β-diketonato)(alkene)$_2$ complexes and of the mechanism of the catalyzed dimerization of ethylene by the formed Rh-ethyl complexes. A point we particularly address is why no oligomerization occurs, despite the fact that the Rh-butyl complexes apparently are stable vis-à-vis β-hydride elimination. This is puzzling since β-hydride elimination has been inferred as the general path to chain termination, and the exclusive formation of dimers in some cases [2,8] (Scheme 1).



1 **2, 3**

Scheme 1.

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2. Results

The reaction of Rh(acac)(ethylene)$_2$ with two equivalents of CF_3SO_3H in d_8-THF proceeds rather slowly at 273 K and after a few hours two Rh-ethyl species are formed. This is clear from the ^1H, ^{13}C and ^{103}Rh NMR spectra. Two sets of resonances from Rh-ethyl and Rh-acac groups are the only significant signals appart from some remaining starting material and some protonated acetylacetone.

This reaction, with different β-diketonato ligands and different alkenes, was investigated by multinuclear and 2D-NMR spectroscopy at low temperatures.

2.1. The results of the protonation reaction and the structure of the products

At 173 K some new peaks appear in the H-NMR spectra between 11 and 17 ppm. A reference experiment without rhodium showed that these signals are due to protonated dissociated acetylacetonate, protonated THF and the free acid. In an electrospray mass spectra protonated THF, a protonated THF-dimer, H_2acac^+ and a THF-H_2acac^+ compound were observed. The free acetylacetonate is presumably formed by protonation of the coordinated acac and subsequent displacement by THF to give the known complex Rh(ethylene)$_2$(THF)$_2^+$ [9]. The dissociation is, however, not complete, and about 50% of the original complex remains.

When the temperature is raised slowly, Rh-ethyl species start to form at 263 K. These are clearly assigned by the CH_3 resonance at 0.6–0.7 ppm and the CH_2 signal at 4–4.5 ppm. The CH_2 signal is 'labeled' by a 2–3 Hz coupling to Rh, (^{103}Rh, $I = 1/2$, 100% abundance) and has a distinct cross peak in the H–Rh 2D-NMR correlation spectrum.

Initially two Rh-ethyl complexes are formed, which both have non-equivalent CH_2 protons. Later, two major products appear with the isomer ratio 3:1, one with equivalent CH_2 protons and one with non-equivalent CH_2 protons. No chemical exchange between the isomers is detectable on the NMR timescale.

We were not able to isolate these products for elemental analysis due to polymerization of the solvent during the reaction [10]. However, a combination of various NMR techniques can often qualitatively deduce the solution structures [11].

It is clear from the H–Rh correlation spectrum, Fig. 1, that the ethyl groups are bonded to rhodium. The two Rh-ethyl isomers are accompanied by acac signals with matching integrals. Their coordination to rhodium is established by a 1 Hz J_{Rh-C} coupling to the acetylacetonate methine carbon. Moreover, NOE effects were detected in NOESY spectra by cross peaks from the ethyl groups to the acetylacetonate ligands establishing

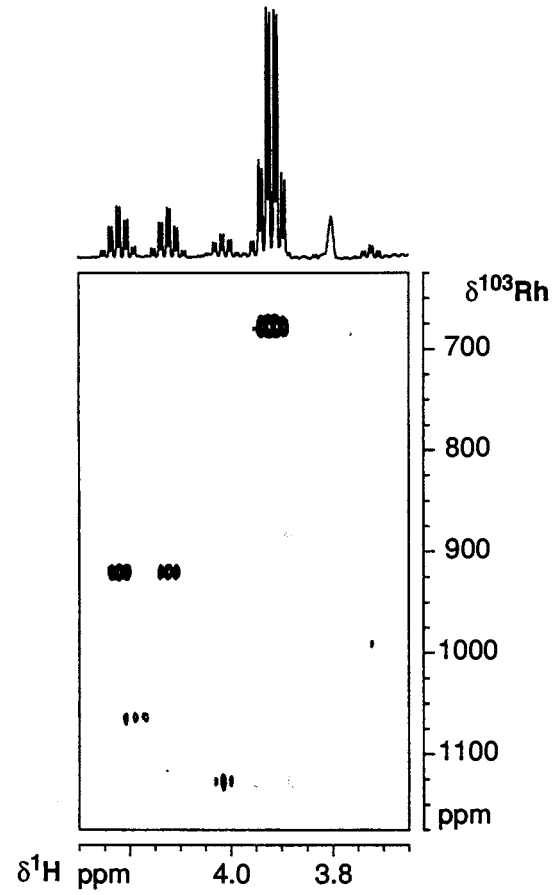


Fig. 1. 2D-NMR Rh–H correlation spectrum (273 K, 11.4 T, after 8 h at this temperature) of the reaction mixture: Rh(acac)(ethylene)$_2$ and two equivalents of CF_3SO_3H in THF-d_8.

that the ethyl and the acac groups are indeed coordinated to the same rhodium atom.

It is apparent that the second ethylene has been displaced since free ethylene was detected and, even after lowering the temperature to 173 K again, no peaks appeared that could be assigned to coordinated ethylene. Furthermore, NMR spectra of protonated Rh(acac)(5-methylene-cycloheptene), **8**, that could potentially give a σ-π-η^3-chelating ligand, show a non-coordinated alkene group in addition to the σ-bound cycloheptyl group.

Rh(III) is normally octahedrally coordinated. The H-NMR signals of the methylene groups show that one isomer has symmetry-related CH_2 protons and the other isomer has not. The acetylacetonate signals behave correspondingly, a single methyl for one complex and split signal for the other. Since these complexes, labeled **2** and **3**, are indeed susceptible to β-hydride elimination, but with the equilibrium completely shifted towards the Rh-alkyl (see below), a structure with three additional ligands, one of them weakly coordinating, is suggested [12].

Electrospray mass spectrometry has recently been applied also to organometallic chemistry [13]. In the

present case, however, no conclusive evidence was obtained for species like [Rh(acac)(ethyl)(CF_3SO_3)*cis*-$(THF)_2$], probably due to undesireable reactions in the mass spectrometer [14].

When the solution was neutralized by addition of $NaHCO_3$ the Rh-ethyl groups were still present, although their chemical shifts and relative amounts changed slightly.

2.2. Probing the protonation reaction mechanism

The same type of reaction as above takes place with other β-diketonates where the methyl groups in acetylacetonate have been changed to *tert*-butyl or phenyl groups. The reaction rates are clearly suppressed by these bulkier groups, see Fig. 2.

The chelating cyclooctadiene, COD, ligand was also used and Rh(acac)(COD) was prepared. However, the NMR spectrum of Rh(acac)(COD) and CF_3SO_3H in THF-d_8 remained unchanged even after prolonged reaction times.

The protonation of Rh(acac)(5-methylene-cycloheptene) **8**, resulted in protonation exclusively at the interior double bond and the formation of **11**. This was clear from the NMR spectra, especially from the TOCSY experiment where the Rh-α-hydrogen at 4.60 ppm showed two relayed series of signals, one with six CH_2-protons (the $(CH_2)_3$-link between CH–Rh and methylene) the other with four protons (the $(CH_2)_2$-link between CH–Rh and methylene) and from the signals (4.48 and 5.40 ppm) of the two different alkene protons from the methylene group. Results obtained with other alkenes are reported in Table 1.

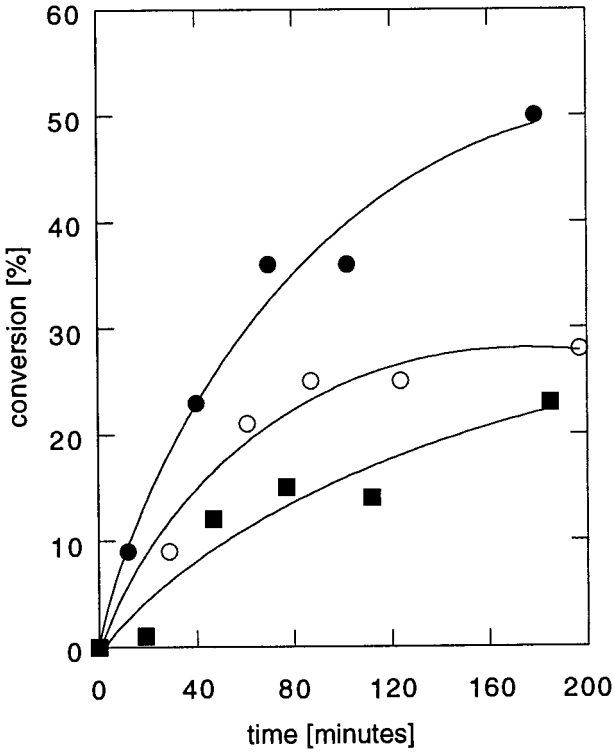


Fig. 2. Formation of Rh–ethyl groups as function of reaction time, monitored by ^{1}H NMR (The formed methyl groups compared to solvent and starting material integrals, yield based on conversion of starting material.) Due to the polymerization of the solvent during the reaction the experiment should only be regarded as qualitative. ● Rh(acac)(ethylene)$_2$; ○, Rh(phacac)(ethylene)$_2$; ■, Rh(hmacac)(ethylene)$_2$. (The lines are guides for the eyes.)

Table 1
Qualitative reaction rates for the formation of Rh–alkyl complexes by the reaction of Rh(acac)(alkene)$_2$ with one equivalent of CF_3SO_3H in THF

Alkene	Yield(%)	Rate	Temperature
Ethylene	50	Fast	263
cis-2-butene	100	Very fast	223
1,4-pentadiene	<10	Slow	273
Cyclooctene	<5	Very slow	273
Cyclooctadiene	0	0	273
5-methylene-cycloheptene	100	Slow[a]	273

The yield is based on ^{1}H NMR integrals of starting material and products. For some alkenes two isomers are formed and the yield is then based on the sum of these.
[a] CF_3COOH as acid.

In order to control that the [Rh(ethylene)$_2$(THF)$_2$]$^+$ complex is not the reactive species [Rh(ethylene)$_2$(THF)$_2$]$^+$ was prepared by reacting Rh_2Cl_2(ethylene)$_4$ with $AgCF_3SO_3$ in THF-d_8 and filtering off the precipitated AgCl [9]. CF_3SO_3H was added but the ^{1}H-NMR spectrum remained unchanged even after 12 h at 278 K.

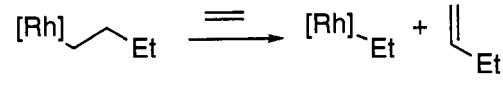
2.3. Oligomerization experiments

In the reaction of Rh(acac)(ethylene)$_2$ with CF_3SO_3H in THF small amounts of *cis*- and *trans*-butene were obtained [15]. When ethylene was added to the Rh-butyl complexes formed by the protonation of Rh(acac)(*cis*-butene)$_2$ in THF, the butyl compounds disappeared and Rh-ethyl complexes **2** and **3** were formed, Scheme 2.

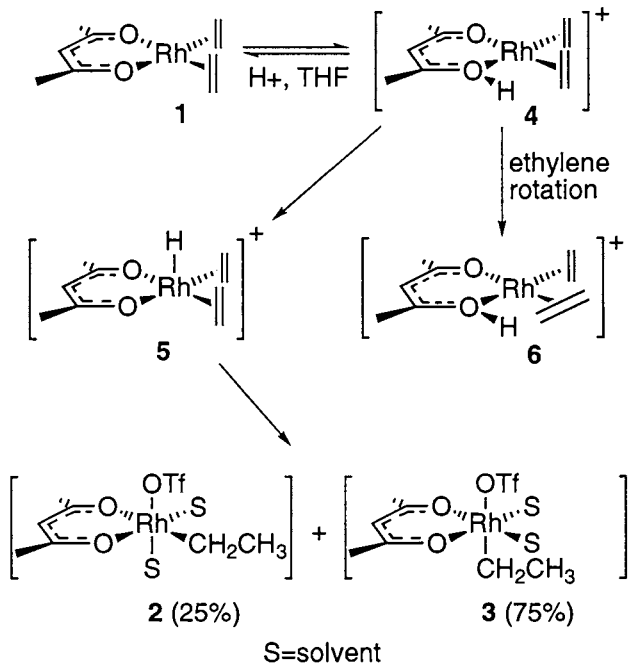
3. Discussion

3.1. Mechanism of the protonation reaction

Two possible mechanisms for the protonation and formation of Rh-ethyl groups are outlined in Scheme 3. The protonation reaction can initially take several



Scheme 2.



Scheme 3.

paths: either protonation of rhodium to give a hydride, or protonation of a free electron-pair on oxygen in the acetylacetonate. Often, protonation at the metal is the thermodynamic product, favoured by the high energy of the HOMO metal orbital, whereas free-electron-pair protonation may be kinetically controlled [2,16,17]. A third possibility is direct protonation of the alkene from the 'solvent side', a mechanism that has been suggested in a few cases [18–20].

No hydrides were observed, even at low temperatures, and no species corresponding to a protonated carbonyl could be detected. However, the dissociation of acetylacetonate, that takes place only in acid solution, most likely goes via a protonated oxygen [21], **4**, followed by displacement with THF. On the other hand, alkene insertions into metal-hydride, **5**, bonds are also well known; thus, the formation of rhodium-ethyl compounds could indicate the hydride path.

The reduced rate of Rh-ethyl group formation with the more bulky substituents on the diketonate supports initial protonation of an oxygen. The two pathways might be combined by considering protonation of oxygen, **4**, followed by transfer to rhodium, **5**, as observed for the reaction between CF_3SO_3H and $[(\mu\text{-}H)Ru_3(CO)_{11}]^-$ [22]. Another, less orthodox explanation, would be a direct proton transfer from oxygen to alkene. Examples of a related reaction exists, the transfer of a proton from a coordinated thiol to a hydride hydrogen to give a non-classical hydrogen complex of the type M(thiolate)(η^2-H_2) [23].

The main conformations **4** and **6** (coordinated alkenes rotate rapidly [24]) are the same in all complexes but less rigid alkenes react faster, and COD, which is locked in a single conformation does not react at all. This could be due to the rigidity of the COD in general, but COD is known to form metal-alkyl bonds both via a hydride route [25], and also via direct protonation [18,19,26]. The apparent inertness of cyclooctadiene may be explained by its energetically very favourable chelating coordination. It is likely that this ligand exchanges protons but that the equilibrium lies totally on the diene side. This is the case for $Fe(CO)_3$(diene) complexes where cyclooctadiene appears to be unreactive towards protonation but where exchange of *endo*-CH_2 protons was observed with deuterated acids [27].

For alkenes without structural constraints on rotation around the metal-alkene bond the meta-stable conformation [28] with the alkene parallel to the coordination plane, 6, will arrange the proton and the carbon in proximate positions possibly facilitating bond making, with or without additional help from Rh *d*-orbitals.

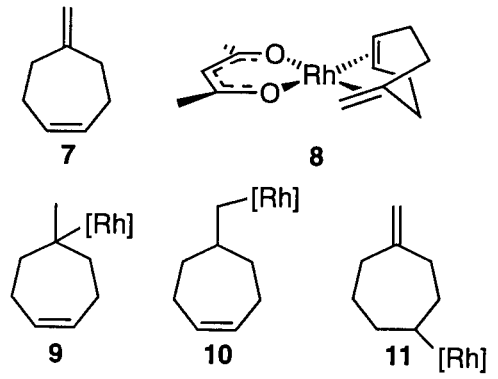
In order to test this hypothesis the Rh(acac)(5-methylene-cycloheptene(**7**)) complex **8** was prepared. This diene has an angle of 90° between the two double bonds, and will therefore have one alkene group perpendicular to the Rh-acetylacetonate plane, and one parallel to the plane, pointing towards an acetylacetonate oxygen [29]. Only a few alkene complexes of this type have been prepared before [30,31]. The square-planar coordination with the exocyclic one double bond 'in plane' has been confirmed by X-ray diffraction for $PtCl_2$(5-methylene-cycloheptene) [32]. A similar structure is consistent with our NMR-data, notably the observation of a smaller value of the J_{Rh-C} for the 'in plane' carbons mirrors the reduction in J_{Pt-C} found for $PtCl_2$(5-methylene-cycloheptene) and $PtCl_2$(5-methylene-cyclooctene) [32].

Clearly, protonation at the methylene carbon, **9** (or **10** after rearrangement) would give support for the oxygen-protonation-rotation-transfer mechanism whereas protonation at the endocyclic double bond, **11**, would indicate a hydride intermediate. A direct protonation would give a mixture of the three species.

The reaction goes cleanly to the isomer **11**, thus indicating the hydride path (Scheme 4).

3.2. Why are only dimers formed?

The insertion of an ethylene into the Rh–ethyl bond is relatively facile, since we observe the production of butenes, but further insertion does not take place. Often, this kind of behaviour has been explained in terms of β-elimination and subsequent dissociation of the alkene. In the present case, however, it is clear that although β-elimination does occur, the alkyl species is the most stable. Since the energetics of bond breaking and bond making of the migratory insertion in



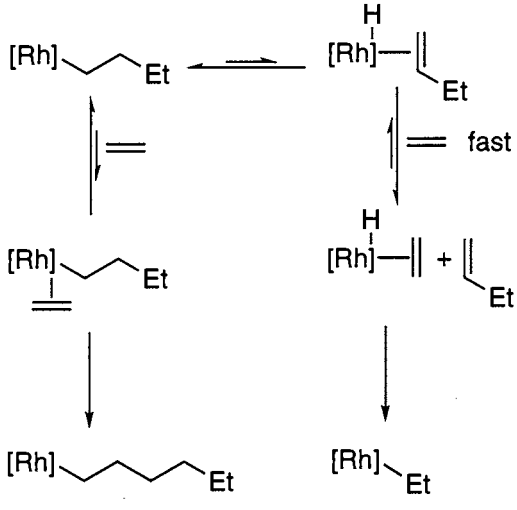
Scheme 4.

Rh(III)(ethylene)(ethyl) and Rh(III)(ethylene)(butyl) can be considered almost identical [33], the key is in a preceding step.

For the oligomerization to propagate, the butyl complex needs to coordinate another ethylene. This implies a displacement of the labile ligand (possibly triflate) by ethylene. However, when a ligand leaves, an empty coordination site is created which can also be used for the β-hydride elimination. This Rh(III)H(alkene) is not observed, but if it can react further the Rh-alkyl complex may be destroyed. One very likely process is alkene exchange, and Cramer concluded already in 1966 that alkene exchange is faster than isomerization [34]. This means that ethylene may have sufficient time to displace the butene from the Rh(hydride)(butene) complex and thus terminate the oligomerization (Scheme 5) [35,36].

Indeed, this is exactly what we observe. When ethylene is added to the *n*-butyl-Rh species, Rh-ethyl complexes **2**, and **3**, are formed quantitatively.

This mechanism (Scheme 5) has both similarities and dissimilarities with the model recently proposed by



Scheme 5.

Brookhart for the polymerization of ethylene by Ni(II) and Pd(II) catalysts [37]. The key point remains the same: in order to form higher oligomers and polymers the subsequent alkene exchange has to be prevented rather than the β-hydride elimination. The difference is that in [37] the alkene exchange is associative since the Pd(II)L_2H(alkene) complex is a d_8-species [38]. Brookhart et al. prevented axial access by introducing bulky diimine ligands, thus reducing the rate of associative exchange. No such possibility exists if the exchange of the Rh(III) catalyst is dissociative.

4. Experimental section

4.1. Reagents and solvents

All reagents were purchased from commercial sources and used without further purification. The deuterated solvents were dried over molecular sieves. Diethyl ether was distilled over sodium before use. 5-Methylene-cycloheptene, bis(η^2-ethylene)(2,4-pentanedionato)rhodium, bis(η^2-*cis*-2-butene)(2,4-pentanedionato)rhodium, bis(η^2-cyclooctene)(2,4-pentane-dionato)rhodium, bis(η^2-ethylene)(1,7-dimethylheptane-3,5-dionato)rhodium and bis(η^2-ethylene) (1,3-diphenyl-1,3-propanedionato)rhodium were prepared by literature methods [39–43].

4.2. Preparation of (η^4-cyclooctadiene)(2,4-pentanedionato)rhodium

This well known complex [44] was prepared in situ by adding one equivalent of cyclooctadiene to a THF-d_8 solution of bis(η^2-ethylene)(2,4-pentanedionato)-rhodium. Bubbling with argon removed displaced ethylene and ^{1}H-NMR showed quantitative conversion. No signal due to coordinated or free ethylene was detected.

4.3. Preparation of (η^4-1,4-pentadiene)(2,4-pentanedionato)rhodium

Bis(η^2-ethylene)(2,4-pentanedionato)rhodium (0.0409 g, 0.16 mmol) was dissolved in 0.8 ml of dry ether. 16 ml (0.16 mmol) of 1,4-pentadiene was added. Bubbles indicated that ethylene was displaced. The solution was stirred for some minutes, ether was evaporated to give (η^4-1,4-pentadiene)(2,4-pentanedionato)rhodium as a yellow solid, pure according to NMR, quantitative yield. ^{1}H-NMR (THF-d_8, 25 C) δ 1.86 (s, 6H), 1.97 (broad, 1H), 2.38 (broad d J_{H-H} 5.3 Hz, 2H), 2.47 (broad d J_{H-H} 11.1 Hz, 2H), 3.22 (broad, 1H), 3.91 (broad, 2H), 5.30 (s, 1H); ^{13}C-NMR (THF-d_8, 25°C) δ 27.00 (s), 32.48 (s), 47.87 (d J_{Rh-C} 8.4 Hz), 58.63 (d

J_{Rh-C} 14.5 Hz) 99.36 (d J_{Rh-C} 2.0 Hz), 186.82 (s) Anal. Calcd. for $C_{10}H_{15}O_2Rh$: C, 44.4; H, 5.65. Found: C, 43.92; H, 5.30.

4.4. Preparation of (η^4-5-methylene-cycloheptene)(2,4-pentanedionato)rhodium, **8**

Bis(η^2-ethylene)(2,4-pentanedionato)rhodium (0.030 g, 0.12 mmol) was dissolved in 2 ml of dry ether. The solution was cooled down to 0°C and 5-methylene-cycloheptene (0.018 g, 0.17 mmol) was added to the yellow solution. Argon was bubbled for 2 h through the solution at 0°C, an addition of 2 ml dry ether was made and the procedure repeated. The solvent was removed by vacuum after a total of 4 h of argon bubbling. Orange crystals were collected in quantitative yield. ^{1}H-NMR (THF-d_8, −40°C) δ 1.75 (s, 3H), 1.93 (app q, 2H), 1.99 (s, 3H), 2.13 (m, 2H), 2.53(m, 2H), 2.62(m, 2H), 3.33 (no coupling to Rh resolved, but this peak correlates to the 76.81 ppm carbon signal that has a 7.4 Hz Rh–C coupling, 2H), 4.20 (m, 2H), 5.39(s, 1H); ^{13}C-NMR δ 26.54 (s), 26.84 (s), 31.30 (s), 39.20 (s), 74.24 (d, J_{Rh-C} 15.0 Hz), 76.81 (d, J_{Rh-C} 7.4 Hz), 99.25 (s), 132.22 (coupling not resolved), 185.25 (s), 185.81 (s) Anal. Calcd. for $C_{13}H_{19}O_2Rh$: C, 50.34; H, 6.17. Found: C, 49.12, 48.55; H, 5.45, 5.88. The compound is sensitive and decomposes slowly at −20°C but can be manipulated for short times at room temperature.

4.5. Protonation experiments

Typically, a 0.05–0.1 M solution of the complex in dry THF-d_8 was prepared. This was transferred (and filtered if necessary) to a 5 mm NMR tube, flushed with argon and the tube sealed with a rubber septum. The solution was cooled to −78°C (CO_2/ethanol), 1–2 equivalents of CF_3SO_3H were added using a syringe. The sample was stirred with a vortex stirrer and inserted into the NMR magnet.

4.6. Rh–ethyl species

For the two complexes labeled as **2** and **3** (isomer ratio 1:3) from the protonation of Rh(acac)(ethylene)$_2$ we have made the following NMR assignments: **2** ^{1}H-NMR (THF-d_8, 25°C) δ 0.63 (t, J_{H-H} 7.5 Hz, 3H) 1.93 (s, 3H), 1.94 (s, 3H), 4.13 (d of m, J_{H-H} 7.5, 7.0 Hz, J_{Rh-H} 2.0 Hz, 1H), 4.23 (d of m, J_{H-H} 7.5, 7.0 Hz, J_{Rh-H} 2.0 Hz, 1H), 5.51 (s, 1H); ^{13}C-NMR (THF-d_8, 15°C) d 17.05 (s), 18.15 (d, J_{Rh-C} 23.6 Hz), 25.09 (s), (another peak probably close by but overlapping with a THF signal), 100.88 (d, J_{Rh-C} 1.1 Hz), 186.00 (s), 187.84 (s). **3** ^{1}H-NMR (THF-d_8, 25°C) δ 0.57 (t, J_{H-H} 7.4 Hz, 3H), 1.96 (s, 6H), 3.92 (d of q, J_{H-H} 7.4 Hz J_{Rh-H} 3.0 Hz, 2H), 5.53 (s, 1H); ^{13}C-NMR (THF-d_8, 15°C) δ 16.58 (s), 18.28 (d, J_{Rh-C} 25.2 Hz), 25.32 (s), 101.39 (d, J_{Rh-C} 1.0 Hz), 187.54 (s). For the two products (**a** and **b**, isomer ratio 4:3) from the protonation of Rh(hmacac)(ethylene)$_2$ we have made the following NMR assignments: **a** ^{1}H-NMR (THF-d_8, 0°C) d 0.56 (t, J_{H-H} 7.5 Hz, 3H) 1.1 (s, overlap with original complex), 3.81 (d of q, J_{H-H} 7.5 Hz, J_{Rh-H} 3.0 Hz, 2H), 5.85 (s, 1H); **b** δ 0.65 (t, J_{H-H} 7.5 Hz, 3H) 1.1 (s, overlap with starting material), 4.01 (m, 2H), 5.84 (s, 1H). For the two products (**c** and **d**, isomer ratio 2:3) from the protonation of Rh(phacac)(ethylene)$_2$ we have made the following NMR assignments: **c** ^{1}H-NMR (THF-d_8, 0°C) δ 0.67 (t, J_{H-H} 7.5 Hz, 3H) 4.15 (d of q, J_{H-H} 7.5 Hz, J_{Rh-H} 2.8 Hz, 2H), 6.97 (s, 1H), 7.4–7.7 (m, overlap with starting material), 7.9–8.3 (m, overlap with starting material) d ^{1}H-NMR (THF-d_8, 0°C) δ 0.74 (t, J_{H-H} 7.5 Hz, 3H) 4.33 (m J_{Rh-H} 2.6 Hz, 1H), 4.41 (m J_{Rh-H} 2.6 Hz, 1H), 7.00 (s, 1H), 7.4–7.7 (m, overlap with starting material), 7.9–8.3 (m, overlap with starting material)

4.7. Rh-n-butyl species

For the major isomer from the protonation reaction of Rh(acac)(*cis*-butene)$_2$ we have made the following NMR assignments: ^{1}H-NMR (THF-d_8, −10°C) δ 0.98 (t, 7.4 Hz, 3H), 1.24 (m, 2H), 1.59 (m, 2H), 1.99 (s, 6H), 3.80 (m, 2H), 5.56 (s, 1H); ^{13}C-NMR (THF-d_8, −10°C) δ 14.65 (s), 18.21 (s), 23.93 (d, J_{Rh-C} 25.0 Hz), 34.16 (s), 101.52 (coupling not resolved), 187.63 (s).

4.8. Rh-(4-methylene-cycloheptyl) complex

For the product from the protonation reaction of Rh(acac)(5-methylene-cycloheptene) we have made the following NMR assignments for **11**: ^{1}H-NMR (THF-d_8, −40°C) d 0.49 (dt, J_{H-H} 15.8, 5.1 Hz, 1H) 1.34 (ddd, J_{H-H} 13.5, 9.5, 4.4 Hz, 1H) 1.60 (m, 1H) 1.75 (m, 1H) 1.77 (m, 1H) 1.84 (s, 3H) 1.85 (m, 1H) 1.90 (m, 1H) 2.11 (m, 1H) 2.14 (s, 3H) 2.27 (m, 1H) 2.31 (m, 1H) 4.48 (d, J_{H-H} 2.4 Hz, 1H) 4.60 (m, 1H) 5.40 (d, J_{H-H} 2.4 Hz, 1H) 5.54 (s, 1H).

4.9. Qualitative kinetic experiment

Equimolar amounts of bis(η^2-ethylene)(2,4-pentanedionato)rhodium, bis(η^2-ethylene)(1,7-dimethylheptane-3,5-dionato)rhodium and bis(η^2-ethylene)(bensoylacetophenone)rhodium, respectively, were dissolved in THF-d_8 in three 5 mm NMR tubes to give a concentration of 0.095 M. The samples were cooled to −78°C. After addition of equimolar amounts of CF_3SO_3H the NMR tubes were kept at 0°C, either in a Dewar flask or in the thermostated NMR probe.

A series of ^{1}H-NMR spectra was recorded during 3 h and the integrals of the arising methyl groups were compared with the solvent integrals.

4.10. NMR spectroscopy

NMR spectra were measured on a Bruker AM-400 (AMX-500 or DMX-500 were also used) spectrometer operating at 400.13 (500.13), 100.6 (125.9) and 12.7 (15.9) MHz for ^{1}H, ^{13}C and ^{103}Rh, respectively. ^{13}C-NMR spectra were recorded with full 1H decoupling employing the Waltz-16 sequence. The chemical shifts are reported in ppm with the solvent as internal standard. For ^{103}Rh NMR spectra the shifts are referenced to X(^{103}Rh) = 3.16 Mhz [45]. The H–Rh HMQC correlations [46–48], the homonuclear COSY, NOESY (with a mixing time of 0.8 s) and TOCSY (MLEV-17 mixing of 60 ms) two-dimensional NMR experiments were acquired and processed according to literature [49–51].

4.11. Electrospray mass spectrometry

A high resolution mass spectrometer (Zab-Spec, VG, Fisons, UK) with an electrospray interface using a hexapole placed before the acceleration path of the ions was used. The hexapole was scanned synchronously with the magnet which increases the transmittance of ions considerably. The electric potentials in the ES-interface, when run in the positive mode, were: spray needle + 8000 V, counter electrode + 5000 V, sampling cone + 4200 V, ring electrode + 4100 V, hexapole and acceleration voltages + 4000 V. The solvent was THF and the flow rate 50 ml min^{-1}.

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