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Synthesis of cyclopentadienyltricarbonylrhenium(I) carboxylic acid from perrhenate☆

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Abstract

The cyclopentadienyltricarbonylrhenium(I) carboxylic acid **1**, $(\eta^5\text{-}C_5H_4COOH)Re(CO)_3$, can be quickly prepared from ammonium perrhenate NH_4ReO_4. The synthetic pathway involves the use of mild conditions to reduce perrhenate to $Re_2(CO)_{10}$ followed by a thermal reaction of $Re_2(CO)_{10}$ with cyclopentadiene carboxylic acid in mesitylene. The yield from perrhenate is 35%. From pure $Re_2(CO)_{10}$, **1** can be obtained with a very good yield of 95%. This new and rapid synthetic pathway may be suitable for the preparation of radiopharmaceuticals.

Keywords: Cyclopentadienyltricarbonylrhenium(I) carboxylic acid; Fast synthesis; Potential radiopharmaceuticals

1. Introduction

Two radioactive isotopes of rhenium, rhenium-186 and rhenium-188, are considered as interesting nucleotides for radiopharmaceutical uses. The main interest lies in the fact that they emit γ and β radiations with suitable energy for their use in diagnosis and therapy (^{186}Re: $T_{1/2} = 3.71$ days, $E_{\beta(avg)} = 0.36$ MeV, $E_\gamma = 137$ keV; ^{188}Re: $T_{1/2} = 16.8$ h, $E_{\beta(avg)} = 0.77$ MeV, $E_\gamma = 155$ keV) [1]. Up to now, rhenium compounds studied with this aim were mainly chelates, as these are easily obtained from perrhenate, the sole oxidation state(VII) for which a radioactive precursor is commercially available [2]. However, such chelates are usually large, lipophilic structures, and moreover, their stability is sometimes rather low. For these reasons, it would be advantageous to use organometallic compounds such as $CpRe(CO)_3$, whose size is smaller and whose stability is excellent. In order to explore these new possibilities, we have used the cyclopentadienyltricarbonylrhenium $(\eta^5\text{-}C_5H_4)Re(CO)_3$ moiety to mark steroids such as oestradiol [3], proteins and antibodies [4]. For use of the organometallic complexes in radioactive form, two features are important: the amount of product used will be extremely small, and the duration of synthesis must be shorter than the half-life of radioactive isotope.

The labelling of aminoacids and proteins by cold rhenium has been demonstrated by using $(\eta^5\text{-}C_5H_4COOH)Re(CO)_3$, **1**, and $(\eta^5\text{-}C_5H_4COCH_2\text{-}CH_2COOH)Re(CO)_3$, **2** [4]. The classical method to obtain acid **1** is to add solid CO_2 to $(\eta^5\text{-}C_5H_4Li)Re(CO)_3$ [5]. Since radioactive rhenium is only commercially available as perrhenate ReO_4^-, we need to find a suitable method to prepare acid **1** from perrhenate. We had recently shown that it is possible to prepare $Re_2(CO)_{10}$ from perrhenate rapidly using mild conditions (1 atm of CO and 1 h of reaction) [6]. We describe now a facile and rapid method for the preparation of acid **1** from $Re_2(CO)_{10}$ and also directly from perrhenate through the intermediacy of $Re_2(CO)_{10}$.

☆ Dedicated to Professor Alberto Ceccon on the occasion of his 65th birthday.

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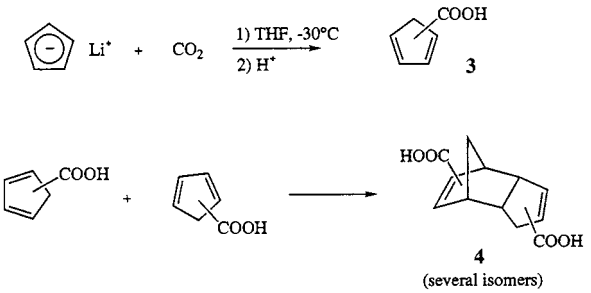


Scheme 1.

2. Results and discussion

2.1. Synthesis

Acid C_5H_5COOH **3** has been prepared by adding crushed solid CO_2 into a solution of cyclopentadienyllithium in THF cooled to $-30°C$ (Scheme 1). After work-up, evaporation of solvent under vacuum without heating over 40°C, acid **3** was obtained as a monomer in 50% yield. This monomeric acid dimerizes slowly into different forms of dimers **4** after several days. Two dimers, **4a** and **4b**, were isolated by chromatography and analysed (Section 4).

Cyclopentadienyltricarbonylrhenium(I) carboxylic acid **1** was prepared from $Re_2(CO)_{10}$ or $Re(CO)_5Br$ and from NH_4ReO_4.

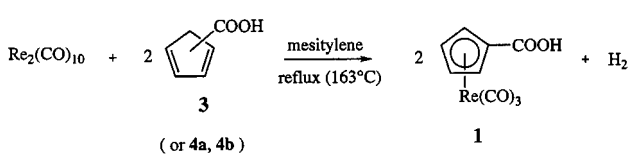
2.1.1. From $Re_2(CO)_{10}$ and $Re(CO)_5Br$

Freshly prepared acid **3** was refluxed with $Re_2(CO)_{10}$ in mesitylene for 1 h (Scheme 2). A 95% yield of acid **1** was obtained after work-up. Under the same reaction conditions, dimer **4a**, or the mixture of the dimers **4a** and **4b**, led to acid **1** with similar yields.

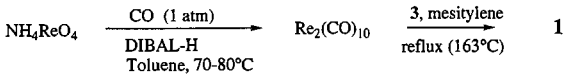
Acid **1** can also be prepared from $Re(CO)_5Br$ in 72% yield, by refluxing with acid **3** in mesitylene for 2 h.

2.1.2. From NH_4ReO_4

Ammonium perrhenate is first reduced to $Re_2(CO)_{10}$ in 60% yield by DIBAL-H at 70–80°C under an 1 atm of CO for 90 min (Scheme 3). The $Re_2(CO)_{10}$ produced in this first step is roughly purified by filtration through silica gel. Acid **3** is then added with mesitylene, and the reaction is carried out as described previously. After purification, acid **1** is obtained in 35% yield based on perrhenate.



Scheme 2.



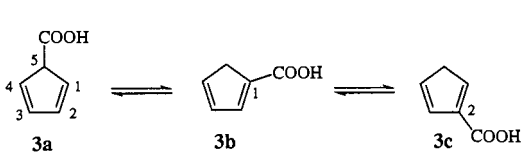
Scheme 3.

2.2. Discussion

Acid **3**, known for a long time, has been prepared by carbonylation of cyclopentadienyl anions [7] but this acid had only been isolated as its dimeric form, as the monomer dimerizes very easily. Under our conditions described above, it is now possible to isolate acid **3** in its monomeric form. Cyclopentadienyllithium is very convenient for the reaction, and gives acid **3** as a white powder with good purity. Cyclopentadienylsodium on the other hand gives only a coloured and less pure product because commercial CpNa solution contains a red impurity. After work-up, evaporation of solvent must be done without heating over 40°C in order to avoid dimerization. The monomer can be kept for a couple of days at $-18°C$ before slowly dimerizing. The monomer potentially has three isomers **3a**, **3b** and **3c** (Scheme 4).

It is known that silyl-substituted cyclopentadienes compounds exist preferentially as the **a** isomer (5-substituted) [8]. But most mono-substituted cyclopentadienyl compounds exist as the **b** isomer (1-substituted) or the **c** isomer (2-substituted) [9]. In order to identify the isomeric form of the monomer, studies have been taken on its methylester. A single UV band at 274 nm has been found for the methylester of acid **3**, which shows a bathochromic shift compared with cyclopentadiene [10]. It may be concluded that the acid function is in a conjugated position. Studies of the Diels–Alder cycloaddition of this ester with cyclopentadiene [11], and with maleic anhydride [12], have led these authors to propose the **b** isomer for ester of **3**. We have recorded the NMR spectrum of acid **3** (Fig. 1). It shows essentially three vinylic multiplets at 7.57, 6.78 and 6.63 ppm, confirming that acid **3** exists as the **b** isomer.

Some very weak resonances that may be attributed to the dimers grow with time, but some weak resonances at 7.43, 6.48 and 3.22 ppm remain at the same intensity. We suggest that these signals belong to the **c** isomer. The resonance of the third vinylic proton could be the 6.80 ppm multiplet, which is partially hidden by a strong neighbouring signal.



Scheme 4.

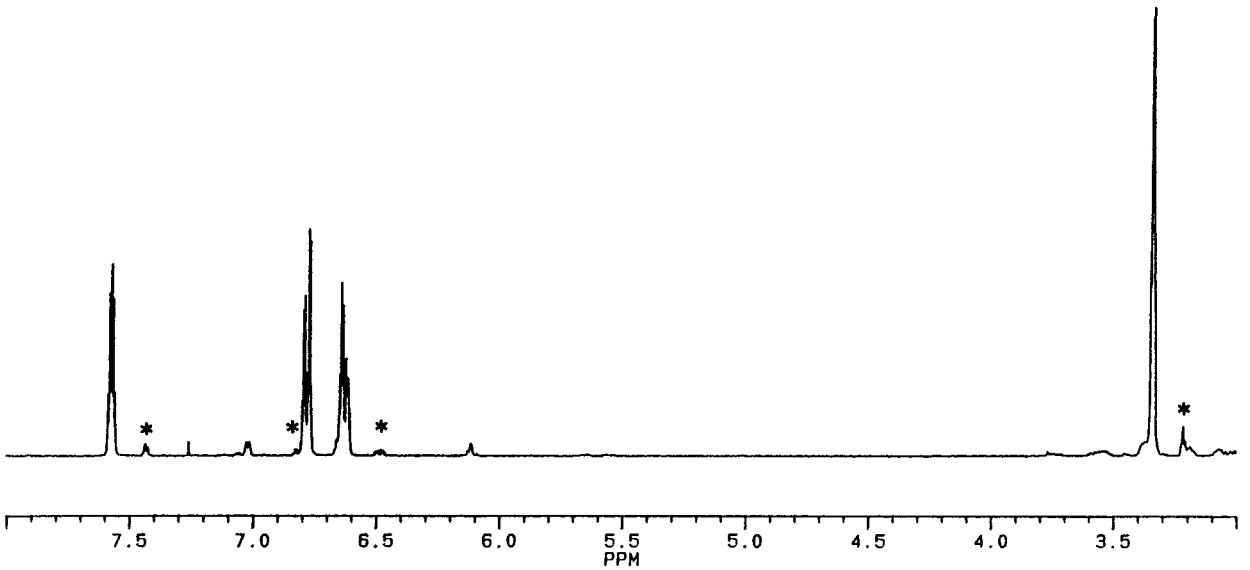
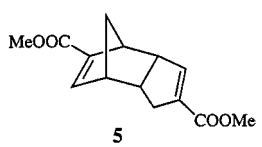


Fig. 1. ^{1}H-NMR spectrum of cyclopentadiene carboxylic acid **3** in $CDCl_3$ (*, probable signals of **3c** isomer).

Acid **3** dimerizes progressively. Many dimers could be formed, but the NMR spectrum shows only two main dimers, **4a** and **4b**, with a ratio of ca. 1:1 (Fig. 2). The dimer **4a** can be isolated in pure form. It is characterized by two vinylic protons at 6.83 and 6.50 ppm, and several signals between 1.40 and 3.55 ppm. Thus, the three other vinylic protons at 6.56, 6.15 and 6.06 ppm belong to the second dimer. The NMR data of dimer **4a** are very similar to that of dimer methylester **5** isolated by Guyon et al. and identified as the isomer shown in Scheme 5 [13].

Dimer **4a** is then identified as the **A** isomer (Scheme 6). The formation of this dimer can only be explained by Diels–Alder cycloaddition between the **b** isomer and the **c** isomer and not between two **b** isomer monomers. It is known that in the Diels–Alder reaction, the electron-withdrawing group activates the dienophile but deactivates the diene. Thus, reaction takes place between the **3c** isomer, which behaves as a diene, and the **3b** isomer, which is a good dienophile.

The presence of the second dimer **4b** can be explained by the possibility of formation of the **B** isomer. The **B** isomer has three vinylic protons and differs from the **A** isomer by the position of the second acid function. As shown in Fig. 2, **4b** has three resonances due to vinylic protons. Thus, we suggest that the second dimer has the **B** structure.



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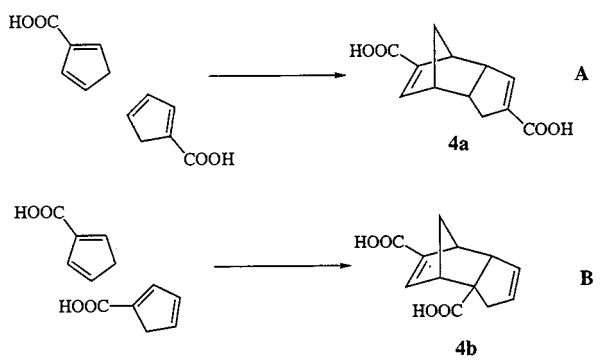
Scheme 5.



3c + 3b Cycloaddition

Scheme 6.

Refluxing the mixture of acids **3** and $Re_2(CO)_{10}$ in mesitylene quickly yields the acid (η^5-$C_5H_4COOH)Re(CO)_3$ **1** with an excellent yield of 95%. This reaction requires a very high temperature, at least at the boiling point of mesitylene (162–164°C). This high temperature is probably needed to break the Re–Re bond of $Re_2(CO)_{10}$ [14]. The reaction may start by the addition of double bond of **3**, acting as a π-donor L ligand, on either the radical $Re(CO)_5$, or on the intermediate $Re_2(CO)_9$ followed by the cleavage of the Re–Re bond. It is of note that $Re(CO)_5Br$ reacts with acid **3** only at high temperature.

It is worth noting that it is not necessary to keep acid **3** as a monomer, since the reaction with dimer **4a** also gives acid **1** in a very good yield (over 90%).

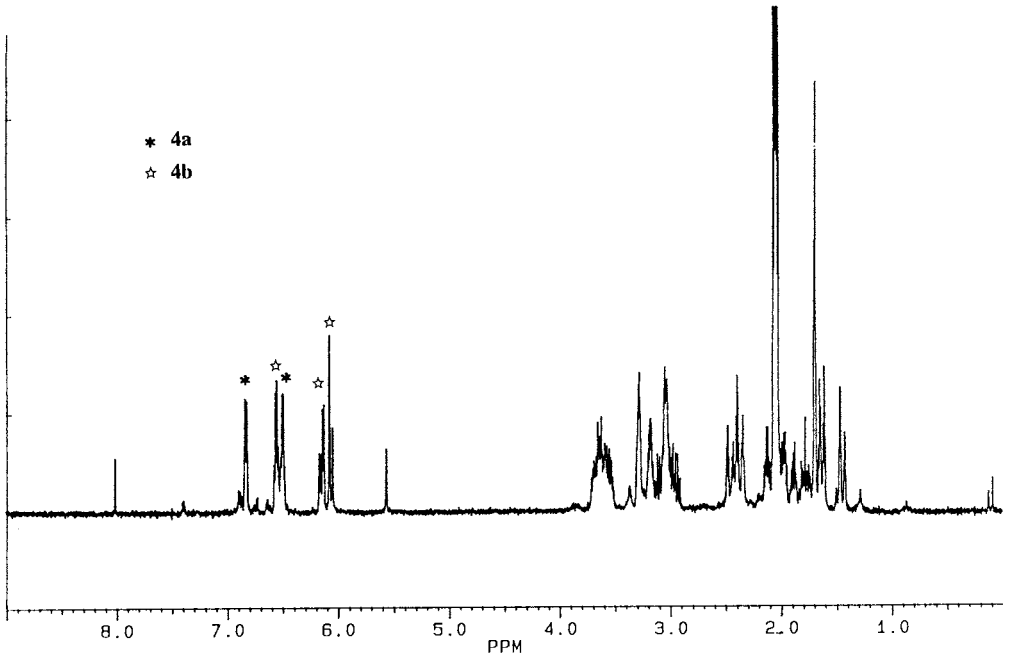


Fig. 2. ^{1}H-NMR spectrum of cyclopentadiene carboxylic acid **3** in CD_3COCD_3 6 months after preparation. The spectrum shows mainly the signals of dimers **4a** and **4b**.

In this case the high temperature is required both to crack the dimer and to cleave the Re–Re bond.

It is also possible to prepare acid **1** directly from perrhenate. Conversion perrhenate to $Re_2(CO)_{10}$ using our smooth and rapid method may be possible with radioactive perrhenate. Using the perrhenate, a purification of the intermediate $Re_2(CO)_{10}$ by filtration is required before reaction with acid **3**. However, this simple purification is easy within the scope of most laboratories dealing with radioactive products.

3. Conclusion

It has been shown that acid **1** is an excellent labelling compound for aminoacids and proteins [3,4]. The new synthetic pathway described in this paper is simple, and should be extended to use with radioactive rhenium. Future research will be focused on radioactive rhenium, and should provide new possibilities for the use of organometallic compounds of rhenium in therapy. The labelling of biological compounds with this acid potentially represents a very substantial application.

4. Experimental

The synthesis of all the compounds was performed under an argon atmosphere, using the Schlenk line technique and Schlenk flasks. Anhydrous THF and anhydrous diethyl ether were obtained by distillation from sodium/benzophenone. Mesitylene (Aldrich) was used without any further purification. NH_4ReO_4 was a gift of Dr E. Roman. $Re_2(CO)_{10}$ was purchased from Strem, $Re(CO)_5Br$ was prepared according to a literature procedure [15]. TLC chromatography was performed on silica gel 60 GF254. IR spectra were obtained on a IRFT BOMEM Michelson-100 spectrometer equipped with a DTGS detector. ^{1}H- and ^{13}C-NMR spectra were recorded on 200 MHz and 250 MHz Bruker spectrometers, respectively. Mass spectrometry was performed with a Nermag R 10-10C spectrometer. Melting points were measured with a Kofler device. Elemental analysis were performed by the regional microanalysis service of Université Pierre et Marie Curie.

*4.1. Cyclopentadiene carboxylic acid **3** C_5H_5COOH and its dimers*

To a Schlenk flask purged with argon, 1.98 g (30 mmol) of cyclopentadiene and 60 ml of anhydrous diethyl ether were added. The solution was cooled to -20°C, and 18.75 ml (30 mmol) of a 1.6 M solution of *n*-BuLi in hexane were added dropwise. Cyclopentadienyllithium (C_5H_5Li) precipitates from the solution as a white solid. The addition was carried out over 20 min, and the stirring maintained for a further 20 min. A further 20 ml of diethyl ether were added and the stirring was stopped. The precipitate was allowed to settle for 1 h, the solvent was then removed with a syringe, and the precipitate was dried under vacuum.

The Schlenk flask containing the cyclopentadienyllithium is cooled to −50°C. Anhydrous THF (30 ml) was added to dissolve completely the cyclopentadienyllithium. The temperature was allowed to rise to −30°C, and 20 g of crushed CO_2 were then added in one portion. The solution turned milky white. The cold bath was removed, and the stirring maintained for an additional 30 min. A 10% HCl solution (50 ml) and 100 ml of diethyl ether were added. The mixture was transferred to a separating funnel. The organic phase was washed once with water and then dried over $MgSO_4$. The solvent was carefully evaporated under reduced pressure without heating the flask over 40°C. The white solid obtained was washed twice with pentane, and then dried under vacuum to give 1.65 g of acid **3** as a white powder (50% yield). ^{1}H-NMR (ppm, $CDCl_3$, 250 MHz). Major monomer: 7.57 (m, 1H, H2); 6.78 (m, 1H, H4); 6.63 (m, 1H, H3); 3.34 (m, 2H, H1); 11.75 (s, 1H, COOH). Minor monomer: 7.43 (m, 1H, H2), 6.80 and 6.48 (m, m, 1H, 1H, H3 and H4); 3.22 (m, 2H, H1). ^{13}C-NMR (ppm, $CDCl_3$, 62.89 MHz). Major monomer: 169.70 (CO); 145.26, 141.37 and 132.63 (C2, C3, and C4); 137.01 (C1); 41.41 (C5). This acid polymerizes slowly.

4.1.1. Isolation of the dimer **4a**

The monomeric acid (1 g), freshly prepared, was dissolved in 15 ml of chloroform. The solution was left at room temperature for 2 days. Filtration provides 150 mg of a beige solid. The NMR spectrum shows only one dimer. Crystallization from acetone/heptane yields white crystals, melting point 246°C. ^{1}H-NMR (ppm, CD_3COCD_3, 200 MHz): 6.83 (d, 1H, H8); 6.50 (dd, 1H, H2); 3.55 (m, 1H, H6); 3.28 (m, 1H, H1); 3.19 (m, 1H, H7); 2.99 (m, 1H, H2); 2.41 (tdd, 1H, H5); 2.10 (m, 1H, H5); 1.63 (td, 1H, H10); 1.45 (md, 1H, H10). All the signals are attributed by comparing the data to those of ester **5** [13]. However, by use of the COSY spectrum of **4a**, we prefer to reverse assignment of the signals H1 and H7, and also H2 and H6. Mass spectrum (EI) m/z: 220 $(M)^+$, 202 $(M-H_2O)^+$.

4.2. (η^5-C_5H_4COOH)$Re(CO)_3$ acid **1**

4.2.1. From $Re_2(CO)_{10}$

C_5H_5COOH (0.132 g, 1.2 mmol) and 0.196 g of $Re_2(CO)_{10}$ (0.3 mmol) were placed in a small flask containing a magnetic stirrer and equipped with a condenser. The flask was purged with argon, and 1 ml of mesitylene was added. The solution was refluxed for 1 h using an oil bath. After cooling to room temperature, the acid was extracted twice with 15 ml of a saturated solution of Na_2CO_3. The aqueous phase was washed with 15 ml of diethyl ether and then acidified with a 20% HCl solution to pH 1. A white precipitate of acid **1** appears. The acid was extracted twice with 25 ml of diethyl ether. The ether phase was washed with water and dried over $MgSO_4$. After removal of solvent, 0.217 g of acid **1** was obtained as a white solid (95% yield). The NMR spectrum shows that the acid **1** is nearly pure without trace of C_5H_5COOH. Crystallization from CH_2Cl_2/pentane produces colourless crystals, m.p.: 210°C. ^{1}H-NMR (ppm, CD_3COCD_3): 6.22 (t, 2H, $J=2.3$ Hz); 5.71 (t, 2H, $J=2.3$ Hz); 11.38 (s, 1H). IR (cm^{-1}, CH_2Cl_2) ν_{CO}: 2032 m, 1938 s, 1741 w, 1721 w, 1697 w. Mass spectrum (EI) m/z for Re = 187: 378 $(M)^+$, 352 $(M-CO)^+$, 296 $(M-3CO)^+$.

4.2.2. From $Re(CO)_5Br$

The procedure is similar to the one used with $Re_2(CO)_{10}$ and described above. A mixture of 0.100 g of C_5H_5COOH (0.9 mmol) and 0.122 g of $Re(CO)_5Br$ (0.3 mmol) in 0.5 ml of mesitylene was heated at 120°C for 3 h. No acid **1** is detected by TLC. The mixture was then refluxed for 2 h. The acid **1** formed was purified by TLC on silica gel. The first elution was done with pure pentane to remove the mesitylene, and then the pentane was replaced by diethyl ether. The acid was extracted from the silica gel with acetone; 0.082 g of acid **1** is isolated, 72% yield.

4.2.3. From ammonium perrhenate

4.2.3.1. Synthesis of $Re_2(CO)_{10}$ [6]. 0.268 g of ammonium perrhenate (1 mmol) was introduced in a 200 ml 2-neck Schlenk flask equipped with a magnetic stirrer, a dropping funnel and a glass tube bearing a frit at one end. The other end of the glass tube was connected to a gas circulating pump and a gas reservoir with gauge. Another tube connects the gas reservoir to the Schlenk flask. This system allows a circulation of gas into the flask. The system is purged with carbon monoxide. Anhydrous toluene was introduced into the flask (12 ml), and into the dropping funnel (3 ml). The pump was turned on to circulate CO gas into the solution and the flask was heated to between 70 and 80°C. DIBAL-H (1.8 ml, 10 mmol) was introduced into the dropping funnel. The solution of DIBAL was added dropwise to the suspension of perrhenate over 90 min. More toluene (10 ml) was introduced in the flask via the dropping funnel. The initial white suspension turns into a limpid black solution. The solution was stirred for one hour and a half more at 70–80°C under CO circulation. The pump was then turned off, and the solution allowed to cool. Methanol (5 ml) was then added dropwise to destroy excess DIBAL. The solution became viscous with evolution of gas. The gas was evacuated and the solvent was evaporated under vacuum to yield a greyish-white powder. The solid was placed in a glass filter funnel filled with silica gel, and then washed several times with dichloromethane and acetone until the remaining solid (alumina produced from DIBAL-H) was white. The yellowish solution was concentrated using a rotavapor and transferred to a 5 ml flask. The solvent

was completely evaporated under vacuum to give a yellow solid (0.157 g) containing mainly $Re_2(CO)_{10}$ (TLC in pentane: $R_f = 0.6$; IR (cm^{-1}, CH_2Cl_2) ν_{CO}: 2070 m, 2011 s, 1967 m).

*4.2.3.2. Synthesis of acid **1**.* Cyclopentadiene carboxylic acid (0.065 g, 0.57 mmol) was introduced to a flask containing the $Re_2(CO)_{10}$ prepared above, a magnetic stirrer and equipped with a condenser. The flask and the condenser were purged with argon, and 2.5 ml of mesitylene were added to the flask. The mixture was then heated at reflux with an oil bath pre-heated to 190–200°C. The yellow suspension turned into a black solution over 5 min. After 1 h of reflux, the solution was allowed to cool to room temperature and then was poured into a saturated Na_2CO_3 solution (30 ml). The aqueous phase was washed with diethyl ether and then acidified with a 20% HCl solution until pH 1. A white precipitate of acid **1** appeared which was then extracted twice with 25 ml of diethyl ether. The solution was then dried over $MgSO_4$, evaporated with a rotavapor and dried under vacuum to yield acid **1**, 0.132 g (35% yield calculated from perrhenate). (TLC in pentane/THF: 1/2: $R_f = 0.67$). NMR and IR spectra show that the acid is almost pure.

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