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Reaction of Cp*(CO)$_2$Re=Re(CO)$_2$Cp* in THF with diethyl fumarate produces Cp*Re(CO)$_3$ and Cp*Re(CO)(η^2-(*E*)-EtO$_2$CCH=CHCO$_2$Et)(THF)

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Abstract

The rhenium dimer complex Cp*(CO)$_2$Re=Re(CO)$_2$Cp* (**1**) (Cp* = C$_5$Me$_5$) reacted in THF with diethyl fumarate in a fragmentation reaction to form Cp*Re(CO)$_3$ (**3**) and Cp*Re(CO)(η^2-(*E*)-EtO$_2$CCH=CHCO$_2$Et)(THF) (**6**). Reaction of **6** with CO resulted in substitution of the THF ligand with CO to form the alkene complex Cp*Re(CO)$_2$(η^2-(*E*)-EtO$_2$CCH=CHCO$_2$Et) (**7**). Variable temperature ^{1}H-NMR spectroscopy of **7** showed that rotation of the alkene ligand is slow below −50°C. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Rhenium; Metal alkene complex; Metal–metal bond scission

1. Introduction

The complex Cp*(CO)$_2$Re=Re(CO)$_2$Cp* (**1**) (Cp* = C$_5$Me$_5$) is a rare example of a dimer of a d^6, 16-electron fragment [1,2]. Complex **1** is thermally stable but is extremely reactive and provides an entry into many interesting organometallic complexes [3–7]. The complex Cp*(CO)$_2$Re=Re(CO)$_2$Cp* (**1**) forms the bridging dihydride Cp*(CO)$_2$Re(μ-H)$_2$Re(CO)$_2$Cp* upon exposure to H$_2$ at −78°C [1], and adds ligands such as CO, PMe$_3$, CH$_2$=CH$_2$, and CH$_3$CN to form the binuclear adducts Cp*(CO)$_2$Re(μ-CO)Re(CO)(L)Cp* [1,8].

The adducts of **1** with CO and CH$_3$CN were stable to fragmentation, but the adducts with PMe$_3$ and CH$_2$=CH$_2$ fragmented in THF to produce Cp*Re(CO)$_2$(THF) and Cp*Re(CO)$_2$L [1,3]. The regiochemistry of this fragmentation can be understood in terms of the stability of the fragments generated. Fragmentation occurs to produce the least unstable complex having a vacant coordination site (Scheme 1). This is consistent with the greater ease of CO loss from Cp*Re(CO)$_3$ compared with loss of CO from Cp*Re(CO)$_2$PMe$_3$.

In the case of the adduct with 2-butyne, a ligand that can shift from being a 2e donor to a 4e donor, a different fragmentation pattern was observed (Scheme 1) [3]. Cleavage of Cp*(CO)$_2$Re(μ-CO)Re(CO)(η^2-CH$_3$C$\equiv$CCH$_3$)Cp* (**2**) occurred to give Cp*Re(CO)$_3$ (**3**) and the 4-electron donor alkyne complex Cp*Re(CO)(η^2-CH$_3$C$\equiv$CCH$_3$) (**4**) (Scheme 2). In addition, some conversion of **2** to the dimetallacyclopentenone Cp*(CO)$_2$Re(μ-η^1,η^3-CMe=CMeCO)-Re(CO)Cp* (**5**) was observed. Subsequent fragmentation of **5** at room temperature gave additional Cp*Re(CO)$_3$ and Cp*Re(CO)(CH$_3$C$\equiv$CCH$_3$) probably via reversal to the initial adduct **2**.

Here we report that reaction of **1** with diethyl fumarate, a second example of a ligand that can act as either a 2 or 4e donor, also leads to cleavage of **1** to give Cp*Re(CO)$_3$ and Cp*Re(CO)(η^2-(*E*)-EtO$_2$CCH=CHCO$_2$Et)(THF) (**6**).

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2. Results and discussion

2.1. Reaction of dimer 1 with diethyl fumarate to form Cp*Re(CO)(η^2-(E)-$EtO_2CCH{=}CHCO_2Et$)(THF) (6)

Diethyl fumarate reacted with a green solution of **1** in THF to give Cp*Re$(CO)_3$ and Cp*Re(CO)(η^2-(*E*)-$EtO_2CCH{=}CHCO_2Et$)(THF) (**6**). Complex **6** was isolated as an orange solid in 40% yield following recrystallization from THF–hexane. Both mass spectrometry and elemental analysis of **6** indicated that THF was present and X-ray crystallography established that THF was coordinated to rhenium in **6**. The ^{1}H-NMR spectrum of **6** in THF-d_8 requires slow rotation about the Re alkene unit. The vinyl hydrogens of the complexed alkene are inequivalent and appear as doublets ($J = 5.7$ Hz) at δ 4.30 and 3.57. These vinyl resonances appear at much lower frequency than for the corresponding free alkene, consistent with complexation of diethyl fumarate to Re. Two different diastereotopic ethyl groups are also observed for the diethyl fumarate ligand as complex overlapping ABX_3 patterns between δ 4.15 and 3.85 for the methylene hydrogens. Two methyl resonances are seen as triplets at δ 1.14 and 1.11. The resonances for the bound THF ligand could not be seen in THF-d_8 due to interference from solvent but were seen in the ^{1}H-NMR spectrum in toluene-d_8 as two broadened quartets at δ 3.60 and 3.17 for the alpha protons and as two partially obscured multiplets at δ 1.06 and 0.96 for the beta protons. The ^{13}C-NMR spectrum of **6** shows two resonances at δ 178.9 and 178.8 for the ester carbonyls along with a resonance at δ 214.8 for the carbonyl bound to rhenium.

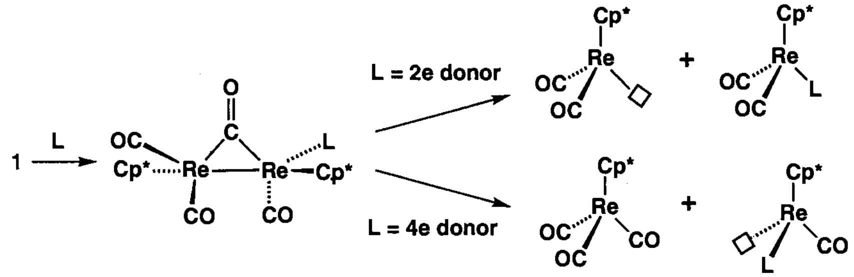
Although there are two possible diastereomers of **6**, only one isomer was observed by 1H-NMR spectroscopy, presumably the same as that seen in the X-ray crystal structure of **6**.

2.2. X-ray crystal structure and bonding of Cp*Re(CO)(η^2-(E)-$EtO_2CCH{=}CHCO_2Et$)(THF) (6)

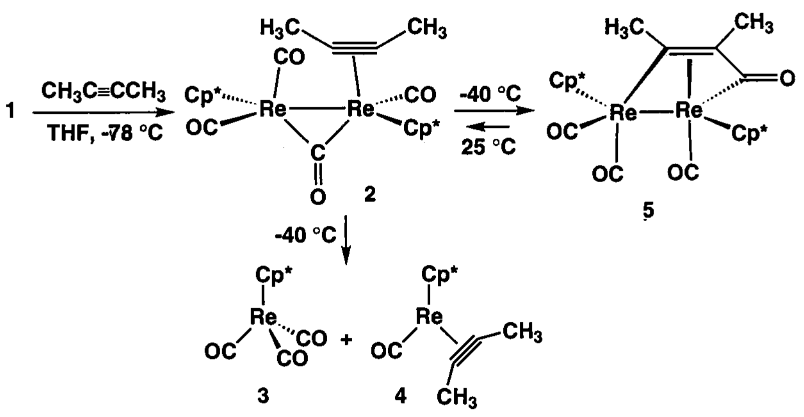
The X-ray crystal structure of **6** confirmed the presence of a THF molecule coordinated to the rhenium (Fig. 1, Tables 1 and 2). The rhenium has a classic three-legged piano stool geometry with a THF, CO and the diethyl fumarate occupying the three legs. The angle between the carbonyl carbon and the THF oxygen is 89.1°. The angle between the centroid of the alkene ligand and the carbonyl is 93.7°. The angle of 107.1° between the THF oxygen and the alkene centroid is slightly larger then the typical angle found in a three-legged piano stool complex and is probably due to steric repulsion between the THF and the diethyl fumarate ligands. The C(2)–C(3) bond length of 1.445 (6) Å is somewhat longer then a normal C=C bond which is typical for coordinated alkenes [9]. The alkene ligand is twisted 27.4° which prevents it from being parallel with the plane of the Cp* ligand [10]. The Re–CO axis is roughly perpendicular to the plane defined by Re and the two alkene carbons (the angle between the planes defined by the carbonyl carbon, Re, and the alkene centroid and the plane of Re and the two alkene carbons is 72.1°).

The observed orientation of the alkene ligand in **6** optimizes backbonding from the metal to the alkene ligand and minimizes steric interactions. The filled d-orbital not involved in π-backbonding to the CO ligand lies in the plane perpendicular to the Re–CO axis and is directed at the π^* orbital of the alkene. In the observed geometry, the alkene ligand and CO do not compete for backbonding with the same d orbital.

There are two possible diastereomers of **6** that differ in which enantioface of the alkene that is coordinated to the metal stereocenter. In the observed diastereomer **6**, an alkene hydrogen is directed towards the sterically large Cp* ring and ester groups occupy a groove parallel to the Cp* ring. For the alternative diastereomer which is not detected, an ester group would either have to be directed towards the sterically large Cp* ring or the alkene would have to twist and compete with CO for backbonding to available d-orbitals. The observation of a single diastereomer of **6** is then understandable in terms of the combination of favorable electronic and steric effects.



Scheme 1.



Scheme 2.

2.3. Kinetics and mechanism of formation of $Cp^*Re(CO)(\eta^2\text{-}(E)\text{-}EtO_2CCH{=}CHCO_2Et)(THF)$ (**6**)

In previous reactions of the dimer **1** with nucleophiles, reactive intermediates from the initial addition of a ligand to the dimer were observable before fragmentation occurred [5,7,8]. In an effort to observe an initial addition product for the diethyl fumarate reaction, the reaction of **1** with excess diethyl fumarate was investigated at low temperature by ^{1}H-NMR spectroscopy. Little reaction was seen below −10°C and then only slow conversion of **1** to **3** and **6** without the observation of detectable intermediates was observed.

The kinetics of the reaction of **1** with excess diethyl fumarate (0.6 M) to form **3** and **6** was monitored by ^{1}H-NMR spectroscopy at −10°C. The disappearance of **1** followed pseudo first order kinetics with an observed rate constant of 3.6×10^{-4} s^{-1} ($t_{1/2} = 32$ min). The reaction of the fumarate with **1** is noticeably slower then the reaction of **1** with other ligands such as CO and alkynes which proceeded very rapidly at −78°C [8]. This slower reaction of diethyl fumarate is attributed to its comparative bulk and low nucleophilicity.

Scheme 3 shows our suggested mechanism for the formation of **6**. Although no intermediate dinuclear addition product was observed, we believe that attack of diethyl fumarate on **1** initially produces the 1:1 adduct **A** similar to intermediates seen in reactions with PMe_3, $CH_2{=}CH_2$, and other nucleophiles [8]. The observation that $Cp^*Re(CO)_3$ is formed in the reaction suggests that diethyl fumarate acts as a 4e donor to promote fragmentation of **A** to give $Cp^*Re(CO)(\eta^4\text{-}(E)\text{-}EtO_2CCH{=}CHCO_2Et)$ (**B**). Conversion of **B** to **6** could occur either by direct displacement of the weakly bound ester oxygen of **B** by THF or by a dissociative mechanism involving coordinatively unsaturated intermediate **C**.

THF readily exchanges with the coordinated THF of **6** at room temperature. In the ^{1}H-NMR spectrum of **6** in toluene-d_8, the resonances for the diastereotopic alpha protons of coordinated THF appeared as two quartets at δ 3.60 and 3.17 and those for the diastereotopic beta protons appeared as partially obscured multiplets at δ 1.06 and 0.96. When 0.12 M THF-d_8 was added to a toluene solution of **6** at 23°C, the downfield resonances for the alpha THF protons at δ 3.60 and 3.17 disappeared and resonances for free THF appeared. The disappearance of the THF signal followed pseudo first order kinetics with a rate constant of 1.9×10^{-4} s^{-1} ($t_{1/2} = 1$ h).

There are two plausible mechanisms for THF exchange: intramolecular displacement of coordinated THF by the ester group to give the intermediate **B** or dissociation of THF to give coordinatively unsaturated intermediate **C**.

2.4. Reaction of **6** with CO to form $Cp^*(CO)_2Re(\eta^2\text{-}(E)\text{-}EtO_2CCH{=}CHCO_2Et)$ (7)

Since complex **6** rapidly exchanged THF, its reaction with CO was investigated. Treatment of an orange–yellow THF-d_8 solution of **6** at 24°C with 1.3 atm CO led

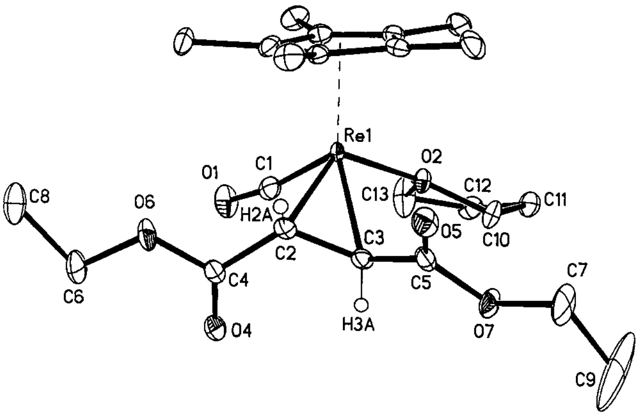


Fig. 1. X-ray crystal structure of $Cp^*Re(CO)(\eta^2\text{-}(E)\text{-}EtO_2CCH{=}CHCO_2Et)(THF)$ (**6**).

Table 1
Selected bond lengths (Å) and angles (°) for Cp*Re(CO)(η^2-(*E*)-$EtO_2CCH{=}CHCO_2Et$)(THF) (**6**)

Bond lengths (Å)			
Re–C(1)	1.872(4)		
Re–C(2)	2.154(4)		
Re–C(3)	2.189(4)		
Re–O(2)	2.164(3)		
C(2)–C(3)	1.445(6)		
C(4)–O(4)	1.209(5)		
C(5)–O(5)	1.222(5)		
Bond angles (°)			
C(1)–Re–C(2)	87.7(2)	C(3)–C(2)–C(4)	119.2(3)
C(1)–Re–O(2)	89.06(14)	C(2)–C(3)–C(5)	116.4(4)
C(2)–Re–C(3)	38.9(2)	Cp*–Re–C(1)	121.3(2)
C(2)–Re–O(2)	125.6(2)	Cp*–Re–C(2)	116.7(2)
C(3)–Re–O(2)	88.65(13)	Cp*–Re–C(3)	133.9(2)
C(2)–C(3)–Re	69.2(2)	Cp*–Re–O(2)	111.0(2)
C(3)–C(2)–Re	71.9(2)		

to the substitution of CO for THF to form the dicarbonyl alkene complex $Cp^*Re(CO)_2$(η^2-(*E*)-$EtO_2CCH{=}CHCO_2Et$) (**7**). The conversion of **6** to **7** occurred in nearly quantitative yield and its rate was followed by ^{1}H-NMR spectroscopy. The pseudo first order rate constant for disappearance of **6** was 2.0×10^{-4} s^{-1} ($t_{1/2} = 9.7$ h). Complex **7** was independently synthesized by the reaction of $Cp^*Re(CO)_2$(THF) with diethyl fumarate.

Table 2
Crystal data and structure refinement for **6**

Empirical formula	$C_{23}H_{35}O_6Re$
Crystal size (mm)	$0.60 \times 0.30 \times 0.20$
Temperature (K)	113(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P–1
Unit cell dimensions	
a (Å)	8.464(3)
b (Å)	9.156(3)
c (Å)	15.366(5)
α (°)	80.90(3)
β (°)	80.90(3)
γ (°)	89.42(3)
V (Å^3)	1175.4(7)
Z	2
Formula weight	593.71
$D_{calc.}$ (mg m^{-3})	1.678
Absorption coefficient (mm^{-1})	5.204
F(000)	592
q Range for data collection	2.25 to 25.03°
Scan range (2θ)	2.20° plus K_α–separation
Limiting indices	$-10 \le h \le 0$, $-10 \le k \le 10$, $-18 \le l \le 18$
Reflections collected	4384
Final *R* indices [$I > 2\sigma(I)$]	$R_1(F) = 0.0240$, $wR_2(F^2) = 0.0610$
R indices (all data)	$R_1(F) = 0.0252$, $wR_2(F^2) = 0.0619$

The mechanism for the conversion of **6** to **7**, which occurred about ten times more slowly than THF exchange, can be understood in terms of the mechanism shown in Scheme 3. Dissociation of THF from **6** is suggested to generate a reactive intermediate (either **B** or **C**) which is attacked by THF solvent (ca. 11 M) to regenerate **6** about ten times more often than it is attacked by low concentrations of CO (ca. 0.01 M) to generate the dicarbonyl complex **7**.

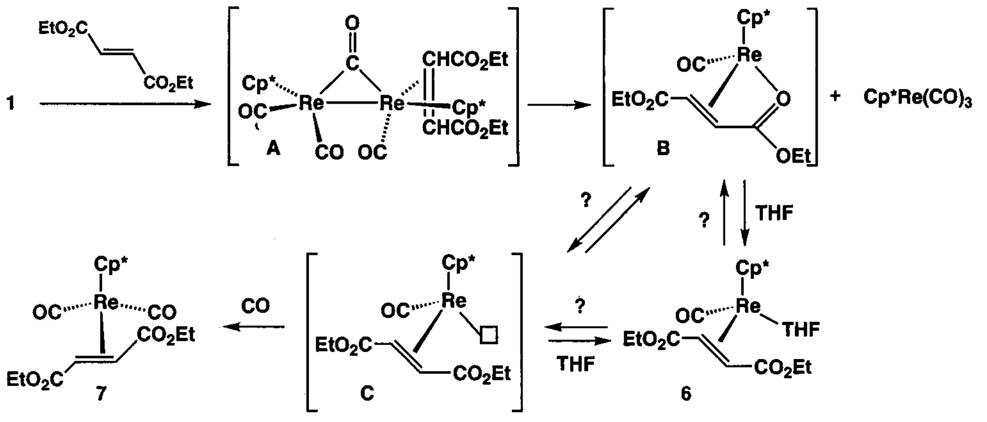
Examination of **7** by variable temperature ^{1}H-NMR spectroscopy in toluene-d_8 showed fluxional behavior of the bound alkene ligand. At −50°C, the rotation about the Re–alkene bond was slow on the NMR timescale and the two 'ends' of the ester were inequivalent. The resonances for the diastereotopic methylene protons of the two different ethyl groups appeared as four doublets of quartets centered at δ 4.30, 4.04, 3.97 and 3.93. The vinyl resonances appeared as doublets at δ 4.17 and 3.25. The methyl groups appeared as two distinct triplets at δ 1.06 and 1.02.

Rotation about the Re–alkene bond interchanges the two ethyl groups but does not interchange the diastereotopic methylene protons of the ethyl groups. At −15°C, significant broadening was observed in all of the signals for the coordinated diethyl fumarate. At 0°C, the methylene and vinyl protons had lost all fine structure and the methyl groups had coalesced into a broad resonance ($\omega_{1/2} = 20$ Hz). Further warming resulted in the sharpening to one ABX_3 signal. One half of the ABX_3 pattern was broader than the other due to the difference in the separation of the two AB patterns at low temperature. At 30°C, the higher frequency half of the ABX_3 pattern broadened into the baseline and the lower frequency half began to sharpen. At 100°C the fine structure of the new single ABX_3 pattern was visible and was simulated to determine the coupling constants. The different halves of the ABX_3 patterns coalesced at different temperatures because of their different chemical shift differences.

The barrier to alkene rotation was calculated from the coalescence of three exchanging resonances in the ^{1}H-NMR: the ester methyl groups and the two diastereotopic CH_2 groups. The average barrier to rotation of the alkene ligand was 13.5 ± 0.3 kcal mol^{-1}, which is higher than the 8.9 kcal mol^{-1} barrier of rotation of ethylene in $Cp^*(CO)_2Re$(η^2-$H_2C{=}CH_2$) [11]. The barrier to fumarate rotation falls in the 12–17 kcal mol^{-1} range seen for the $Cp^*(CO)_2Re$(η^2-alkyne) complexes [12].

3. Experimental

All manipulations were performed under a nitrogen atmosphere in an inert atmosphere glovebox or by standard high-vacuum techniques. ^{1}H-NMR spectra



Scheme 3.

were obtained on a Bruker WP200, WP250, WP270, AC300, or AM500 spectrometer. $^{13}C\{H\}$-NMR spectra were obtained on Bruker AC300 (75 MHz) or AM500 (126 MHz) spectrometer. IR spectra were obtained on an ATI Mattson Genesis spectrometer. Mass spectra were determined on a Kratos MS-80 spectrometer (EI). Elemental analyses were performed by Desert Analytics (Tucson, AZ). Toluene-d_8, THF-d_8, and C_6D_6 were distilled from purple solutions of sodium benzophenone ketyl immediately prior to use. Diethyl fumarate was distilled and dried over molecular sieves.

3.1. $Cp^*Re(CO)(\eta^2$-(E)-$EtO_2CCH{=}CHCO_2Et)(THF)$ (6)

Diethyl fumarate (55 μl, 336 mmol) was added in portions to a green solution of $Cp^*Re(CO)_2Re{=}Re(CO)_2Cp^*$ (**1**) (256 mg, 339 μmol) in THF (15 ml). The reaction mixture slowly turned brown over 3 h. the solvent was evaporated and the dark brown residue was dissolved in 2 ml THF, layered with 2 ml hexane and cooled to −40°C. The resulting orange X-ray quality crystals were washed once with hexane and dried under vacuum to give $Cp^*Re(CO)(\eta^2$-(*E*)-$EtO_2CCH{=}CHCO_2Et)(THF)$ (**6**) (81 mg, 40%). ^1H-NMR (200 MHz, THF-d_8): δ 4.30 (d, $J = 5.7$ Hz, =CH), 4.10 (dq, $J = 11$, 7.1 Hz, C*H*HCH$_3$), 4.03 (dq, $J = 11$, 7.1 Hz, CH*H*CH$_3$), 3.99 (dq, $J = 11$, 7.1 Hz, C*H*HCH$_3$), 3.93 (dq, $J = 11$, 7.1 Hz, CH*H*CH$_3$), 3.57 (d, $J = 5.7$ Hz, =CH), 1.76 (s, Cp*), 1.14 (t, $J = 7.1$ Hz, CH$_3$), 1.11 (t, $J = 7.1$ Hz, CH$_3$). ^1H-NMR (250 MHz, toluene-d_8, to observe bound THF hydrogens) δ 3.60 (br q, $J = 5.0$ Hz, OC*H*H, 3.17 (br q, $J = 5.0$ Hz, OCH*H*, 1.06 (m, OCH$_2$C*H*H), 0.96 (m, OCH$_2$CH*H*). $^{13}C\{^1H\}$-NMR (68 MHz, THF-d8): δ 214.8 (CO); 178.9 and 178.8 (CO_2); 99.7 (C_5Me_5); 58.8 and 58.7 (OCH_2); 43.9 and 38.0 (=CH); 15.2 (both CH_3); 9.8 (Cp^*CH_3). IR (THF): 1851 (vs), 1711 (m), 1690 (m) cm^{-1}. HRMS calc. (found) for $C_{23}H_{35}O_6^{187}Re$ (M+): *m*/*z* 594.196 (594.198). Anal. Calc. for $C_{23}H_{35}O_6Re$: C, 46.23; H, 5.94. Found: C, 46.36; H, 5.68.

3.2. $Cp^*Re(CO)_2(\eta^2$-(E)-$CH_3CH_2O_2CCH{=}CHCO_2CH_2CH_3)$ (7)

3.2.1. Method 1

An orange THF solution (0.3 ml) of **6** (4.7 μmol) was stirred under 1.3 atm CO (80 μmol) for 27 h to give a yellow solution of **7** (98% yield by ^1H-NMR).

3.2.2. Method 2

A yellow solution of $Cp^*Re(CO)_2(THF)$ (100 mg, 0.22 mmol) and diethyl fumarate (400 mg, 2.32 mmol) in 1 ml THF was stirred for 16 h to give a brown solution. Evaporation of the solvent gave a brown oily residue which was purified by column chromatography on silica gel. Excess diethyl fumarate was eluted with 4:1 hexane:CH_2Cl_2. Elution with CH_2Cl_2 gave a pale yellow fraction which was evaporated to give **7** (42 mg, 35%) as a yellow powder. ^1H-NMR (500 MHz, toluene-d_8, −50°C): δ 4.30 (dq, $J = 10.5$, 7.0 Hz, C*H*HCH$_3$), 4.17 (d, $J = 9.0$ Hz, CH=), 4.04 (dq, $J = 10.5$, 7.0 Hz, CH*H*CH$_3$), 3.96 (overlapping dq, 2H, C*H*$_2$CH$_3$, $J_{AB} = 10.5$, $J_{AX} = J_{BX} = 7.0$ Hz), 3.26 (d, $J = 8.5$ Hz, =CH), 1.63 (s, Cp*), 1.06 (t, $J = 7.0$ Hz, CH$_3$), 1.03 (t, $J = 7.0$ Hz, CH$_3$). $^{13}C\{^1H\}$-NMR [126 MHz, C_6D_6, 0.07 M $Cr(acac)_3$]: δ 213.0 (CO), 208.5 (CO), 169.8 (CO_2), 100.8 (C_5Me_5), 99.5 (=CH), 50.9 (OCH_2), 10.2 (C_5Me_5). IR (THF): 1986 (vs), 1908 (vs), 1705 (m) cm^{-1}. HRMS calc. (found) for $C_{20}H_{27}O_6^{187}Re$: *m*/*z* 550.1367 (550.1382).

The barrier to rotation of the fumarate ligand was determined from the coalescence of three different sets of peaks in the ^1H-NMR spectrum of **7**: ester Me ($\Delta\nu = 22$ Hz, $T_c = 273$ K, $\Delta G = 13.8$ kcal mol^{-1}); ester C*H*H ($\Delta\nu = 165$ Hz, $T_c = 288$ K, $\Delta G = 13.5$ kcal mol^{-1}); ester CH*H* ($\Delta\nu = 60$ Hz, $T_c = 273$ K, $\Delta G = 13.3$ kcal mol^{-1}).

3.3. NMR kinetics

The rate of conversion of **1** to **6** and **3** was determined by monitoring the Cp* resonances of **1** (δ 2.10), **6** (δ 1.75), and **3** (δ 2.17) utilizing ^{1}H-NMR spectroscopy. The disappearance of **1** (5.3 μmol) in a THF-d_8 solution (0.3 ml) was measured versus an internal standard of *para*-$(TMS)_2(C_6H_4)$ (6.3 μmol) at −10°C over a period of 90 min. The temperature was calibrated versus a methanol standard. A plot of ln [**1**] versus time was linear and gave a $k_{obs} = 3.6 \times 10^{-4}$ s^{-1}, $t_{1/2} = 32$ min.

The conversion of **6** (4.7 μmol) to **7** in the presence of 1.3 atm CO (80 μmol) was monitored by taking periodic ^{1}H-NMR spectra. Between spectra, the sample tube was immersed in a 24°C oil bath. The disappearance of the Cp* resonance of **6** (δ 1.75) was monitored versus an internal standard of *para*-$(TMS)_2(C_6H_4)$ (4.5 μmol). A plot of ln [**6**] versus time was linear and gave a $k_{obs} = 2.0 \times 10^{-5}$ s^{-1}, $t_{1/2} = 9.7$ h.

The rate of exchange of solvent THF-d_8 with coordinated THF of **6** was measured at 23°C by ^{1}H-NMR spectroscopy by observing the disappearance of the resonances for the diastereotopic alpha protons of the coordinated THF at δ 3.60 and 3.17 versus the doublet resonance for the alkene hydrogen at δ 4.84 in a toluene-d_8 solution of **6** containing 0.12 M THF-d_8. The disappearance of the coordinated THF signal followed pseudo first order kinetics with a rate constant of 1.9×10^{-4} s^{-1} ($t_{1/2} = 1$ h).

3.4. X-ray crystal structure determination and refinement of **6**

Intensity data were obtained with graphite monochromated Mo–K_α radiation on a Nicolet (Siemens) P3/F diffractometer at −160°C. Crystallographic computations were carried out with SHELXTL [13]. A semi-empirical (psi) absorption correction was applied. The initial position of the Re atom was obtained by direct methods. Other nonhydrogen atoms were obtained from successive Fourier difference maps coupled with isotropic least-squares refinement. All nonhydrogen atoms were refined anisotropically. Idealized positions were used for the hydrogen atoms. The atomic positional parameters for **6** have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgements

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