

Dinuclear metal complexes with saturated and unsaturated hydrocarbon bridges¹

Ekkehard Lindner^{*}, Thomas Leibfritz, Riad Fawzi, Manfred Steimann

Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

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Abstract

The reaction of the bis(triflates) $[Y-(CH_2)_m-Y]$ [$Y = F_3CSO_3$, $m = 4, 6-9, 12, 14, 16$ (**1a-h**)] with the carbonyl metalates $M'[M(CO)_5]$ ($M' = Na, K$; $M = Mn, Re$) affords the alkanediyl bridged metal complexes $[(OC)_5M-(CH_2)_m-M(CO)_5]$ [$m = 6-9, 12, 14, 16$; $M = Mn$ (**2b-h**) and $m = 4, 6-9, 12, 14, 16$; $M = Re$ (**3a-h**)]. Starting with $K[Mn(CO)_5]$ and the bis(triflates) **1d** and **1e** the diesters $[H_3CO(O)C(CH_2)_mC(O)OCH_3]$ [$m = 8, 9$ (**4d,e**)] are obtained in a one-pot reaction. The unsaturated hydrocarbon bridged rhenium complexes *trans*- $[Re]-(CH_2)_2-CH=CH-(CH_2)_2-[Re]$ (**6**), *cis*- $[Re]-(CH_2)_3-CH=CH-(CH_2)_3-[Re]$ (**8**), and $[Re]-(CH_2)_p-CH_2-C\equiv C-CH_2-(CH_2)_p-[Re]$ [$[Re] = Re(CO)_5$, $p = 1, 3$ (**11, 12**)] are formed by reaction of the bis(triflates) *trans*- $Y-(CH_2)_2-CH=CH-(CH_2)_2-Y$ (**5**), *cis*- $Y-(CH_2)_3-CH=CH-(CH_2)_3-Y$ (**7**), and $Y-(CH_2)_p-CH_2-C\equiv C-CH_2-(CH_2)_p-Y$ [$Y = F_3CSO_3$, $p = 1, 3$ (**9, 10**)] with $Na[Re(CO)_5]$ in THF. The structure of **8** was determined by an X-ray structural analysis. Crystal data for **8**: space group $P2_1/n$ with $a = 12.501(2)$, $b = 6.592(2)$, $c = 26.875(5)$ Å, $\beta = 93.28(2)^\circ$, $V = 2211.0(9)$ Å³, $Z = 4$. The structure was refined to $R = 0.039$, $wR = 0.090$. © 1997 Elsevier Science S.A.

Keywords: Manganese complexes; Rhenium complexes; Saturated hydrocarbon bridges; Unsaturated hydrocarbon bridges; Diesters

1. Introduction

Hydrocarbon bridged metal complexes are still of considerable attraction in organometallic chemistry [1], because they may serve as model compounds for reactive intermediates in transition metal catalyzed processes. Typical examples are the Fischer–Tropsch synthesis [2], the polymerization of alkenes [3] and alkynes [4] and unsaturated hydrocarbons which are chemisorbed on metal surfaces [5]. This is an important step in heterogeneous catalysis. Since hydrocarbon bridged complexes are also available with two different metal atoms it is possible to combine the properties of early and late transition metals via a hydrocarbon chain [6,7]. Recently Gladysz reported on one-dimensional carbon allotropes with terminal metal complex fragments containing alternative $C\equiv C$ triple and $C-C$ single bonds. Hitherto up to 20 carbon atoms could be arranged in one molecule [8].

For the access of hydrocarbon bridged complexes several approaches are described in the literature. Beck et al. studied the nucleophilic addition of carbonyl metalates to unsaturated η^2 -coordinated hydrocarbons leading to homo- and heteronuclear species [9]. Moss et al. allowed carbonyl metalates to react with bifunctional acid halides [10]. Subsequent thermolysis or photolysis results in the formation of hydrocarbon bridged complexes. The first dinuclear polymethylene complex was described by King many years ago [11]. This author employed α,ω -dihalogenoalkanes as starting materials. However, the applicability of this method is restricted [12]. Halides are insufficient leaving groups, hence side reactions are gaining prevalence. For the synthesis of compounds with two or even more metal–carbon σ bonds the bis(triflate) way is the method of choice. Lately alkanediylbis(trifluoromethanesulfonates) were successfully applied for the synthesis of metallacyclophanes [13] and of medium- and large-sized metallacycloalkanes with up to three $Os(CO)_4$ units in the framework [14].

Herein we want to report on homodinuclear complexes in which both transition metals are linked either via four to 16 methylene groups, or via *trans*-hexenediyl,

^{*} Corresponding author.

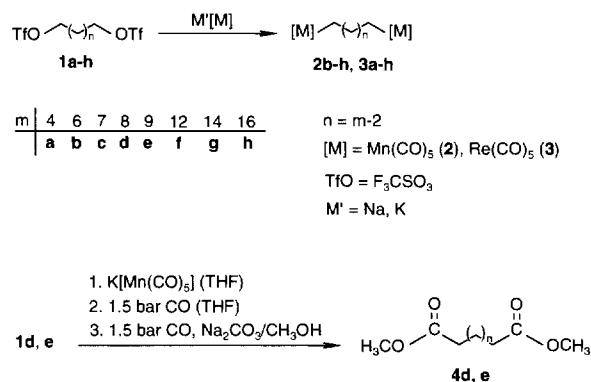
¹ Dedicated to Professor Gottfried Huttner on the occasion of his 60th birthday.

cis-octenediyl, hexynediyl, and decynediyl bridges respectively. Comparable species with only one C–C double or triple bond hitherto are only known with C₂ [6,15], C₄ [16], or C₅ [17] and C₂ [6] and C₄ [11,18] units respectively. Further experiments are engaged in migratory CO insertion reactions into both M–C σ bonds. Cleavage of both metal fragments of the diacyl intermediates leads to organic compounds with two additional carbon atoms in the chain.

2. Results and discussion

2.1. Complexes with saturated hydrocarbon chains

Treatment of the bis(triflates) **1a–h** with the carbonyl metalates [M(CO)₅][−] in diethyl ether at −30 °C (M = Mn) or THF at −10 °C (M = Re) afforded in a one-step reaction the alkanediyl bridged dinuclear manganese and rhenium complexes (OC)₅M–(CH₂)_m–M(CO)₅ **2b–h** and **3a–h** with six to 16 and four to 16 methylene groups respectively (Scheme 1). Compounds **2b–d** and **3a–d** were already described by Moss et al. by reacting the corresponding bifunctional acid halides with [M(CO)₅][−] followed by a decarbonylation of the intermediary occurring diacyl species [10]. Hence a two-step reaction is necessary to get satisfying yields of the final products. Only the rhenium complex **3e** was directly obtained from 1,9-dibromononane and [Re(CO)₅][−] [10]. The last mentioned method is only applicable in a few cases, in particular in the presence of strong organometallic Lewis bases [10,11]. Because of the weak nucleophilic character of [Mn(CO)₅][−] [19] the reaction between this anion and α,ω -dihaloalkanes leads preferably to undesirable side products [12]. If bis(triflates) are employed in place of dihaloalkanes the lacking basic character of [Mn(CO)₅][−] [19] is compensated by the strong electrophilicity of the terminal carbon atoms [20]. Hence the formation of the dinuclear complexes **2b–h** and **3a–h** proceeds under very mild conditions.



Scheme 1.

While the manganese compounds **2b–h** are pale yellow solids the rhenium analogues **3a–h** are colorless. Both fairly air-stable species dissolve readily in chlorinated hydrocarbons, but **2b–h** undergo a slow decomposition in these solvents. In saturated hydrocarbons the solubility increases with growing chain length. The easy decomposability of the manganese complexes **2b–h** in solution when exposed to air, which is in contrast to **3a–h**, is in agreement with the decreasing stability of the metal–carbon σ bond on going from 5d to 3d transition metals [21].

The composition of the compounds **2b–h** and **3c–h** was confirmed by their field desorption mass spectra displaying the molecular peaks. The spectra of **3a,b** reveal only the [M⁺–Re(CO)₅] peaks as the highest mass. In the 5 μm region of the IR spectra of **2b–h** and **3a–h** three sharp bands for the terminal CO ligands are observed, being consistent with a local C_{4v} symmetry of the M(CO)₅ fragments. The length of the bridging hydrocarbon chain has no significant influence on the position of the CO absorptions.

In the ¹H NMR spectra of **3a** and the complexes **2b–h**, **3b–h** appear two complex multiplets and three groups of signals respectively. An AA'BB' and an AA'BB'CC' spin system are established for the α - and β -methylene protons respectively, suggesting a hindered rotation of the C _{α} –C _{β} bonds. By rotation along that axis the equatorial carbonyl groups and the geminal γ -CH₂ protons approach too closely [22]. Between these two spin systems a third signal occurs, the shape of which changes from a complex multiplet for **2b,c**, **3b,c** to a broad signal for **2d–h**, **3d–h**. According to the integration of all ¹H peaks this third signal is ascribed to methylene protons other than α - and β -CH₂.

In the alkane part of **2b–e** and **3a–f** the ¹³C{¹H} NMR spectra reveal *m*/2 signals for even and (*m* + 1)/2 signals for odd numbers *m* of methylene carbon atoms. In the corresponding spectra of **2f–h** and **3g,h** not all signals are well resolved. The high field shifts are assigned to the metal adjacent carbon atoms. In the low field part of the spectra a further two signals are observed with relative intensities of approximately 1:4 which are attributed to the axially and equatorially positioned carbonyl ligands.

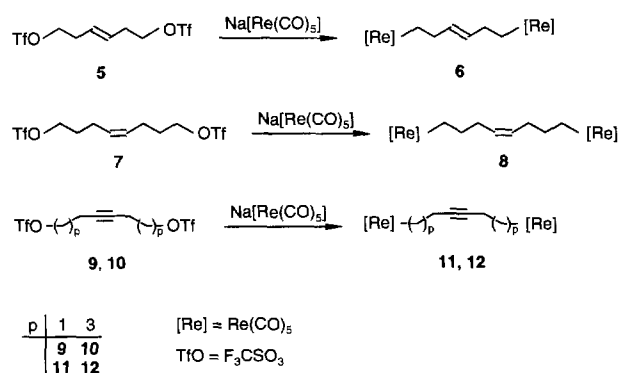
The behavior of hydrocarbon bridged and alkyl manganese and rhenium complexes toward carbon monoxide is thoroughly investigated [10,23]. Migratory insertion reactions into Mn–C σ bonds take place even under mild conditions [24]. This observation is in marked contrast to Re–C σ bonds, in which carbon monoxide insertions are only known in very few cases [25]. For example, solutions of the manganese complexes **2b–h** in CH₂Cl₂ or THF undergo a partial carbonylation even in the absence of carbon monoxide. In the IR spectra of these solutions an additional absorption at about 1650 cm^{−1} is observed which is indicative of a >C=O

group. Accordingly it should be possible to employ hydrocarbon bridged manganese complexes to extend a hydrocarbon chain by two carbon atoms. If the bis(triflates) **1d,e** are reacted with $\text{K}[\text{Mn}(\text{CO})_5]$ in THF, **2d,e** are formed as intermediates [IR (THF) 2106, 2004, 1974 cm^{-1} (CO)]. Subsequently the same solution was pressurized with 1.5 bar carbon monoxide leading to the diacyl compounds $(\text{OC})_5\text{MnC}(\text{O})(\text{CH}_2)_m\text{C}(\text{O})\text{Mn}(\text{CO})_5$ ($m = 8, 9$) [IR (THF) 2113, 2045, 2008 (CO), 1648 cm^{-1} ($> \text{C}=\text{O}$)]. Finally THF was replaced by a suspension of Na_2CO_3 in methanol and the resulting mixtures were exposed to carbon monoxide [26]. The occurrence of an IR band at 1720 cm^{-1} indicates the formation of the dicarboxylic diesters **4d,e** (Scheme 1). Additional absorptions at 1876 and 1907 cm^{-1} are attributed to the presence of $[\text{Mn}(\text{CO})_5]^-$ [27]. After purification by column chromatography the diesters **4d,e** were obtained as colorless viscous liquids and characterized by their IR, MS, ^1H , and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra.

2.2. Complexes with unsaturated hydrocarbon chains

Dinuclear complexes with unsaturated bridging units containing more than four carbon atoms and one C–C double or triple bond are scarcely described in the literature [17]. Basically they offer the possibility for the introduction of functional groups by addition reactions or to bind other metal complex fragments via a π bond [28]. According to this method molecules with well defined properties can be made accessible [29]. For the synthesis of complexes with two transition metals linked by an unsaturated hydrocarbon chain the bis(triflate) method can be employed.

The formation of the rhenium complexes *trans*-[Re]– $(\text{CH}_2)_2\text{--CH=CH--}(\text{CH}_2)_2\text{--[Re]}$ (**6**), *cis*-[Re]– $(\text{CH}_2)_3\text{--CH=CH--}(\text{CH}_2)_3\text{--[Re]}$ (**8**), and [Re]– $(\text{CH}_2)_p\text{--CH}_2\text{--C}\equiv\text{C--CH}_2\text{--}(\text{CH}_2)_p\text{--[Re]}$ (**11, 12**) succeeds by reaction of $\text{Na}[\text{Re}(\text{CO})_5]$ with the corresponding bis(triflates) **5, 7, 9, and 10** in THF (Scheme 2). After work up of the reaction mixtures the complexes **6, 8, 11, and 12** resulted as colorless solids in good yields. They are



Scheme 2.

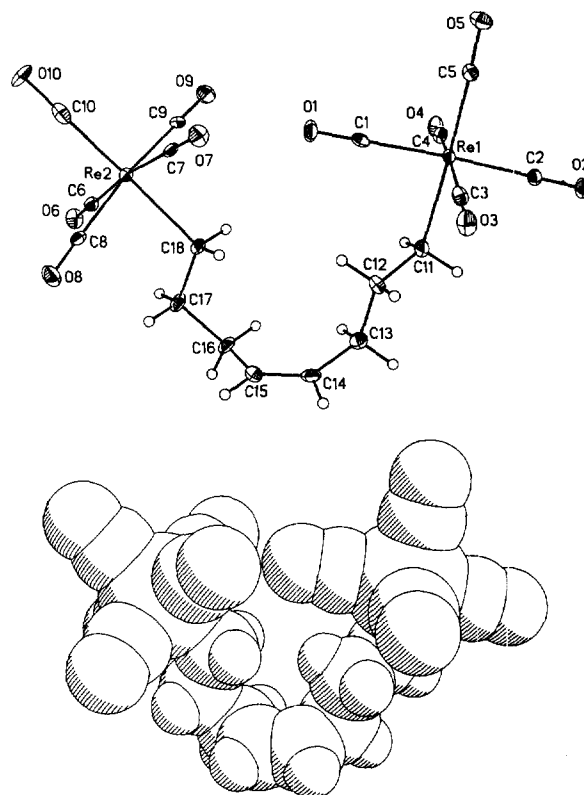


Fig. 1. Top: ORTEP plot of **8**. Bottom: space filling model of **8**.

remarkably stable toward atmospheric oxygen and easily soluble in chlorinated hydrocarbons and ethers, but less soluble in saturated hydrocarbons.

The occurrence of molecular peaks in the FD and FAB mass spectra with characteristic isotopic patterns corroborates the composition of the complexes **6, 8, 11, and 12**. Between 2130 and 1970 cm^{-1} the IR spectra (*n*-pentane) of these species exhibit three CO absorptions, as expected for both $\text{Re}(\text{CO})_5$ moieties.

In the ^1H NMR spectra of **6, 8, 11, and 12** each multiplet can be assigned to the protons of a specific methylene group and to the olefinic function. With the exception of the doubly and triply bonded carbon atoms the signals of which are located in the expected region the $^{13}\text{C}\{^1\text{H}\}$ NMR data of the mentioned unsaturated complexes are similar to those of the corresponding saturated species [22].

To confirm the structure of the *cis*-octenediyl bridged rhenium complex **8** an X-ray structural analysis was carried out. The ORTEP plot (Fig. 1, top) shows the *cis*-configuration of the C13–C14–C15–C16 unit. In contrast to the *trans*-[Re]– $\text{CH}_2\text{--CH=CH--CH}_2\text{--[Re]}$ structure published by Beck et al. [$d(\text{C}=\text{C}) = 1.43 \text{ \AA}$] [16] the C14–C15 bond length in **8** is in the range of a C=C double bond [1.32(1) \AA] (Table 1). In the solid state the bulky $\text{Re}(\text{CO})_5$ fragments are located surprisingly on the same side of the molecule in such a manner that the C1–O1 carbonyl group points to the gap be-

Table 1
Selected interatomic distances (Å) and angles (°) for **8**

Selected bond lengths	
Re(1)–C(5)	1.952(8)
Re(1)–C(1)	2.003(9)
Re(1)–C(11)	2.284(9)
C(11)–C(12)	1.514(11)
C(14)–C(15)	1.317(14)
Selected bond angles	
C(4)–Re(1)–C(3)	170.3(4)
C(5)–Re(1)–C(11)	177.8(3)
Re(1)–C(11)–C(12)	117.6(6)
C(13)–C(14)–C(15)	126.0(10)
C(14)–C(15)–C(16)	129.3(10)

tween the ligands C7–O7 and C9–O9, which is demonstrated in a space filling model (Fig. 1, bottom). The reason for such an arrangement is probably packing effects. The steric congested Re(CO)₅ groups lead to an expansion of the angles C13–C14–C15 and C14–C15–C16.

3. Conclusion

Recently we could demonstrate that the bis(triflate) route is a successful method for the access of hydrocarbon bridged homodinuclear metal complexes [22,30]. This type of chemistry was extended by the introduction of dialkyl substituted aromatic backbones as hydrocarbon bridges between two transition metal fragments [31]. Herein we report on the general applicability of the bis(triflate) method which was transferred to the synthesis of homodinuclear complexes being bridged by large saturated and unsaturated hydrocarbon chains with one C–C double or triple bond. The terminal carbon atoms each carrying a triflate group are strongly electrophilic. Therefore the reactions with a carbonyl rhenate and even with the less nucleophilic manganate proceed under very mild conditions in a straightforward way.

The Mn–C σ bond is capable of undergoing a facile migratory carbon monoxide insertion reaction. In this context the manganese complexes **2b–h** were suitable precursors for the synthesis of hydrocarbons with two additional carbon atoms which could be verified by the formation of the carboxylic diesters **4d,e**.

4. Experimental section

All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were dried over appropriate reagents and stored under argon. IR spectra were recorded on a Bruker IFS 48 FT-IR spectrometer. FD mass spectra were recorded on a Finnigan MAT 711 A instrument (8 kV), modified

by AMD and FAB mass spectra were obtained on a Finnigan TSQ 70 (10 kV). Elemental analyses were performed with a Carlo Erba 1106 analyzer and a Perkin–Elmer Model 4000 atomic absorption spectrometer. ¹H NMR and ¹³C{¹H} NMR spectra were measured at 25 °C with a Bruker DRX 250 spectrometer at 250.13 and 62.90 MHz respectively. Chemical shifts were recorded relative to partially deuterated solvent peaks which are reported relative to TMS. K[Mn(CO)₅] [32] and the bis(triflates) [33] were synthesized according to literature methods.

4.1. General procedure for the preparation of the alkane-bridged manganese complexes **2b–h**

To a suspension of K[Mn(CO)₅] in 50 ml of diethyl ether a solution of the bis(triflates) **1b–h** in 50 ml of the same solvent was added dropwise (2 h) at –30 °C. After stirring this mixture for 4 h the solvent was removed in vacuo at room temperature. The residue was extracted three times with 50 ml of *n*-pentane. The insoluble components were separated by filtration (D4). The filtrate was concentrated in vacuo to ca. 4 ml and subsequently cooled to –80 °C which results in the formation of a pale yellow precipitate. Purification of raw **2b–h** succeeded by recrystallization from CH₂Cl₂/*n*-pentane (1/4) at –60 °C.

4.1.1. Hexane-1,6-diylbis(pentacarbonylmanganese) (**2b**)

Starting materials 371 mg (1.59 mmol) of K[Mn(CO)₅] and 296 mg (0.77 mmol) of **1b**. Yield 208 mg (57%) of **2b**; m.p. 108 °C (dec.). IR (*n*-pentane): 2106, 2009, 1989 (CO)cm⁻¹. ¹H NMR (CDCl₃): δ 1.03 (m, 4H, CH₂Mn); 1.40 (m, 4H, CH₂(CH₂)₂Mn); 1.67 (m, 4H, CH₂CH₂Mn). ¹³C{¹H} NMR (CDCl₃): δ 6.9 (s, CH₂Mn); 35.1, 37.2 (s, (CH₂)₂CH₂Mn); 209.5 (s, axial CO); 213.7 (s, equatorial CO). MS (FD, 30 °C), *m/z* 474.4 [M⁺]. Anal. Found: C, 40.72; H, 2.64; Mn, 23.35. C₁₆H₁₂O₁₀Mn₂ (474.14) Calc.: C, 40.53, H, 2.55; Mn, 23.17%.

4.1.2. Heptane-1,7-diylbis(pentacarbonylmanganese) (**2c**)

Starting materials 431 mg (1.84 mmol) of K[Mn(CO)₅] and 362 mg (0.91 mmol) of **1c**. Yield 288 mg (65%) of **2c**; m.p. 72 °C (dec.). IR (*n*-pentane): 2106, 2009, 1989 (CO)cm⁻¹. ¹H NMR (CDCl₃): δ 1.04 (m, 4H, CH₂Mn); 1.40 (m, 6H, (CH₂)₂(CH₂)₂Mn); 1.67 (m, 4H, CH₂CH₂Mn). ¹³C{¹H} NMR (CDCl₃): δ 7.0 (s, CH₂Mn); 28.7 (s, CH₂(CH₂)₃Mn); 35.7, 37.3 (s, (CH₂)₂CH₂Mn); 210.2 (s, axial CO); 213.7 (s, equatorial CO). MS (FD, 30 °C), *m/z* 488.4 [M⁺]. Anal. Found: C, 41.51; H, 2.85; Mn, 22.74. C₁₇H₁₄O₁₀Mn₂ (488.17) Calc.: C, 41.83; H, 2.89; Mn, 22.51%.

4.1.3. Octane-1,8-diylbis(pentacarbonylmanganese) (**2d**)

Starting materials 250 mg (1.07 mmol) of $K[Mn(CO)_5]$ and 216 mg (0.53 mmol) of **1d**. Yield 175 mg (66%) of **2d**; m.p. 73 °C (dec.). IR (*n*-pentane): 2106, 2009, 1989 (CO) cm^{-1} . 1H NMR ($CDCl_3$): δ 1.03 (m, 4H, CH_2Mn); 1.35 (br, 8H, $(CH_2)_2(CH_2)_2Mn$); 1.66 (m, 4H, CH_2CH_2Mn). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 6.9 (s, CH_2Mn); 24.3, 35.5, 37.2 (s, $(CH_2)_3CH_2Mn$); 209.5 (s, axial CO); 213.6 (s, equatorial CO). MS (FD, 30 °C), m/z 502.2 [M^+]. Anal. Found: C, 42.78; H, 3.39; Mn, 21.93. $C_{18}H_{16}O_{10}Mn_2$ (502.20) Calc.: C, 43.05; H, 3.21; Mn, 21.88%.

4.1.4. Nonane-1,9-diylbis(pentacarbonylmanganese) (**2e**)

Starting materials 250 mg (1.07 mmol) of $K[Mn(CO)_5]$ and 228 mg (0.54 mmol) of **1e**. Yield 192 mg (69%) of **2e**; m.p. 69 °C (dec.). IR (*n*-pentane): 2106, 2009, 1989 (CO) cm^{-1} . 1H NMR ($CDCl_3$): δ 1.03 (m, 4H, CH_2Mn); 1.32 (br, 10H, $(CH_2)_3(CH_2)_2Mn$); 1.67 (m, 4H, CH_2CH_2Mn). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 7.0 (s, CH_2Mn); 22.7 (s, $CH_2(CH_2)_4Mn$); 24.4, 35.7, 37.3 (s, $(CH_2)_3CH_2Mn$); 210.2 (s, axial CO); 213.7 (s, equatorial CO). MS (FD, 30 °C), m/z 516.2 [M^+]. Anal. Found: C, 43.83; H, 3.40; Mn, 21.05. $C_{19}H_{18}O_{10}Mn_2$ (516.22) Calc.: C, 44.21; H, 3.51; Mn, 21.28%.

4.1.5. Dodecane-1,12-diylbis(pentacarbonylmanganese) (**2f**)

Starting materials 229 mg (0.98 mmol) of $K[Mn(CO)_5]$ and 229 mg (0.49 mmol) of **1f**. Yield 193 mg (70%) of **2f**; m.p. 78 °C (dec.). IR (*n*-pentane): 2106, 2009, 1989 (CO) cm^{-1} . 1H NMR ($CDCl_3$): δ 1.04 (m, 4H, CH_2Mn); 1.26 (br, 16H, $(CH_2)_4(CH_2)_2Mn$); 1.66 (m, 4H, CH_2CH_2Mn). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 7.0 (s, CH_2Mn); 29.2, 29.7, 35.7, 37.3 (s, $(CH_2)_5CH_2Mn$); 210.2 (s, axial CO); 213.7 (s, equatorial CO). MS (FD, 30 °C), m/z 558.4 [M^+]. Anal. Found: C, 46.93; H, 4.60; Mn, 19.23. $C_{22}H_{24}O_{10}Mn_2$ (558.30) Calc.: C, 47.33; H, 4.33; Mn, 19.68%.

4.1.6. Tetradecane-1,14-diylbis(pentacarbonylmanganese) (**2g**)

Starting materials 196 mg (0.84 mmol) of $K[Mn(CO)_5]$ and 207 mg (0.42 mmol) of **1g**. Yield 165 mg (67%) of **2g**; m.p. 71 °C (dec.). IR (*n*-pentane): 2106, 2008, 1989 (CO) cm^{-1} . 1H NMR ($CDCl_3$): δ 1.02 (m, 4H, CH_2Mn); 1.25 (br, 20H, $(CH_2)_5(CH_2)_2Mn$); 1.66 (m, 4H, CH_2CH_2Mn). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 7.0 (s, CH_2Mn); 29.2, 29.4, 29.7, 35.7, 37.3 (s, $(CH_2)_6CH_2Mn$); 210.2 (s, axial CO); 213.7 (s, equatorial CO). MS (FD, 35 °C), m/z 586.5 [M^+]. Anal. Found: C, 48.81; H, 4.94; Mn, 18.49.

$C_{24}H_{28}O_{10}Mn_2$ (586.36) Calc.: C, 49.16; H, 4.81; Mn, 18.74%.

4.1.7. Hexadecane-1,16-diylbis(pentacarbonylmanganese) (**2h**)

Starting materials 248 mg (1.06 mmol) of $K[Mn(CO)_5]$ and 273 mg (0.52 mmol) of **1h**. Yield 232 mg (72%) of **2h**; m.p. 84 °C (dec.). IR (*n*-pentane): 2106, 2008, 1989 (CO) cm^{-1} . 1H NMR ($CDCl_3$): δ 1.01 (m, 4H, CH_2Mn); 1.24 (br, 24H, $(CH_2)_6(CH_2)_2Mn$); 1.65 (m, 4H, CH_2CH_2Mn). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 7.0 (s, CH_2Mn); 29.2, 29.5, 29.7, 35.7, 37.3 (s, $(CH_2)_7CH_2Mn$); 210.2 (s, axial CO); 213.7 (s, equatorial CO). MS (FD, 30 °C), m/z 614.5 [M^+]. Anal. Found: C, 50.84; H, 5.67; Mn, 18.04. $C_{26}H_{32}O_{10}Mn_2$ (614.41) Calc.: C, 50.83; H, 5.25; Mn, 17.88%.

4.2. General procedure for the preparation of the diesters **4d,e**

To a suspension of $K[Mn(CO)_5]$ in 50 ml of THF a solution of the bis(triflates) **1d** and **1e** in 50 ml of the same solvent was added dropwise (2 h) at -30 °C. After stirring for 4 h the mixture was pressurized with 1.5 bar CO for 1 day. The solvent was removed under vacuum and replaced by a suspension of two equivalents of Na_2CO_3 in 50 ml of MeOH. The mixture was stirred under a pressure of 1.5 bar CO for 4 days. After removing the solvent the residue was extracted two times with 100 ml of CH_2Cl_2 , the insoluble components were separated by filtration (D4) and the filtrate was concentrated to a volume of ca. 5 ml. The dicarboxylic diesters were purified by column chromatography using activated silica gel/ CH_2Cl_2 (column 2.5×20 cm^2). The first fraction contains $Mn_2(CO)_{10}$, the second fraction the diesters **4d** and **4e**. The solvent of the latter fraction was removed under reduced pressure leaving the colorless, viscous liquids.

4.2.1. 1,8-Decanedioic acid dimethyl ester (**4d**)

Starting materials 503 mg (2.15 mmol) of $K[Mn(CO)_5]$, 432 mg (1.05 mmol) of **1d** and 222 mg (2.09 mmol) of Na_2CO_3 . Yield 141 mg (58%) of **4d**; m.p. 18 °C [lit. [34] 27 °C]. IR (CH_2Cl_2): 1733 ($>C=O$) cm^{-1} . 1H NMR ($CDCl_3$): δ 1.28 (br, 8H, $(CH_2)_2(CH_2)_2COO$); 1.56 (m, 4H, CH_2CH_2COO); 2.26 (t, 4H, CH_2COO); 3.63 (s, 6H, OCH_3) [lit. [35] 1.30, 1.53–1.69, 2.30, 3.67]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.6, 28.8, 29.0, 34.0 (s, $(CH_2)_4CO$); 51.3 (s, OCH_3); 174.2 (s, CO) [lit. [35] 24.79, 28.90, 28.93, 33.94, 51.20, 174.30]. MS (FD, 30 °C), m/z 230.5 [M^+].

4.2.2. 1,9-Undecanedioic acid dimethyl ester (**4e**)

Starting materials 576 mg (2.46 mmol) of $K[Mn(CO)_5]$, 509 mg (1.20 mmol) of **1e** and 254 mg

(2.40 mmol) of Na_2CO_3 . Yield 158 mg (54%) of **4e**; m.p. 15 °C [lit. [34] 18 °C]. IR (CH_2Cl_2): 1733 ($> \text{C}=\text{O}$) cm^{-1} . ^1H NMR (CDCl_3): δ 1.22 (br, 10H, $(\text{CH}_2)_3(\text{CH}_2)_2\text{COO}$); 1.54 (m, 4H, $\text{CH}_2\text{CH}_2\text{COO}$); 2.23 (t, 4H, CH_2COO); 3.60 (s, 6H, OCH_3) [lit. [35] 1.28, 1.52–1.63, 2.26–2.32, 3.66]. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 24.8, 29.0, 29.1, 33.9 (s, $(\text{CH}_2)_3\text{CO}$); 51.3 (s, OCH_3); 174.2 (s, CO) [lit. [35] 24.97, 29.13, 29.17, 29.22, 34.13, 51.35, 174.21]. MS (FD, 30 °C), m/z 244.4 [M^+].

4.3. General procedure for the preparation of the hydrocarbon bridged rhenium complexes **3a–h**, **6**, **8**, **11**, **12**

A solution of $\text{Re}_2(\text{CO})_{10}$ in 50 ml of THF was stirred for 3 h in the presence of 0.6% sodium amalgam at room temperature. The orange solution of mainly $\text{Na}[\text{Re}(\text{CO})_5]$ was transferred into a Schlenk tube, cooled to -10°C and then the bis(triflates) **1a–h**, **5**, **7**, **9**, and **10** were added. After stirring at -10°C for 30 min the reaction mixture was allowed to warm up to room temperature and the solvent was removed under vacuum. The residue was extracted two times with 50 ml of CH_2Cl_2 . The insoluble components were separated by filtration (D4). After removing the solvent under reduced pressure the residue was pre-purified by column chromatography (silica gel/*n*-pentane, $\varnothing = 2$ cm, length 5 cm for the saturated and 2.5 cm for the unsaturated rhenium complexes). Evaporation of the solvent in vacuo and recrystallization from *n*-pentane at -80°C (saturated complexes **3a–h**) and at -60°C (unsaturated complexes **6**, **8**, **11**, **12**) result in the colorless rhenium complexes.

4.3.1. Butane-1,4-diylbis(pentacarbonylrhenium) (**3a**)

Starting materials 414 mg (0.63 mmol) of $\text{Re}_2(\text{CO})_{10}$ and 222 mg (0.63 mmol) of **1a**. Yield 279 mg (62%) of **3a**; m.p. 162 °C (dec.). IR (*n*-pentane): 2122, 2013, 1982 (CO) cm^{-1} . ^1H NMR (CDCl_3): δ 1.00 (m, 4H, CH_2Re); 1.76 (m, 4H, $\text{CH}_2\text{CH}_2\text{Re}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -9.7 (s, CH_2Re); 47.0 (s, $\text{CH}_2\text{CH}_2\text{Re}$); 181.6 (s, axial CO); 186.1 (s, equatorial CO). MS (FD, 35 °C), m/z 382.1 [$\text{M}^+ - \text{Re}(\text{CO})_5$]. Anal. Found: C, 23.66; H, 1.26; Re, 52.31. $\text{C}_{14}\text{H}_8\text{O}_{10}\text{Re}_2$ (708.63) Calc.: C, 23.73; H, 1.14; Re, 52.55%.

4.3.2. Hexane-1,6-diylbis(pentacarbonylrhenium) (**3b**)

Starting materials 517 mg (0.79 mmol) of $\text{Re}_2(\text{CO})_{10}$ and 294 mg (0.77 mmol) of **1b**. Yield 376 mg (66%) of **3b**; m.p. 116 °C. IR (*n*-pentane): 2124, 2012, 1983 (CO) cm^{-1} . ^1H NMR (CDCl_3): δ 0.94 (m, 4H, CH_2Re); 1.29 (m, 4H, $\text{CH}_2(\text{CH}_2)_2\text{Re}$); 1.75 (m, 4H, $\text{CH}_2\text{CH}_2\text{Re}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -9.1 (s, CH_2Re); 36.8, 39.2 (s, $(\text{CH}_2)_2\text{CH}_2\text{Re}$); 181.5 (s, axial CO); 186.1 (s, equatorial CO). MS (FD, 35 °C), m/z

409.0 [$\text{M}^+ - \text{Re}(\text{CO})_5$]. Anal. Found: C, 26.30; H, 1.74; Re, 50.23. $\text{C}_{16}\text{H}_{12}\text{O}_{10}\text{Re}_2$ (736.68) Calc.: C, 26.09; H, 1.64; Re, 50.55%.

4.3.3. Heptane-1,7-diylbis(pentacarbonylrhenium) (**3c**)

Starting materials 301 mg (0.46 mmol) of $\text{Re}_2(\text{CO})_{10}$ and 177 mg (0.45 mmol) of **1c**. Yield 249 mg (74%) of **3c**; m.p. 79 °C (dec.). IR (*n*-pentane): 2124, 2012, 1984 (CO) cm^{-1} . ^1H NMR (CDCl_3): δ 0.93 (m, 4H, CH_2Re); 1.29 (m, 6H, $(\text{CH}_2)_2(\text{CH}_2)_2\text{Re}$); 1.77 (m, 4H, $\text{CH}_2\text{CH}_2\text{Re}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -9.1 (s, CH_2Re); 28.6 (s, $\text{CH}_2(\text{CH}_2)_3\text{Re}$); 37.5, 39.2 (s, $(\text{CH}_2)_2\text{CH}_2\text{Re}$); 181.5 (s, axial CO); 186.1 (s, equatorial CO). MS (FD, 35 °C), m/z 750.0 [M^+]. Anal. Found: C, 26.91; H, 1.90; Re, 49.90. $\text{C}_{17}\text{H}_{14}\text{O}_{10}\text{Re}_2$ (750.71) Calc.: C, 27.20; H, 1.88; Re, 49.61%.

4.3.4. Octane-1,8-diylbis(pentacarbonylrhenium) (**3d**)

Starting materials 598 mg (0.92 mmol) of $\text{Re}_2(\text{CO})_{10}$ and 367 mg (0.89 mmol) of **1d**. Yield 487 mg (71%) of **3d**; m.p. 94 °C. IR (*n*-pentane): 2124, 2012, 1984 (CO) cm^{-1} . ^1H NMR (CDCl_3): δ 0.94 (m, 4H, CH_2Re); 1.27 (br, 8H, $(\text{CH}_2)_2(\text{CH}_2)_2\text{Re}$); 1.74 (m, 4H, $\text{CH}_2\text{CH}_2\text{Re}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -9.1 (s, CH_2Re); 29.2, 37.5, 39.2 (s, $(\text{CH}_2)_3\text{CH}_2\text{Re}$); 181.5 (s, axial CO); 186.1 (s, equatorial CO). MS (FD, 35 °C), m/z 763.7 [M^+]. Anal. Found: C, 27.89; H, 1.88; Re, 48.66. $\text{C}_{18}\text{H}_{16}\text{O}_{10}\text{Re}_2$ (764.73) Calc.: C, 28.27; H, 2.11; Re, 48.70%.

4.3.5. Nonane-1,9-diylbis(pentacarbonylrhenium) (**3e**)

Starting materials 451 mg (0.69 mmol) of $\text{Re}_2(\text{CO})_{10}$ and 279 mg (0.66 mmol) of **1e**. Yield 392 mg (76%) of **3e**; m.p. 64 °C. IR (*n*-pentane): 2124, 2012, 1984 (CO) cm^{-1} . ^1H NMR (CDCl_3): δ 0.92 (m, 4H, CH_2Re); 1.27 (br, 10H, $(\text{CH}_2)_3(\text{CH}_2)_2\text{Re}$); 1.75 (m, 4H, $\text{CH}_2\text{CH}_2\text{Re}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -9.1 (s, CH_2Re); 29.2, 37.4, 39.2 (s, $(\text{CH}_2)_3\text{CH}_2\text{Re}$); 29.8 (s, $\text{CH}_2(\text{CH}_2)_4\text{Re}$); 181.4 (s, axial CO); 186.0 (s, equatorial CO). MS (FD, 35 °C), m/z 777.9 [M^+]. Anal. Found: C, 29.35; H, 2.54; Re, 47.57. $\text{C}_{19}\text{H}_{18}\text{O}_{10}\text{Re}_2$ (778.76) Calc.: C, 29.30; H, 2.33; Re, 47.82%.

4.3.6. Dodecane-1,12-diylbis(pentacarbonylrhenium) (**3f**)

Starting materials 808 mg (1.24 mmol) of $\text{Re}_2(\text{CO})_{10}$ and 571 mg (1.23 mmol) of **1f**. Yield 785 mg (78%) of **3f**; m.p. 82 °C. IR (*n*-pentane): 2124, 2011, 1984 (CO) cm^{-1} . ^1H NMR (CDCl_3): δ 0.93 (m, 4H, CH_2Re); 1.25 (br, 16H, $(\text{CH}_2)_4(\text{CH}_2)_2\text{Re}$); 1.74 (m, 4H, $\text{CH}_2\text{CH}_2\text{Re}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -9.2 (s, CH_2Re); 29.1, 29.7, 29.8, 37.5, 39.2 (s, $(\text{CH}_2)_5\text{CH}_2\text{Re}$); 181.5 (s, axial CO); 186.0 (s, equatorial CO). MS (FD, 35 °C), m/z 819.8 [M^+]. Anal. Found: C, 32.17; H, 2.87; Re, 45.02. $\text{C}_{22}\text{H}_{24}\text{O}_{10}\text{Re}_2$ (820.84) Calc.: C, 32.19; H, 2.95; Re, 45.37%.

4.3.7. Tetradecane-1,14-diylbis(pentacarbonylrhenium) (3g)

Starting materials 457 mg (0.70 mmol) of $\text{Re}_2(\text{CO})_{10}$ and 344 mg (0.70 mmol) of **1g**. Yield 465 mg (79%) of **3g**; m.p. 69°C. IR (*n*-pentane): 2124, 2011, 1984 (CO) cm^{-1} . ^1H NMR (CDCl_3): δ 0.93 (m, 4H, CH_2Re); 1.24 (br, 20H, $(\text{CH}_2)_5(\text{CH}_2)_2\text{Re}$); 1.74 (m, 4H, $\text{CH}_2\text{CH}_2\text{Re}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -9.1 (s, CH_2Re); 29.2, 29.7, 29.8, 37.5, 39.2 (s, $(\text{CH}_2)_6\text{CH}_2\text{Re}$); 181.6 (s, axial CO); 186.1 (s, equatorial CO). MS (FD, 35°C), m/z 850.2 [M^+]. Anal. Found: C, 33.66; H, 3.62; Re, 43.42. $\text{C}_{24}\text{H}_{28}\text{O}_{10}\text{Re}_2$ (848.89). Calc.: C, 33.96; H, 3.32; Re, 43.87%.

4.3.8. Hexadecane-1,16-diylbis(pentacarbonylrhenium) (3h)

Starting materials 235 mg (0.36 mmol) of $\text{Re}_2(\text{CO})_{10}$ and 179 mg (0.34 mmol) of **1h**. Yield 243 mg (81%) of **3h**; m.p. 65°C. IR (*n*-pentane): 2124, 2011, 1984 (CO) cm^{-1} . ^1H NMR (CDCl_3): δ 0.93 (m, 4H, CH_2Re); 1.24 (br, 24H, $(\text{CH}_2)_6(\text{CH}_2)_2\text{Re}$); 1.74 (m, 4H, $\text{CH}_2\text{CH}_2\text{Re}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -9.1 (s, CH_2Re); 29.2, 29.7, 29.8, 37.5, 39.2 (s, $(\text{CH}_2)_7\text{CH}_2\text{Re}$); 181.5 (s, axial CO); 186.1 (s, equatorial CO). MS (FD, 31°C), m/z 877.9 [M^+]. Anal. Found: C, 35.54; H, 3.60; Re, 42.51. $\text{C}_{26}\text{H}_{32}\text{O}_{10}\text{Re}_2$ (876.95) Calc.: C, 35.61; H, 3.68; Re, 42.47%.

4.3.9. *trans*-3-Hexene-1,6-diylbis(pentacarbonylrhenium) (6)

Starting materials 459 mg (0.70 mmol) of $\text{Re}_2(\text{CO})_{10}$ and 262 mg (0.69 mmol) of **5**. Yield 293 mg (58%) of **6**; m.p. 156°C (dec.). IR (*n*-pentane): 2124, 2013, 1984 (CO) cm^{-1} . ^1H NMR (CDCl_3): δ 0.99 (m, 4H, CH_2Re); 2.45 (m, 4H, $\text{CH}_2\text{CH}_2\text{Re}$); 5.41 (m, 2H, $=\text{CH}(\text{CH}_2)_2\text{Re}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -9.5 (s, CH_2Re); 41.0 (s, $\text{CH}_2\text{CH}_2\text{Re}$); 134.9 (s, $=\text{CH}(\text{CH}_2)_2\text{Re}$); 181.3 (s, axial CO); 185.8 (s, equatorial CO). MS (FD, 31°C), m/z 734.3 [M^+]. Anal. Found: C, 26.53; H, 1.60; Re, 50.92. $\text{C}_{16}\text{H}_{10}\text{O}_{10}\text{Re}_2$ (734.66) Calc.: C, 26.16; H, 1.37; Re, 50.69%.

4.3.10. *cis*-4-Octene-1,8-diylbis(pentacarbonylrhenium) (8)

Starting materials 591 mg (0.91 mmol) of $\text{Re}_2(\text{CO})_{10}$ and 356 mg (0.87 mmol) of **7**. Yield 422 mg (63%) of **8**; m.p. 66°C (dec.). IR (*n*-pentane): 2124, 2013, 1984 (CO) cm^{-1} . ^1H NMR (CDCl_3): δ 0.96 (m, 4H, CH_2Re); 1.80 (m, 4H, $\text{CH}_2\text{CH}_2\text{Re}$); 2.03 (m, 4H, $\text{CH}_2(\text{CH}_2)_2\text{Re}$); 5.38 (m, 2H, $=\text{CH}(\text{CH}_2)_3\text{Re}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -9.5 (s, CH_2Re); 35.2, 39.4 (s, $(\text{CH}_2)_2\text{CH}_2\text{Re}$); 129.5 (s, $=\text{CH}(\text{CH}_2)_3\text{Re}$); 181.3 (s, axial CO); 185.9 (s, equatorial CO). MS (FAB, 50°C), m/z 760.9 [M^+]. Anal. Found: C, 28.61; H, 2.08; Re, 48.62. $\text{C}_{18}\text{H}_{14}\text{O}_{10}\text{Re}_2$ (762.72) Calc.: C, 28.35; H, 1.85; Re, 48.83%.

4.3.11. 3-Hexyne-1,6-diylbis(pentacarbonylrhenium) (11)

Starting materials 332 mg (0.51 mmol) of $\text{Re}_2(\text{CO})_{10}$ and 192 mg (0.51 mmol) of **9**. Yield 204 mg (55%) of **11**; m.p. 151°C (dec.). IR (*n*-pentane): 2126, 2015, 1983 (CO) cm^{-1} . ^1H NMR (CDCl_3): δ 1.17 (m, 4H, CH_2Re); 2.72 (m, 4H, $\text{CH}_2\text{CH}_2\text{Re}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -9.5 (s, CH_2Re); 26.6 (s, $\text{CH}_2\text{CH}_2\text{Re}$); 86.4 (s, $\equiv\text{C}(\text{CH}_2)_2\text{Re}$); 181.1 (s, axial CO); 185.3 (s, equatorial CO). MS (FD, 35°C), m/z 732.0 [M^+]. Anal. Found: C, 26.30; H, 1.52; Re, 50.77. $\text{C}_{16}\text{H}_8\text{O}_{10}\text{Re}_2$ (732.65) Calc.: C, 26.23; H, 1.10; Re, 50.83%.

4.3.12. 5-Decyne-1,10-diylbis(pentacarbonylrhenium) (12)

Starting materials 311 mg (0.48 mmol) of $\text{Re}_2(\text{CO})_{10}$ and 203 mg (0.47 mmol) of **10**. Yield 214 mg (58%) of **12**; m.p. 118°C (dec.). IR (*n*-pentane): 2124, 2012, 1985 (CO) cm^{-1} . ^1H NMR (CDCl_3): δ 0.91 (m, 4H, CH_2Re); 1.46 (m, 4H, $\text{CH}_2(\text{CH}_2)_2\text{Re}$); 1.83 (m, 4H, $\text{CH}_2\text{CH}_2\text{Re}$); 2.15 (m, 4H, $\text{CH}_2(\text{CH}_2)_3\text{Re}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -10.3 (s, CH_2Re); 18.0, 36.4, 38.2 (s, $(\text{CH}_2)_3\text{CH}_2\text{Re}$); 80.3 (s, $\equiv\text{C}(\text{CH}_2)_4\text{Re}$); 181.4 (s, axial CO); 185.8 (s, equatorial CO). MS (FD, 31°C), m/z 788.1 [M^+]. Anal. Found: C, 30.67; H, 2.11; Re, 46.74. $\text{C}_{20}\text{H}_{16}\text{O}_{10}\text{Re}_2$ (788.76) Calc.: C, 30.46; H, 2.04; Re, 47.22%.

Table 2
Crystal data and collection parameters for **8**

Formula	$\text{C}_{18}\text{H}_{14}\text{O}_{10}\text{Re}_2$
<i>FW</i>	762.69
Crystal size (mm^3)	$0.43 \times 0.12 \times 0.05$
Crystal system	Monoclinic
Space group	$P2_1/n$
<i>a</i> (Å)	12.501(2)
<i>b</i> (Å)	6.592(2)
<i>c</i> (Å)	26.875(5)
β (°)	93.28(2)
<i>V</i> (Å ³)	2211.0(9)
<i>Z</i>	4
Calc. density (g cm^{-3})	2.291
<i>h, k, l</i> range	$\pm 14, \pm 7, \pm 31$
<i>T</i> (K)	173(2)
<i>F</i> (000)	1408
Wavelength (Mo K α) (Å)	0.71073
Reflections collected	14760
Independent reflections	3887
Reflections observed [$I > 2\sigma(I)$]	3083
No. of parameters	272
Goodness of fit	1.500
R_1^a	0.039
wR_2^b	0.090

^a $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$.

^b $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \{\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **8**

Atom	x	y	z	U_{eq}
Re(1)	-3308(1)	4640(1)	5865(1)	23(1)
Re(2)	1784(1)	9749(1)	5960(1)	24(1)
C(1)	-1925(6)	5951(14)	5704(3)	31(2)
O(1)	-1148(5)	6713(11)	5616(3)	44(2)
C(2)	-4690(6)	3454(13)	6072(3)	30(2)
O(2)	-5476(4)	2812(11)	6187(3)	42(2)
C(3)	-2575(6)	1997(13)	6011(3)	31(2)
O(3)	-2171(5)	525(11)	6112(3)	48(2)
C(4)	-4048(6)	7306(13)	5845(3)	28(2)
O(4)	-4455(5)	8821(10)	5855(3)	41(2)
C(5)	-3646(6)	4095(14)	5160(3)	29(2)
O(5)	-3835(5)	3846(12)	4737(2)	46(2)
C(6)	2062(6)	12308(14)	6340(3)	33(2)
O(6)	2194(5)	13797(10)	6551(3)	44(2)
C(7)	1419(6)	7101(13)	5641(3)	26(2)
O(7)	1222(5)	5573(10)	5466(3)	42(2)
C(8)	3012(6)	8424(13)	6338(3)	27(2)
O(8)	3704(5)	7578(11)	6540(3)	46(2)
C(9)	452(6)	10937(15)	5638(3)	33(2)
O(9)	-309(5)	11617(12)	5456(3)	48(2)
C(10)	2675(7)	10558(16)	5423(4)	44(2)
O(10)	3217(6)	11057(13)	5105(3)	56(2)
C(11)	-2870(6)	5378(16)	6682(3)	38(2)
C(12)	-1737(7)	4922(16)	6880(4)	41(2)
C(13)	-1481(7)	5624(17)	7417(3)	41(2)
C(14)	-328(8)	5169(16)	7583(3)	40(2)
C(15)	470(8)	6475(17)	7602(4)	44(2)
C(16)	445(8)	8697(17)	7529(3)	43(2)
C(17)	1163(8)	9389(18)	7119(3)	47(3)
C(18)	769(6)	8789(15)	6599(3)	33(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

4.4. Structure determination of **8**

Crystal data and details of data collection are summarized in Table 2. The atomic coordinates and equivalent isotropic displacement parameters for **8** are given in Table 3. Single crystals were obtained from diethyl ether solution, mounted on a glass fiber and transferred to a P4 Siemens diffractometer by taking rotation photographs and performing a photo search to find a suitable reduced cell. The lattice constants were determined with 25 precisely centered high-angle reflections and refined by least-squares methods. The structure was solved by the Patterson method [36] and refined by the least-squares method (based on F^2) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions (riding model). An absorption correction (Ψ scan) was applied. Max. and min. transmission were 1.00 and 0.305 respectively. Maximum and minimum peaks in the final difference synthesis were 1.895 and $-2.343 \text{ e \AA}^{-3}$. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische

Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-406092, the names of the authors, and the journal citation.

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