Organometallic Rhenium Chemistry

Synthesis of Cyclopentadienyl-Based Tricarbonyl Rhenium Complexes and Some Unusual Reactivities of Cyclopentadienyl Substituents

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Abstract: Cyclopentadienyl-based (Cp-based) tricarbonyl rhenium complexes [Cp′Re(CO)$_3$] are convenient precursors for the corresponding Cp-based trioxorhenium complexes (Cp′ReO$_3$), which are potential catalysts for the deoxydehydration (DODH) of diols to olefins. To evaluate the influence of different Cp substituents in Cp′ReO$_3$ complexes in DODH, a series of alkyl-substituted Cp′Re(CO)$_3$ complexes (**1a**–**8a**) were synthesized. High yields (86–98 %) were obtained from the reactions of Re$_2$(CO)$_{10}$ with the corresponding Cp′H ligands (**1**–**8**). The C–O infrared absorptions of **1a**–**8a** indicate that the electron-donating character of the Cp ligand increases with the number of substituents attached directly to the Cp ring. Analogous aryl-substituted complexes **10a**–**12a** containing bulky phenyl groups were accessed through the salt metathesis of ReBr(CO)$_5$ with

the lithium salt of the deprotonated ligand (Cp′Li), and the aryl groups decreased the electron donation. Furthermore, an unusual [6+4] cycloaddition reaction of (CpMe$_4$H)Re(CO)$_3$ (**8a**) with excess ligand resulted in the highly asymmetric Cp′Re(CO)$_3$ complex **9a**. Finally, the reaction of the tetraphenylcyclopentadienone ligand with Re$_2$(CO)$_{10}$ was investigated and led to the isolation of two unusual compounds, namely, Re(CO)$_3$ complexes of the Shvo-type hydroxytetraphenylcyclopentadienyl ligand, [Ph$_4$Cp(OH)]Re(CO)$_3$ (**13a**), and a benzofuran-fused cyclopentadienyl ligand, [Ph$_3$Cp(C$_6$H$_4$O)]Re(CO)$_3$ (**14a**). X-ray crystal structures were obtained for the new Cp′Re(CO)$_3$ complexes (CptBu$_2$H$_3$)Re(CO)$_3$ (**2a**), [1,2,3-Me$_3$(tetrahydroindenyl)]Re(CO)$_3$ (**7a**), **9a**, **13a**, and **14a**, which all have the typical three-legged "piano-stool" configuration.

Introduction

Currently, chemical industries rely on petroleum-based feedstocks for the production of bulk chemicals. Owing to the volatile prices of fossil fuels and their anticipated depletion, the search for alternative and renewable feedstocks has received much attention.[1,2] Among these, lignocellulosic biomass holds promise for the sustainable production of commodity chemicals and other building blocks.[3–5] However, in contrast to petroleum-derived hydrocarbons, its components are highly oxygenated, mostly in the form of hydroxy groups. Thus, the synthesis of industrially relevant chemical building blocks requires several consecutive dehydroxylation reactions through reductive deoxygenation methods.[6,7] Particularly attractive is the combination of deoxygenation[8,9] and dehydration[10] in the single-step deoxydehydration (DODH)[11–13] of biomass-derived sugars and polyols to obtain the corresponding deoxygenated olefinic products.[14–16]

In this context, the rhenium-catalyzed DODH of vicinal diols to olefins is attracting considerable attention, mainly focused on the use of methyltrioxorhenium (MTO) as the catalyst. This is likely due to its commercial availability, easy handling, and versatility in catalytic applications.[17] However, in addition to the sensitivity of MTO to base or acid hydrolysis (to form poly-MTO) and easy poisoning with N-donor bases, many different unidentified and structurally elusive rhenium species were found under DODH conditions.[11,12] Furthermore, there are longstanding issues with the potential expansion of the series of MTO catalysts for catalytic applications, as their longer-chain alkyl analogues are not very stable, unlike MTO itself (e.g., Et-ReO$_3$ decomposes at ambient temperature).[18,19]

Cyclopentadienyl-based trioxorhenium complexes (Cp′ReO$_3$) [Cp′ = substituted cyclopentadienyl ligand, including fused-ring structures such as indenyl (Ind) or tetrahydroindenyl] have been known for over three decades,[20–22] and Cp*ReO$_3$ (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) was the first demonstrated catalyst (1996) for the DODH of diols and polyols to olefins.[16] We recently expanded the scope of DODH catalysts by using the bulkier Cp^{ttt}ReO$_3$ complex (Cp^{ttt} = 1,2,4-tri-*tert*-butylcyclopentadienyl) and found it to be an efficient catalyst [turnover numbers (TONs) of up to 1400 for the conversion of 1,2-octanediol to octenes with 73 % selectivity for 1-octene].[23,24] To obtain insights into the structure–activity relationships and, accordingly, improve the catalytic properties of these

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Cp'ReO$_3$ catalysts, the synthesis and study of other closely related complexes are of interest.[11,25,26]

Both Cp*ReO$_3$ and Cp^{ttt}ReO$_3$ are synthesized through oxidative decarbonylation methods from the corresponding Cp-based tricarbonylrhenium complexes Cp'Re(CO)$_3$.[27–29,62] The synthesis of Cp'Re(CO)$_3$ compounds is commonly achieved by two methods, that is, ligand exchange of rhenium(I) carbonyl species such as XRe(CO)$_5$ (X = Cl, Br) with the substituted cyclopentadienyl anion (Cp'$^–$)[29–31] or thermal reactions (150–210 °C) of the protonated ligand Cp'H with Re$_2$(CO)$_{10}$ under neat conditions[23,32,33] or in a high-boiling solvent mixture for Cp'H compounds with high-melting points (e.g., solid materials containing aryl substituents).[34] In addition, several other synthetic methods are available to obtain Cp'Re(CO)$_3$ from Re$_2$(CO)$_{10}$ such as Cp transfer from Cp$_2$TiCl$_2$[35] or cascade C–H activation reactions starting from ketimines.[36] The thermolysis of tetracarbonyl(1,2,3-triphenylpropenetriyl)rhenium with alkynes (PhCCR, R = Ph, H) can also lead to aryl-substituted Cp'Re(CO)$_3$.[37,38] Furthermore, in situ generated Cp'SnBu$_3$ reacts with BrRe(CO)$_5$ or (Et$_4$N)$_2$[ReBr$_3$(CO)$_3$] conveniently at ambient temperature to produce Cp'Re(CO)$_3$.[39] The latter rhenium precursor was also successfully employed for functionalized Cp'Re(CO)$_3$ derivatives bearing carboxylic acid or boronic acid substituents with C$_5$H$_4$N$_2$ as the Cp source.[40]

Here, we report on the synthesis of alkyl- and aryl-appended Cp'Re(CO)$_3$ compounds with varying electronic and steric properties. Firstly, we focused on the synthesis of a series of Cp'Re(CO)$_3$ complexes bearing alkyl-appended Cp' ligands (1–8), including the previously mentioned Cp* and Cp^{ttt} ligands (Figure 1). In comparison with the bulky Cp^{ttt}H (1), ligands 2–4 contain a lower number of tBu groups (2) or these groups are replaced with less bulky isopropyl groups (3 and 4). Similarly, ligands 6–8 are related to the electron-rich Cp*H (5) ligand, either by an increase (6 and 7) or a decrease (8) in steric demand. Cp'Re(CO)$_3$ complexes bearing aryl-appended Cp' ligands derived from the cyclopentadiene (10 and 11), indene (12), and cyclopentadienone (13) scaffolds were subsequently investigated (vide infra). During the exploration of the syntheses of the corresponding Cp'Re(CO)$_3$ complexes, some unusual reactivity induced by the Cp substituents to afford cyclopentadienyl-ligated Cp'Re(CO)$_3$ structures was observed.
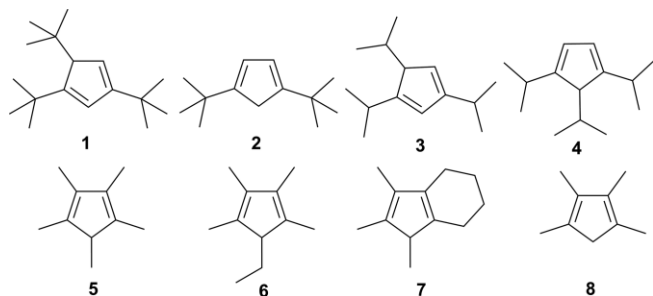

Figure 1. Alkyl-appended Cp'H ligands 1–8 used in this study. Different double-bond isomers are possible for all ligands except 5.

Results and Discussion

The alkyl-appended Cp'H ligands were either obtained commercially (2, 5, 6, and 8) or synthesized through literature procedures (1,[41,42] 3,[42] 4,[42] and 7[43]). The Cp'Re(CO)$_3$ compounds 1a–8a were prepared through a slight modification of a procedure by Gladysz et al.,[32] which had previously been applied to 1a,[23] 5a,[32] and 6a[33] (the synthesis of 8a through salt metathesis reactions was reported previously).[31,44] The Cp'H ligand (1.5–3.0 equiv. per Re center) was treated with Re$_2$(CO)$_{10}$ in neat reaction conditions under an inert N$_2$ atmosphere (Scheme 1). The reaction flask was heated to 150 °C for 30 min and then gradually to 200 °C for 5–20 h. If necessary, the reaction temperature was raised to 210 °C for 1–3 h to achieve complete conversion of the Re$_2$(CO)$_{10}$. After the completion of the reaction, the solidified mixture was purified by silica column chromatography to afford Cp'Re(CO)$_3$ as white or off-white crystalline materials in very good yields (89–98 % based on rhenium).
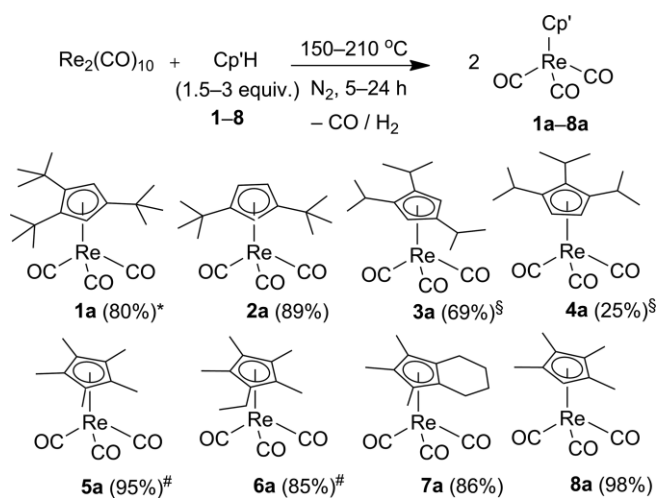
Scheme 1. Synthesis of alkyl-appended cyclopentadienyl tricarbonyl rhenium complexes 1a–8a. * Improved yield (80 %) for 1a.[23] § Obtained as inseparable mixture. # Literature yields for 5a[32] and 6a.[33]

The synthesis of the triisopropyl derivatives 3a and 4a was complicated by the fact that the parent triisopropylcyclopentadiene ligands 3 and 4 could only be obtained as a mixture of isomers (including isomers containing an exocyclic double bond).[42] The mixture was subjected to the standard metalation reaction to afford a mixture of 3a and 4a as a colorless liquid (94 % total yield) after column chromatography, and the isomers could not be separated. The ^{1}H NMR spectrum of the mixture revealed the two isomers (1,2,4-iPr$_3$CpH$_2$)Re(CO)$_3$ (3a) and (1,2,3-iPr$_3$CpH$_2$)Re(CO)$_3$ (4a) with two different Cp–H singlets at δ = 4.99 and 5.22 ppm in a ratio of 73:27 (3a/4a), alongside the corresponding four septets in the range δ = 2.6–2.8 ppm for the –CHMe$_2$ moieties. An enriched mixture containing 95 % of 3a (and 5 % of 4a) was obtained after the removal of 4a in the form of its corresponding oxidized (1,2,3-iPr$_3$CpH$_2$)ReO$_3$ complex, for which the iPr substitution pattern was confirmed.[45]

Selected spectroscopic and crystallographic characterization data of 1a–8a are collected in Table 1. All Cp'Re(CO)$_3$ complexes 1a–8a exhibit a single Re–CO ^{13}C NMR signal between δ = 195 and 199 ppm and two IR absorptions corresponding to the asymmetric (ν_{asym}, $\tilde{\nu}$ = 1880–1910 cm^{-1}) and symmetric (ν_{sym},

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$\tilde{\nu}$ = 1990–2010 cm^{-1}) CO normal modes typical of the three-legged "piano-stool" geometry. Two types of Cp'Re(CO)$_3$ complexes can be distinguished on the basis of these spectroscopic data, that is, those with partially substituted Cp' ligands (**1a**–**4a** and **8a**) and those with peralkylated ligands (**5a**–**7a**). As shown in Table 1, a lower-frequency ν_{sym} band is observed for the peralkylated systems **5a**–**7a** ($\tilde{\nu}$ = 1995–1996 cm^{-1}) than for the less-substituted Cp analogues ($\tilde{\nu}$ = 2005–2007 cm^{-1}), and the corresponding ^{13}C NMR signals of the former complexes appear at relatively low field (δ = 198 ppm); both effects are ascribed to π backbonding into the antibonding CO orbitals in **5a**–**7a** (i.e., Re→CO). A similar trend for an increasing number of methyl substituents in (CpMe$_{1-5}$)Re(CO)$_3$ was reported previously.[31] Thus, it is clearly demonstrated that the peralkylated Cp ligands are more electron-rich than the less-substituted Cp ligands **1a**–**4a**. The same effect is seen in **1a** and **2a**: the CO frequency increases when the number of tBu substituents decreases from three in **1a** to two in **2a**. The electronic environments of the isopropyl-appended complexes **3a** and **4a** are between those of **1a** and **2a**. Therefore, the relative order of electron donation from the Cp' ligands in the Cp'Re(CO)$_3$ complexes is **5a** ≈ **6a** ≈ **7a** > **8a** ≥ **1a** ≥ **3a**, **4a** ≥ **2a**. This order of electronic effect is in close agreement with that reported previously for a different selection of Cp ligands on the basis of the carbonyl IR vibrations of Cp'RuBr(CO)$_2$.[46]

The recrystallization of **2a** and **7a** in CH$_2$Cl$_2$/hexane (2:1) afforded crystals suitable for X-ray diffraction. As expected from the spectroscopic data, these two complexes exhibit typical three-legged piano-stool geometries similar to those observed for **1a**[23] and **5a**[47] (Figure 2). The Cp centroid to rhenium [Cp–Re = 1.9538(6)–1.9584(6) Å] and Re–CO [1.9130(16)–1.9183(14) Å] distances are nearly the same for **1a**, **2a**, and **7a**, but the crystal structure of **5a** at T = 293(1) K contains a slightly wider range of Re–CO distances [1.875(10)–1.908(10) Å].[47] Furthermore, the Cp rings are perfectly planar with a well-centered η^5-bonding to the rhenium center with no ring slippage (Δ = 0 Å) for **1a**, **2a**, and **5a** and a very small ring slippage (Δ = 0.023 Å) for **7a** (Δ is the distance between the ring centroid and the perpendicular projection of the metal onto the least-squares plane of the ring).[48] The latter is likely caused by the decreased symmetry owing to the fused cyclohexyl ring. The puckering of the saturated ring is similar to that observed in Fe and Ru complexes of **7**.[43,49] Indeed, the two rear methylene groups in **7a** are significantly above and below the plane of the Cp ring with torsion angles of –15.07(18) and –14.21(18)°, respectively. The molecular structure of **2a** has an approximate noncrystallographic C_s symmetry with a root mean square (rms) deviation of 0.0944 Å.[50] The mirror plane contains (Cp)C–Re–CO. For all of these complexes, the OC–Re–CO bonds are close to perpendicular and have angles in the range 89.18(9) to 92.3(4)° (Table 1).

In the course of our optimization of the synthesis of the tetramethylcyclopentadienyl derivative **8a**, an interesting side-product was isolated. When a mixture of **8** (3.6 equiv.) and Re$_2$(CO)$_{10}$ was heated for an extended reaction time of 11 h, **8a** was isolated in only 60 % yield; an additional product was

Table 1. Selected analytical data of Cp'Re(CO)$_3$ complexes **1a**–**8a**.

Cp'Re(CO)$_3$	^{13}C NMR[a] δ(Re–CO) [ppm]	IR (CO)[a] asym, sym $\tilde{\nu}$ [cm^{-1}]	Cp–Re[e] [Å]	Δ[f] [Å]	X-ray crystal structures Re–C(O) [Å]	OC–Re–CO [°]
1a[c]	196.62	1887, 2005	1.9569(7)	0	1.9126(18)–1.9140(19)	89.18(9)–90.84(7)
2a	195.85	1889, 2007	1.9584(6)	0	1.9130(16)–1.9161(15)	89.90(6)–91.07(7)
3a, **4a**[b]	196.33, 196.55	1892, 2007	–	–	–	–
5a[d]	198.28	1885, 1996	1.959(8)	0	1.875(10)–1.908 (10)	89.4(2)–90.2(5)
6a[b]	198.18	1889, 1997	–	–	–	–
7a	198.45	1884, 1995	1.9538(6)	0.023	1.9129(14)–1.9180(14)	89.73(6)–91.75(6)
8a[b]	197.38	1887, 2005	–	–	–	–

[a] The NMR spectra were recorded with samples in CDCl$_3$. The FTIR spectroscopic data of solid samples are reported here. [b] No X-ray data available. [c] The X-ray data were taken from ref.[23] [d] The X-ray data were taken from ref.[47] [e] Distance between the ring centroid and the metal center. [f] The ring slippage Δ is defined as the distance between the Cp ring centroid and the perpendicular projection of the metal center onto the least-squares plane of the ring.
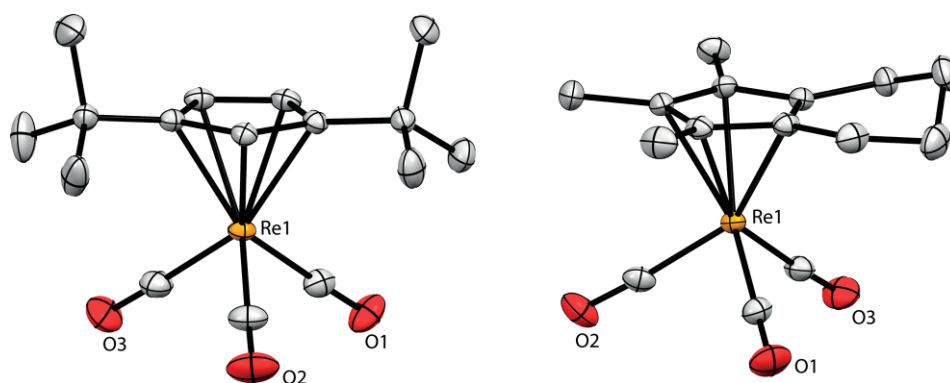

Figure 2. Molecular crystal structures of **2a** (left) and **7a** (right), drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

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obtained in low yield (7 %) and identified crystallographically as the Cp'Re(CO)$_3$ compound **9a**, which incorporates a complex tricyclic Cp' ligand (Scheme 2). A shorter reaction time of 5 h resulted in the clean and nearly quantitative formation of **8a**; this suggests that **9a** is formed through a subsequent reaction of **8a** rather than a parallel pathway. This was confirmed by the treatment of the pure complex **8a** with a slight excess of **8** (1.1 equiv.) at 160–200 °C for 10 h, which resulted in a low conversion of **8a** (20 %) to **9a** (5 %).
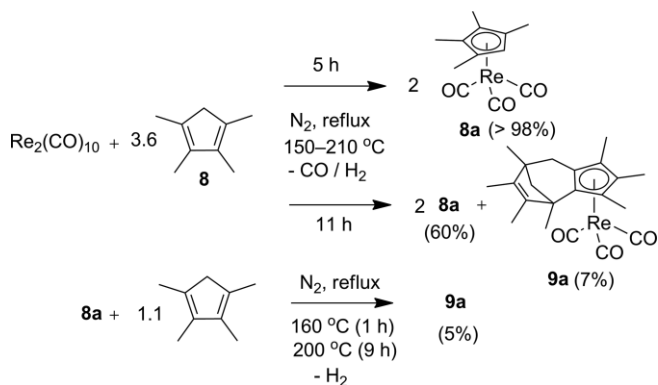
Scheme 2. Synthesis and reactivity of **8a** with the free ligand **8**.

The X-ray crystal structure of **9a** exhibits a three-legged piano-stool conformation comprising a peralkylated Cp' ligand appended with a bicyclic, partially unsaturated unit. Overall, a highly asymmetric Cp ligand was found (Figure 3). The Cp ring is perfectly planar in a well-centered η^5-bonding environment with no ring slippage, and the corresponding Re–C(Cp) distances are between 2.3061(17) and 2.3186(17) Å. The Re–C(O) and (Re)C–O bond lengths are in the ranges 1.910(2)–1.9139(19) and 1.152(2)–1.158(2) Å, respectively, and the OC–Re–CO angles are
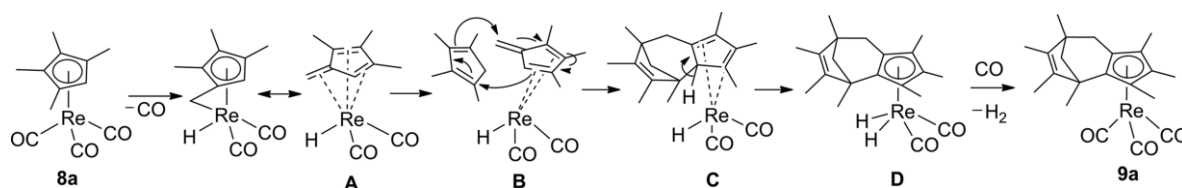
in the range 89.53(8)–90.44(9)°. These data closely match those of the other piano-stool complexes described herein.

As we have demonstrated that the reaction of **8a** with excess **8** can yield **9a**, we propose the mechanism depicted in Scheme 3 for the formation of **9a**. The initial thermal dissociation of CO from **8a** leads to the fulvene-bound rhenium hydride complex **A** through β-hydride elimination from one of the Cp–CH$_3$ groups.[51] A change in hapticity from η^6 to η^4 then generates the reactive 16-electron species **B**, which undergoes a [6+4] cycloaddition with the free ligand **8** to form the 16-electron species **C**. The oxidative addition of the C–H bond then restores the aromaticity of the Cp ring to yield the rhenium(III) dihydride species **D**. Finally, the reductive elimination of H$_2$ followed by CO association results in the final product **9a**.

This mechanism finds support in the literature. Fulvene-based (η^6-C$_5$Me$_4$–CH$_2$)Re(CO)$_2$X (X = Cl, I, Br) species analogous to the proposed intermediate **A** are known and undergo addition reactions with nucleophiles (e.g., halides, phosphines, or amines).[52,53] The [6+4] cycloaddition reactions of fulvene with dienes are well known,[54] and metal-mediated pathways have been studied in detail for (η^6-1,3,5-cycloheptatriene)tricarbonyl chromium(0).[54,55] The formation of the rhenium(III) dihydride intermediate **D** correlates with the previously reported and well-characterized complex Cp*Re(CO)$_2$(H)$_2$ and its conversion to Cp*Re(CO)$_3$.[56,57]

Furthermore, an understanding of the mechanism of this reaction would provide insights into the development of direct, target-oriented synthetic procedures for planar chiral Cp-based metal complexes.[58,59] The planar chirality of **9a** could be exploited for asymmetric catalytic transformations, such as the previously reported enantioselective phenyl transfer to aldehydes catalyzed by a planar chiral Cp'Re(CO)$_3$ complex.[60]

Aryl-appended cyclopentadiene ligands have long been known to afford robust metal complexes.[60] They can be employed for the steric protection of a metal center owing to the ability of the aryl substituents to rotate out of the plane of the Cp ring and also provide tunable electronic environments for the metal center. Prompted by the absence of previous reports on Cp'ReO$_3$ complexes with aryl substituents on the Cp ring, the perarylated pentaphenylcyclopentadiene (**10**) and its smaller analogues tetraphenylcyclopentadiene (**11**) and tetraphenylcyclopentadienone (**13**) were considered as Cp' ligands. Additionally, the related indenyl ligand 1,2,3-triphenylindene (**12**) was also considered (Figure 4).

Originally, Berke and co-workers reported the complexes (CpPh$_5$)Re(CO)$_3$ (**10a**, 72 %) and (CpPh$_4$H)Re(CO)$_3$ (**11a**, 68 %) formed by the thermolysis of tetracarbonyl(triphenylpropene-triyl)rhenium in the presence of alkynes (i.e., PhCCR, R = H or Ph) in hexanes at reflux temperature.[37,38] However, owing to
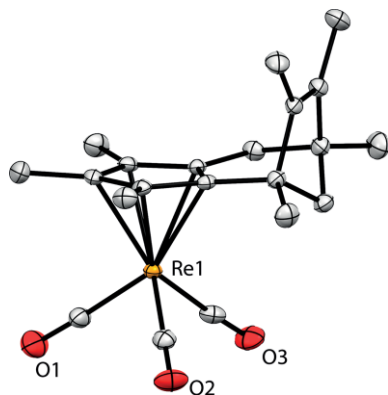

Figure 3. Molecular crystal structure of **9a**, drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

Scheme 3. Proposed mechanism for the formation of **9a** through the [6+4] cycloaddition of fulvene species **B** with 1,2,3,4-tetramethylcyclopentadiene **8**.

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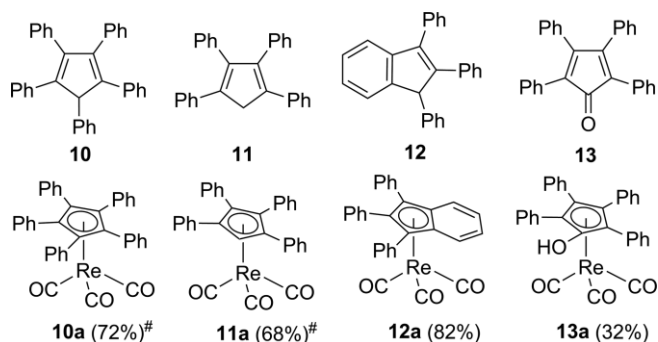of Inorganic Chemistry

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Figure 4. Aryl-appended Cp'H ligands **10**–**13** and the corresponding Cp' Re(CO)$_3$ complexes (Cp' = cyclopentadienyl or indenyl). #Literature yields for **10a** and **11a**.[38]

the commercial availability of ligands **10** and **11** as solid materials, salt metathesis reactions were performed with a slight modification of the published procedure by George and co-workers (Scheme 4).[30] Proligand **12** was prepared by a literature procedure.[63] As shown in Scheme 4, the deprotonation of the aryl-substituted cyclopentadiene or indene (**10**–**12**) with nBuLi at –78 °C in tetrahydrofuran (THF) for 4–5 h was followed by the addition of Re(CO)$_5$Br at room temp. Next, the reaction mixture was heated under reflux for 2 d to afford **10a** (30 %), **11a** (93 %), and **12a** (82 %).
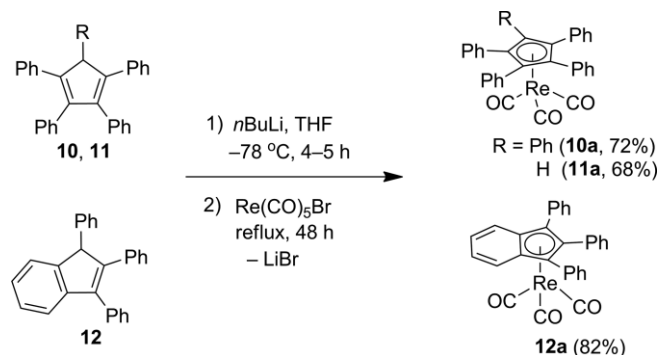
Scheme 4. Synthesis of aryl-substituted Cp'Re(CO)$_3$ complexes **10a**, **11a**, and **12a**.

The analytical data of **10a** and **11a** agree with the previously reported values.[38] Complex **12a** was identified from the disappearance of the (1,2,3-Ph$_3$)Ind–H signal at δ = 5.10 ppm in the ^{1}H NMR spectrum and the shift of the signals of the aromatic

protons to slightly higher field (δ = 6.96–7.36 ppm compared with δ = 7.03–7.43 ppm for **12**). Accordingly, 14 ^{13}C NMR signals were found, including a singlet at δ = 194.14 ppm for the Re–CO moiety, which appeared in a similar range for **10a** (δ = 195.7 ppm) and **11a** (δ = 195.6 ppm). Furthermore, IR bands were observed at $\tilde{v}$ = 1906 and 2011 cm^{-1} for (ReC–O)$_{asym}$ and (ReC–O)$_{sym}$, respectively, for both **11a** and **12a**. The pentaphenyl-appended **10a** has absorptions at slightly higher energies owing to a slight decrease in electron donation compared with those in **11a** and **12a**. Owing to the electron-withdrawing nature of the aryl substituents in **10a**–**12a**, these vibrations are at relatively higher frequencies than those for the alkyl-Cp analogues **1a**–**8a** (vide supra). A similar trend was observed for the ^{13}C NMR signals (δ = 194–196 ppm) of the (Re–CO) moieties in **10a**–**12a** (Table 2).

Crystals suitable for X-ray diffraction were obtained from a solution of **11a** in CH$_2$Cl$_2$/hexane (2:1) at –30 °C and from a CDCl$_3$ solution of **12a** at room temperature. The molecular structures of these complexes display piano-stool conformations similar to those of the alkyl-appended Cp'Re(CO)$_3$ complexes, and the phenyl groups are oriented in propeller-like geometries (Figure 5).[61] The Cp centroid to rhenium (Cp–Re) distances of **11a** and **12a** of 1.9694(11) and 1.9707(10) Å, respectively, are somewhat longer than those in the alkyl-appended complexes (ca. 1.95 Å, Table 1). Similar Cp–Re distances of 1.955, 1.968, and 1.983 Å were reported for the highly electron-poor complexes [Cp(C$_6$F$_5$)$_2$H$_3$]Re(CO)$_3$, [Cp(C$_6$F$_5$)$_3$H$_2$]Re(CO)$_3$, and [Cp(C$_6$F$_5$)$_4$H]Re(CO)$_3$, respectively.[64,65] The ring slippage is somewhat larger in **12a** (Δ = 0.069 Å) than in **11a** (Δ = 0.019 Å). The Re–C(O) and (Re)C–O bond lengths are in the ranges 1.908(2)–1.913(3) and 1.149(3)–1.155(3) Å for **11a** and 1.896(3)–1.927(3) and 1.143(4)–1.151(3) Å for **12a**, respectively. The OC–Re–CO angles are in the range 87.87(12)–92.92(13)°.

Tetraphenylcyclopentadienone (**13**) is a peculiar aryl-substituted proligand, as it contains no acidic Cp–H bond. The reactivity of **13** with an equivalent amount of Re$_2$(CO)$_{10}$ under reflux conditions over 5 d in a mesitylene/xylene (1:1) solvent mixture was studied (Scheme 5). This is a slight modification of the literature procedure for the synthesis of pentabenzylcyclopentadienyl tricarbonyl rhenium.[34] After the completion of the reaction, the purple suspension was centrifuged, and the solvent was decanted to afford an insoluble off-white solid. The IR spectroscopic analysis of this solid strongly suggested the formation of a mixture of rhenium carbonyl species on the basis of the

Table 2. Selected analytical data of aryl-substituted Cp'Re(CO)$_3$.[a]

Cp'Re(CO)$_3$	^{13}C NMR δ(Re–CO) [ppm]	IR (CO) asym, sym $\tilde{v}$ [cm^{-1}]	X-ray crystal structure			
			Cp–Re[b] [Å]	Δ[c] [Å]	Re–C(O) [Å]	OC–Re–CO [°]
10a[d]	195.72	1911, 2012				
11a	195.63	1906, 2012	1.9694(11)	0.019	1.908(2)–1.913(3)	87.99(12)–90.15(10)
12a	194.14	1906, 2011	1.9707(10)	0.069	1.896(3)–1.927(3)	87.87(12)–92.92 (13)
13a[e]	195.67	1910, 2011	1.9588(7)	0.039	1.9152(18)–1.9180(18)	89.67(8)–92.15(8)
			[1.9619(7)]	[0.025]	[1.9081(18)–1.9187(17)]	[87.72(8)–91.35(7)]
14a	194.69	1908, 2013	1.9666(9)	0.035	1.9016(19)–1.914(2)	89.66(9)–90.48(8)

[a] The NMR spectra were recorded with samples in CDCl$_3$. The FTIR spectroscopic data of solid samples were measured under air. [b] Distance between the ring centroid and the metal center. [c] The ring slippage Δ is defined as the distance between the ring centroid and the perpendicular projection of the metal center onto the least-squares plane of the ring. [d] The X-ray data was not available. [e] The X-ray data of a second independent molecule of **13a** are given in brackets.

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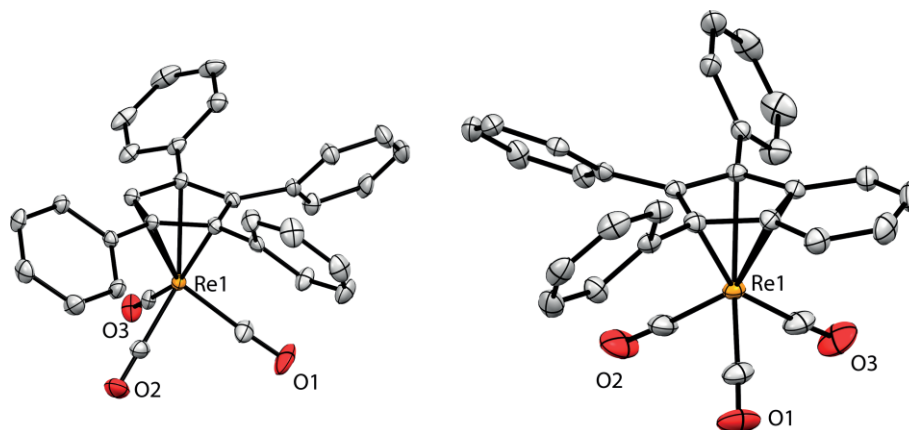EurJIC
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Figure 5. Molecular crystal structures of **11a** (left) and **12a** (right), drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

observation of many different strong Re(C–O) vibrations at $\tilde{v}$ = 1860, 1894, 1913, 1936, 1988, 2014, and 2055 cm^{-1}. The solid did not dissolve in CH$_2$Cl$_2$, CHCl$_3$, acetone, pyridine, or dimethyl sulfoxide (DMSO) and was not analyzed further. The high-boiling solvent mixture (mesitylene/xylene) of the purple solution was removed by distillation, and the residue was subjected to column chromatography. This allowed the recovery of some unreacted purple **13** (17 %) and the isolation of two new products, that is, (hydroxy)tetraphenylcyclopentadienyl tricarbonyl rhenium (**13a**, 32 %) and benzofuran-fused triphenylcyclopentadienyl tricarbonyl rhenium (**14a**, 13 %; Scheme 5). Recrystallization from CH$_2$Cl$_2$/hexane at –30 °C afforded crystals of sufficient quality for X-ray crystallography, which provided a convenient identification of **13a** and **14a** (Figure 6). The presence of a hydroxy moiety in **13a** was further supported by the ^{1}H NMR signal at δ = 4.65 ppm and the (Cp)O–H IR absorption at $\tilde{v}$ = 3525 cm^{-1}.

The asymmetric unit in the X-ray crystal structure of **13a** contains two independent molecules, which contain very small differences in bond lengths [e.g., the Cp centroid to Re distances are 1.9588(7) and 1.9619(7) Å] and bond angles [e.g., the OC–Re–CO angles are 89.67(8)–92.15(8) and 87.72(8)–91.35(7)°]. The ring-slippage values are also slightly different (Δ = 0.039 and 0.025 Å) between these two conformers of **13a**. Similarly to that in **13a**, the Cp ring in **14a** is η^5-bonded with a small ring slippage (Δ = 0.035 Å), but **14a** contains slightly longer
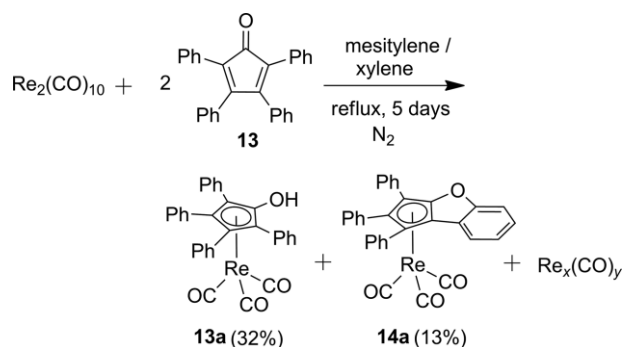
Scheme 5. Synthesis of aryl-substituted Cp′Re(CO)$_3$ complexes **10a**, **11a**, and **12a**.

Cp–Re [1.9666(9) Å] and shorter Re–C(O) distances than those in **13a** (Table 2); therefore, the Cp′ ligand in **14a** is less electron donating than that in **13a**. This can be ascribed to the partial delocalization of the electron density of the Cp moiety into the fused benzofuran ring, similarly to the observation for **12a** owing to the indene ring. The comparatively weak donor strength of the Cp′ ligand in **14a** was further corroborated by a (Re–CO) ^{13}C NMR signal at relatively low field (δ = 194.7 ppm) and the corresponding (ReC–O)$_{sym}$ IR vibration at $\tilde{v}$ = 2013 cm^{-1} (Table 2).
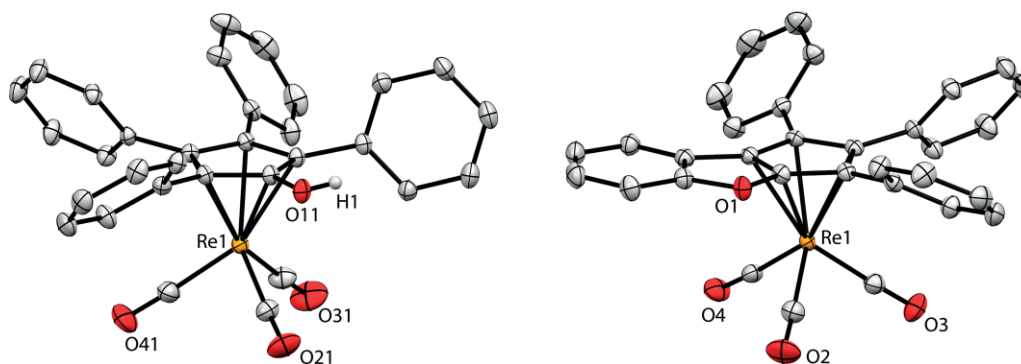

Figure 6. Molecular crystal structures of **13a** (left) and **14a** (right), drawn at the 50 % probability level. Phenyl-bound hydrogen atoms and the CH$_2$Cl$_2$ molecule in the crystal structure of **14a** are omitted for clarity.

The precise mechanism leading to the formation of **13a** and **14a** is not fully understood; the reaction likely proceeds through the thermal dissociation of $Re_2(CO)_{10}$ followed by complexation with **13** to form the π complex **E**, which is an unstable Re^0 species containing 17 valence electrons (Scheme 6).[66,67] Intermediate **E** can likely undergo an intramolecular C–H bond activation to yield the rhenium(III) hydride species **F**. Further, a concerted pathway might occur for the hydrogen abstraction by another molecule of **E** to form **13a** and **G** simultaneously. Complex **14a** is obtained as the final product through a formal reductive coupling in **G**.
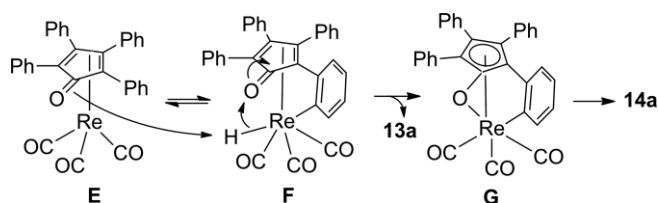
Scheme 6. Proposed pathway for the formation of **13a** and **14a** via the π complex **E**.

To the best of our knowledge, there is no literature precedent for an oxygen-containing five-membered heterocycle (furan) fused with a Cp ring in general for any of the Cp-ligated metal complexes, but an example of an oxygen-containing fused six-membered $Cp'Re(CO)_3$ has been reported.[36] Thiophene- and pyrrole-fused cyclopentadienyl complexes with early transition metals (i.e., Sc, Ti, and Zr) have been reported. For these complexes, the corresponding heterocyclic cyclopentadienes were introduced through conventional deprotonation followed by metalation procedures.[68–71]

Conclusions

A series of multiply substituted cyclopentadienyl-based tricarbonyl rhenium complexes were synthesized as potential precursors for the synthesis of the corresponding trioxorhenium complexes as DODH catalysts.[45] To evaluate structure–activity relationships for the corresponding $Cp'ReO_3$ complexes, the Cp ligands **1**–**8** were used to synthesize the corresponding $Cp'Re(CO)_3$ complexes **1a**–**8a** from $Re_2(CO)_{10}$. Additionally, several $Cp'Re(CO)_3$ complexes incorporating bulky aryl substituents (**10a**–**12a**) were synthesized through the substitution of $Re(CO)_5Br$ with the cyclopentadienyl anion. The X-ray crystal structures of the new complexes $(CptBu_2)Re(CO)_3$ (**2a**), [1,2,3-Me_3(tetrahydroindenyl)]Re(CO)_3 (**7a**), and [1,2,3-Ph_3(indenyl)-Re(CO)_3] **12a** exhibit typical three-legged piano-stool conformations. Furthermore, an unusual [6+4] cycloaddition reactivity of $(CpMe_4)Re(CO)_3$ (**8a**) with excess ligand resulted in a highly asymmetric Cp-ligated **9a**. When the tetraphenylcyclopentadienone ligand was used in conjunction with $Re_2(CO)_{10}$, a formal intermolecular hydrogen transfer resulted in the serendipitous formation of the Shvo-type complex $[Ph_4Cp(OH)]Re(CO)_3$ (**13a**) and the benzofuran-fused $[Ph_3Cp(C_6H_4O)]Re(CO)_3$ (**14a**) product.

From the ReC–O IR absorption bands of the alkyl-appended (Me, *i*Pr, or *t*Bu) $Cp'Re(CO)_3$ complexes, an increase in the electron-donating properties of the Cp' ligand was found when more substituents were attached directly to the Cp ring, whereas the opposite was observed for the phenyl-appended complexes, that is, the electron-donating properties decreased with an increased number of substituents. The variations in the electronics and bulkiness of the $Cp'Re(CO)_3$ complexes reported in this article have allowed us to study the performance of a series of new $Cp'ReO_3$ complexes in catalytic DODH reactions, which has provided valuable insights towards the rational development of Cp-based trioxorhenium catalysts.[45]

Experimental Section

General Considerations: All chemicals including the rhenium compounds were degassed either by exposure to a vacuum or freeze–pump–thaw cycles. All reactions were performed under an inert N_2 atmosphere by standard Schlenk techniques. Benzene, xylene, mesitylene, and THF were distilled with Na/benzophenone. Hexane was obtained from an MBraun MB SPS-800 solvent purifier and stored over 4 Å molecular sieves. Unless otherwise stated, all other commercial chemicals were used without further purification. The compounds di-*tert*-butylcyclopentadiene (**2**), pentamethylcyclopentadiene (**5**), ethyltetramethylcyclopentadiene (**6**), tetramethylcyclopentadiene (**8**), and $Re(CO)_5Br$ were received from Aldrich, and $Re_2(CO)_{10}$ was received from Acros. The NMR spectra were recorded with a Varian VNMRS400 spectrometer (400 MHz) at 298 K. The IR spectra were recorded with a Perkin–Elmer Spectrum One FTIR spectrometer in the wavenumber range 650–4000 cm^{-1}. The ESI-MS spectra were recorded with a Waters LCT Premier XE instrument.

(CptBu$_2$H$_3$)Re(CO)$_3$ (2a): In a dried Schlenk flask, $Re_2(CO)_{10}$ (1.3629 g, 2.09 mmol) was degassed under vacuum for 30 min, and di-*tert*-butylcyclopentadiene (883 mg, 4.67 mmol, 1.2 equiv.) was added. The reaction system was connected to a gas bubbler to allow the release of the formed CO. The reaction mixture was heated at 150 °C for 30 min, and subsequently the temperature was increased to 200 °C and maintained for 19 h, during which the reaction mixture turned into a dark brown suspension. After cooling to ambient temperature, a sample was analyzed by TLC, which showed the presence of some unreacted $Re_2(CO)_{10}$ and the formation of the desired product. The reaction mixture was then dissolved in hexane and separated by silica column chromatography with hexane as the eluent. The column fractions containing the product only were combined and dried in vacuo to yield the product as a white crystalline solid (1.662 g, 3.713 mmol, 89 %). ^{1}H NMR (400 MHz, 25 °C, CDCl$_3$): δ = 1.21 (s, 18 H, *t*Bu), 5.16 (d, $^4J_{H,H}$ = 2 Hz, 2 H, Cp–H), 5.33 (t, $^4J_{H,H}$ = 2 Hz, 1 H, Cp–H) ppm. ^{1}H NMR (400 MHz, 25 °C, C$_6$D$_6$): δ = 0.985 (s, 18 H, *t*Bu), 4.62 (d, $^4J_{H,H}$ = 2 Hz, 2 H, Cp–H), 5.07 (t, $^4J_{H,H}$ = 2 Hz, 1 H, Cp–H) ppm. ^{13}C NMR (400 MHz, 25 °C, CDCl$_3$): δ = 31.20, 32.17, 76.84, 80.63, 81.92, 120.02, 195.85 ppm. FTIR: $\tilde{v}$ = 669, 843, 890, 920, 1031, 1059, 1113, 1166, 1201, 1252, 1295, 1364, 1396, 1446, 1465, 1485, 1889, 2007, 2419, 2872, 2908, 2970, 3115, 3895 cm^{-1}. ESI-MS (CH$_2$Cl$_2$): calcd. for C$_{16}$H$_{21}$ClReO$_3$ [M + Cl]$^+$ 483.0728; found 483.0769; this cationic Re^{III} species containing Re–Cl is formed inside the spectrometer through the facile oxidation of **2a**. C$_{16}$H$_{21}$O$_3$Re (448.10): calcd. C 42.94, H 4.73; found C 42.95, H 4.29.

Improved Synthesis of (CptBu$_3$H$_2$)Re(CO)$_3$ (1a): In a similar reaction procedure to that for **2a**, $Re_2(CO)_{10}$ (1.0 g, 1.53 mmol) was degassed under vacuum for 30 min, and 1,2,4-tri-*tert*-butylcyclopentadiene (1.65 mL, 6.19 mmol) was added under N$_2$. After the completion of the reaction (150 °C for 0.5 h, 200 °C for 1 h, and

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210 °C for 6 h), purification by silica column chromatography with hexane as the eluent afforded **2a** (1.23 g, 2.45 mmol, 80 %). The analytical data matched those reported.[23]

Mixture of 1,2,4-(Cp*i*Pr₃H₂)Re(CO)₃ (3a) and 1,2,3-(Cp*i*Pr₃H₂)-Re(CO)₃ (4a): In a dried Schlenk flask, Re₂(CO)₁₀ (1.6418 g, 2.516 mmol) was degassed in vacuo for 30 min, and then a mixture of 1,2,4-triisopropylcyclopentadiene and 1,2,3-triisopropylcyclo-pentadiene (2.830 g, 14.71 mmol, 3.0 equiv. based on Re) was added. The reaction mixture was immersed in a preheated oil bath at 150 °C and heated for 2 h. Subsequently, the temperature was increased to 200 °C and maintained for 20 h and eventually to 210 °C for another 2.5 h. After cooling to ambient temperature, a dark brown liquid reaction mixture was obtained. A sample was analyzed by TLC, which showed the full conversion of Re₂(CO)₁₀ and the formation of new products. The crude reaction mixture was then concentrated in vacuo and separated by silica column chroma-tography with petroleum ether as the eluent. A colorless, viscous liquid product was obtained (2.1183 g, 4.590 mmol, 94 %). The ^{1}H and ^{13}C NMR spectroscopic analysis revealed a mixture of isomers **3a** and **4a** in a ratio of 0.73:0.27. ^{1}H NMR (400 MHz, 25 °C, CDCl₃): δ = 1.11 (s, 6 H, Me, **3a**), 1.17–1.13 (four overlapping doublets, no splitting was observed, 12 H, Me, **4a/3a**), 1.37 (s, 6 H, Me, **3a**), 2.61 (sept, $^3J_{H,H}$ = 6.8 Hz, 1 H, C*H*Me₂, **3a**), 2.66 (sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, C*H*Me₂, **3a**), 2.79 (two overlapping septets, $^3J_{H,H}$ = 6.8 Hz, 3 H, C*H*Me₂, **4a**), 4.99 (s, 2 H, Cp–H, **4a**), 5.22 (s, 2 H, Cp–H, **3a**) ppm. ^{1}H NMR (400 MHz, 25 °C, C₆D₆): δ = 0.88 (s, 6 H, Me, **4a**), 0.89 (s, 6 H, Me, **3a**), 0.91 (s, 6 H, Me, **3a**), 0.97 (s, 6 H, Me, **4a**), 1.01 (s, 6 H, Me, **3a**), 1.13 (s, 6 H, Me, **4a**), 2.24 (sept, $^3J_{H,H}$ = 6.8 Hz, 1 H, C*H*Me₂, **3a**), 2.31 (sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, C*H*Me₂, **3a**), 2.40 (sept, $^3J_{H,H}$ = 6.8 Hz, 1 H, C*H*Me₂, **4a**), 2.44 (sept, $^3J_{H,H}$ = 6.8 Hz, 2 H, C*H*Me₂, **4a**), 4.47 (s, 2 H, Cp–H, **4a**), 4.91 (s, 2 H, Cp–H, **3a**) ppm. ^{13}C NMR (400 MHz, 25 °C, CDCl₃): δ = 24.35, 24.71, 25.38, 25.60, 25.69, 25.85, 25.92, 26.05, 26.29, 26.83, 53.57, 79.78, 81.13, 110.02, 110.99, 113.30, 118.05, 196.33, 196.55 ppm. FTIR [attenuated total reflectance (ATR)]: $\tilde{v}$ = 511, 596, 722, 823, 887, 1011, 1025, 1205, 1271, 1367, 1385, 1461, 1892, 2007, 2968 cm^{-1}. ESI-MS (CH₃CN with pyridine and HCOOH as additives): calcd. for C₁₇H₂₄O₃Re [M + H]$^+$ 463.1284; found 463.1319. C₁₇H₂₃O₃Re (462.12): calcd. C 44.24, H 5.02; found C 44.36, H 4.99.

[1,2,3-Me₃(tetrahydroindenyl)]Re(CO)₃ (7a): In a dried Schlenk flask, Re₂(CO)₁₀ (0.944 g, 1.447 mmol) was degassed in vacuo for 30 min, and 1,2,3-trimethyl-4,5,6,7-tetrahydroindene (0.767 g, 4.730 mmol, 1.6 equiv. based on Re) was added. The reaction mix-ture was immersed in a preheated oil bath at 150 °C and heated for 30 min. Subsequently, the temperature was increased to 200 °C and maintained for 17 h and then to 210 °C for another 3 h. After cooling to ambient temperature, a dark brown solidified reaction mixture was obtained. A sample was analyzed by TLC, which showed full conversion of Re₂(CO)₁₀ and the formation of a new product. The crude reaction mixture was then dissolved in hexane, and separated by silica column chromatography with petroleum ether as the eluent to afford **7a** (98 %). The collected product frac-tion was recrystallized from hexane at –30 °C to yield a white, crys-talline product (1.076 g, 2.501 mmol, 86 %). ^{1}H NMR (400 MHz, 25 °C, CDCl₃): δ = 1.67 (br m, 2 H, CH₂ *exo*), 1.78 (br m, 2 H, CH₂ *endo*), 2.13 (s, 6 H, Me), 2.18 (s, 3 H, Me), 2.58 (br m, 2 H, Cp–CH₂ *exo*), 2.68 (br m, 2 H, Cp–CH₂ *endo*) ppm. ^{1}H NMR (400 MHz, 25 °C, C₆D₆): δ = 1.29 (br m, 2 H, CH₂ *exo*), 1.48 (br m, 2 H, CH₂ *endo*), 1.71 (s, 6 H, Me), 1.75 (s, 3 H, Me), 2.01 (br m, 2 H, Cp–CH₂ *exo*), 2.36 (br m, 2 H, Cp–CH₂ *endo*) ppm. ^{13}C NMR (400 MHz, 25 °C, CDCl₃): δ = 10.55, 10.58, 22.29, 23.05, 77.361, 95.42, 100.15, 102.00, 198.45 ppm. IR (KBr): $\tilde{v}$ = 752, 817, 853, 909, 953, 1034, 1069, 1106, 1147, 1181, 1244, 1258, 1330, 1345, 1378, 1384, 1442, 1884, 1995, 2408, 2508,

2857, 2923, 2943, 3788, 3879 cm^{-1}. ESI-MS (THF): calcd. for [M – H]$^+$ 431.0657; found 431.0665; this dehydrogenated cationic Re^I species indicates the possible modification of the Cp ligand into a fulvene analogue.

(CpMe₄H)Re(CO)₃ (8a): In a dried Schlenk flask, Re₂(CO)₁₀ (1.5 g, 2.3 mmol) was degassed in vacuo for 30 min, and an excess of tetramethylcyclopentadiene (1.27 mL, 8.43 mmol, 1.83 equiv.) was added. The resulting mixture was heated at 150 °C for 40 min. At regular time intervals, the reaction temperature was increased to reach 210 °C in 5 h (i.e., the temperature was raised to 165, 180, 200, and 210 °C after each 1 h). The reaction mixture was kept at 210 °C to allow the complete conversion of the Re₂(CO)₁₀. After cooling to ambient temperature, a sample of the solidified reaction mixture was analyzed by TLC with hexane, which showed the com-plete conversion of Re₂(CO)₁₀ and the formation of a new product. The crude reaction mixture was dissolved in CH₂Cl₂ and subjected to silica column chromatography: hexane was used as the first elu-ent to collect an organic fraction containing mainly the unreacted ligand (2.34 mmol), and elution with CH₂Cl₂/hexane (1:3) afforded **8a** as an off-white solid in nearly quantitative yield (>98 %). The analytical data matched the literature values of **8a** prepared by the reactions of Re(CO)₅Cl with NaCp or TlCp.[31,44] ^{1}H NMR (400 MHz, CDCl₃): δ = 2.155 (s, 6 H, Me), 2.158 (s, 6 H, Me), 4.99 (s, 1 H, CpH) ppm. ^{13}C NMR (400 MHz, CDCl₃): δ = 10.8, 12.42, 80.69, 99.87, 101.12, 197.37 ppm. FTIR (ATR): $\tilde{v}$ = 692, 823, 1033, 1382, 1447, 1887, 2005, 2924, 2960 cm^{-1}. ESI-MS (CH₂Cl₂): calcd. for C₁₃H₁₃ClO₃Re [M + Cl]$^+$ 427.0111; found 426.9627; this cationic Re^{III} species contain-ing Re–Cl formed inside the spectrometer through the facile oxid-ation of **8a**.

(C₁₉H₂₅)Re(CO)₃ (9a): In a dried Schlenk flask, Re₂(CO)₁₀ (1.5 g, 2.3 mmol) was degassed in vacuo for 30 min, and an excess of tetramethylcyclopentadiene (1.27 mL, 8.43 mmol, 1.83 equiv.) was added. Then the mixture was heated for 11 h (150, 165, 190, 200, and 210 °C for 1, 1, 6, 1.5, and 1.5 h, respectively). After cooling to ambient temperature, the reaction mixture was repeatedly ex-tracted into hexane (3 × 5 mL) from an insoluble white solid. Then, the concentrated hexane fractions were purified by column chro-matography to afford **8a** (2.77 mmol, 60 %). The insoluble white solid **9a** was obtained in 7 % yield (0.16 g, 0.314 mmol) after drying. Recrystallization in CH₂Cl₂/hexane (2:1, 0.7 mL) at –30 °C gave crys-tals of **9a** suitable for X-ray analysis. ^{1}H NMR (400 MHz, CDCl₃): δ = 1.13 (s, 3 H, Me), 1.44 (s, 3 H, Me), 1.49 (d, $^4J_{H,H}$ = 0.8 Hz, 3 H, Me), 1.57 (d, $^4J_{H,H}$ = 1.2 Hz, 3 H, Me), 1.60 (dd, ^2J = 10.4 Hz, ^4J = 1.6 Hz, 1 H, CH₂), 1.965 (d, ^2J = 10.4 Hz, 1 H, CH₂), 2.06 (s, 3 H, Me), 2.13 (s, 3 H, Me), 2.275 (dd, ^2J = 15.6 Hz, ^4J = 1.6 Hz, 1 H, CH₂), 2.29 (s, 3 H, Me), 2.49 (d, ^2J = 15.6 Hz, 1 H, CH₂) ppm. ^{13}C NMR (400 MHz, CDCl₃): δ = 9.21, 10.58, 10.85, 11.01, 12.63, 20.83, 23.74, 31.55, 45.29, 47.22, 58.5, 95.40, 95.80, 99.25, 101.83, 110.87, 133.75, 141.88, 198.65 ppm. FTIR (ATR): $\tilde{v}$ = 472, 511, 594, 803, 1260, 1381, 1442, 1677, 1889, 1994, 2864, 2922, 2961 cm^{-1}. ESI-MS (CH₂Cl₂): calcd. for C₂₁H₂₅ClO₃Re [M + Cl]$^+$ 547.105; found 547.0965; this cationic Re^{III} species containing Re–Cl formed inside the spectrometer through the facile oxidation of **9a**.

[1,2,3-Ph₃(indenyl)]Re(CO)₃ (12a): 1,2,3-Triphenylindene (**12**, 2 g, 5.81 mmol) was degassed for 30 min in a dried Schlenk flask, and THF (50 mL) was added. The homogeneous solution was cooled to –78 °C, and *n*BuLi (1.6 M in hexanes, 4 mL) was added dropwise. The deprotonation reaction proceeded for 3.5 h at –78 °C; the reac-tion mixture was then warmed to ambient temperature, and Re(CO)₅Br (2.36 g, 5.81 mmol) was added. The reaction mixture was heated to reflux for 2 d, after which the THF was evaporated, and the product mixture was extracted into CH₂Cl₂. After solvent evapo-

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ration, the NMR spectrum showed a small amount of unreacted **12** (16 %), which was removed by silica column chromatography with CH_2Cl_2/hexane (1:1) as the eluent to afford **12a** as light yellowish off-white solid (2.92 g, 82 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95–7.64 (m, 19 H, Ph) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 94.36, 106.45, 116.83, 123.04, 126.75, 127.89, 128. 03, 128. 21, 128.73, 130. 41, 131.96, 132.00, 132.81, 194.14 ppm. FTIR (ATR): $\tilde{v}$ = 698, 742, 756, 798, 1028, 1073, 1393, 1443, 1503, 1906, 1928, 2011 cm^{-1}. ESI-MS (CH_3CN): calcd. for $C_{30}H_{19}ReO_3$ [M]$^+$ 614.0893; found 614.0889.

[CpPh$_4$(OH)]Re(CO)$_3$ (13a) and [CpPh$_3$(C$_6$H$_4$O)]Re(CO)$_3$ (14a): In a dried Schlenk flask, $Re_2(CO)_{10}$ (3.26 g, 5 mmol) and tetraphenyl-cyclopentadienone **13** (1 mL, 2 mmol) were degassed in vacuo for 30 min. Then, the distilled solvents mesitylene (50 mL) and xylene (50 mL) were added, and the mixture was heated gently under reflux (170 °C) for 5 d. The reaction progress was monitored through the release of CO gas from an overpressure valve containing silicone oil. After the CO release ceased, TLC showed an incomplete conversion of **13** and the presence of two new products. The purple suspension was centrifuged, and the solvent was decanted to remove the off-white solid. The solvent from the purple solution was removed through vacuum distillation. Then, silica column chromatography with CH_2Cl_2/hexane (1:1) afforded **13 (**17 %, 0.652 g) together with **13a** (2.09 g, 32 %) and **14a** (0.8296 g, 13 %). Recrystallization of both **13a** and **14a** was performed in CH_2Cl_2/hexane (2:1) at –30 °C. Complex **14** cocrystallized with CH_2Cl_2, which was removed completely by the solvent evaporation of a hexane solution of **14**. The off-white solid did not dissolve in $CDCl_3$, acetone, DMSO, benzene, or pyridine, and the IR spectrum showed multiple carbonyl vibrations, indicating a mixture of rhenium carbonyls. FTIR (ATR): $\tilde{v}$ = 683, 695, 746, 799, 832, 1921, 1105, 1233, 1375, 1437, 1504, 1860, 1894, 1913, 1936, 1988, 2014, 2055 cm^{-1}. Elemental analysis: found C 37.62, H 2.09, O 25.99. Complex **13a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.65 (s, 1 H, CpOH), 6.90–7.32 (m, 20 H, Ph) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 89.46, 102.36, 127.92, 127.96, 128.40, 128.88, 129.86, 130.52, 132.27, 132.60, 135.13, 195.67 ppm. FTIR (ATR): $\tilde{v}$ = 698, 708, 744, 755, 795, 921, 1027, 1072, 1100, 1125, 1159, 1184, 1273, 1290, 1432, 1505, 1601, 1910, 2011, 3525 cm^{-1}. ESI-MS (CH_3CN): calcd. for [M – H]$^-$ $C_{32}H_{20}ReO_4$ 655.0921; found 655.0913. $C_{32}H_{21}O_4Re$ (656.10): calcd. C 58.61, H 3.23; found C 58.79, H 3.35. Complex **14a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16–7.67 (m, 19 H, Ph) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 83.61, 90.01, 93.63, 106.31, 113.11, 121.28, 123.16, 124.21, 127.49, 128.02, 128.40, 128.45, 128.50, 128.56, 128.59, 130.13, 130.26, 130.70, 130.92, 131.36, 133.11, 140.27, 161.93, 194.69 ppm. FTIR (ATR): $\tilde{v}$ = 692, 714, 736, 751, 844, 1185, 1399, 1908, 2013 cm^{-1}. ESI-MS (CH_3CN): calcd. for [M]$^+$ $C_{32}H_{19}ReO_4$ 654.0841 found 654.0728. $C_{32}H_{19}O_4Re$ (654.08): calcd. C 58.76, H 2.93; found C 58.89, H 2.95.

Compound 2a: $C_{16}H_{21}O_3Re$, Fw = 447.53, colorless plate, 0.40 × 0.22 × 0.07 mm, orthorhombic, *Pbca* (no. 61), *a* = 11.6695(3), *b* = 15.9645(4), *c* = 17.3621(5) Å, *V* = 3234.52(15) Å^3, *Z* = 8, $D_{calcd.}$ = 1.838 g/cm^3, μ = 7.52 mm^{-1}. 57658 reflections were measured with a Bruker Kappa ApexII diffractometer with a sealed tube and a Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin $\theta/\lambda)_{max}$ = 0.70 Å^{-1}. The intensity data were integrated with the Eval15 software.[75] Analytical absorption correction and scaling were performed with SADABS[81] (correction range 0.15–0.62). 4716 reflections were unique (R_{int} = 0.019), of which 4355 were observed [$I > 2\sigma(I)$]. The structure was solved with the program SHELXT.[76] Least-squares refinement against F^2 for all reflections was performed with SHELXL-2013.[77] Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps. Hydrogen atoms H2, H4, and H5 of the Cp ring were refined freely

with isotropic displacement parameters. The methyl hydrogen atoms were refined with a riding model. 200 parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0111/0.0251. R_1/wR_2 (all reflections): 0.0128/0.0255. S = 1.055. Extinction parameter EXTI = 0.000354(16). Residual electron density between –0.42 and 0.40 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[48]

Compound 7a: $C_{15}H_{17}O_3Re$, Fw = 431.48, colorless plate, 0.58 × 0.27 × 0.10 mm, triclinic, *P*$\bar{1}$ (no. 2), *a* = 6.90487(4), *b* = 7.8670(2), *c* = 14.2039(3) Å, α = 75.313(2), β = 83.540(2), γ = 72.486°, *V* = 711.20(3) Å^3, *Z* = 2, $D_{calcd.}$ = 2.015 g/cm^3, μ = 8.54 mm^{-1}. 14136 reflections were measured with a Bruker Kappa ApexII diffractometer with a sealed tube and a Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin $\theta/\lambda)_{max}$ = 0.70 Å^{-1}. The intensity data were integrated with the Eval15 software.[75] Analytical absorption correction and scaling were performed with SADABS[81] (correction range 0.13–0.65). 4124 reflections were unique (R_{int} = 0.013), of which 4080 were observed [$I > 2\sigma(I)$]. The structure was solved with the program SHELXT.[76] Least-squares refinement against F^2 for all reflections was performed with SHELXL-2013.[77] Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. 176 parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0089/0.0220. R_1/wR_2 (all reflections): 0.0092/0.0221. S = 1.174. Extinction parameter EXTI = 0.0045(2). Residual electron density between –0.52 and 0.49 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[48]

Compound 9a: $C_{21}H_{25}O_3Re$, Fw = 511.61, colorless block, 0.45 × 0.41 × 0.17 mm, monoclinic, *Pn* (no. 7), *a* = 9.4758(7), *b* = 7.1045(5), *c* = 14.3536(10) Å, β = 103.3716(9)°, *V* = 940.10(12) Å^3, *Z* = 2, $D_{calcd.}$ = 1.807 g/cm^3, μ = 6.48 mm^{-1}. 14639 reflections were measured with a Bruker Kappa ApexII diffractometer with a sealed tube and a Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin $\theta/\lambda)_{max}$ = 0.64 Å^{-1}. The intensity data were integrated with the Saint software.[72] Analytical absorption correction and scaling were performed with SADABS[81] (correction range 0.19–0.47). 4301 reflections were unique (R_{int} = 0.013), of which 4289 were observed [$I > 2\sigma(I)$]. The structure was solved by direct methods with the program SIR2011.[78] Least-squares refinement against F^2 for all reflections was performed with SHELXL-97.[74] Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. 235 parameters were refined with two restraints (floating origin). R_1/wR_2 [$I > 2\sigma(I)$]: 0.0087/0.0218. R_1/wR_2 (all reflections): 0.0088/0.0218. S = 1.143. Extinction parameter EXTI = 0.00282(15). Flack parameter[79] x = 0.045(4). Residual electron density between –0.49 and 0.62 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[48]

Compound 11a: $C_{32}H_{21}O_3Re$, Fw = 639.69, colorless plate, 0.42 × 0.27 × 0.06 mm, monoclinic, *P*2$_1$/*c* (no. 14), *a* = 10.6960(3), *b* = 8.3778(3), *c* = 27.2134(9) Å, β = 90.046(3)°, *V* = 2438.58(14) Å^3, *Z* = 4, $D_{calcd.}$ = 1.742 g/cm^3, μ = 5.02 mm^{-1}. 40663 reflections were measured with a Bruker Kappa ApexII diffractometer with a sealed tube and a Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin $\theta/\lambda)_{max}$ = 0.64 Å^{-1}. The intensity data were integrated with the Eval15 software.[75] Analytical absorption correction and scaling were performed with SADABS[81] (correction range 0.26–0.77). 5585 reflections were unique (R_{int} = 0.029), of which 5500 were observed [$I > 2\sigma(I)$]. The structure

was solved by Patterson methods with the program DIRDIF-08.[73] Least-squares refinement against F^2 for all reflections was performed with SHELXL-97.[74] The structure was refined as a pseudo-orthorhombic twin with a twofold rotation about hkl = (0,0,1) as the twin operation. The twin fraction refined to BASF = 0.3203(4). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps. Hydrogen atom H5 of the Cp ring was refined freely with an isotropic displacement parameter. The phenyl hydrogen atoms were refined with a riding model. 330 parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0131/0.0331. R_1/wR_2 (all reflections): 0.0135/0.0333. S = 1.074. Residual electron density between –0.67 and 0.51 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[48]

Compound 12a: $C_{30}H_{19}O_3Re$, Fw = 613.65, pale yellow block, 0.54 × 0.52 × 0.33 mm, orthorhombic, $P2_12_12_1$ (no. 19), a = 8.4824(3), b = 11.6544(2), c = 26.8796(12) Å, V = 2343.97(14) Å^3, Z = 4, $D_{calcd.}$ = 1.739 g/cm^3, μ = 5.21 mm^{-1}. 40664 reflections were measured with a Bruker Kappa ApexII diffractometer with a sealed tube and a Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.64 Å^{-1}. The intensity data were integrated with the Eval15 software.[75] Multiscan absorption correction and scaling were performed with SADABS[81] (correction range 0.28–0.43). 5372 reflections were unique (R_{int} = 0.021), of which 5348 were observed [$I > 2\sigma(I)$]. The structure was solved by direct methods with the program SHELXS-97.[74] Least-squares refinement against F^2 for all reflections was performed with SHELXL-97.[74] Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. 308 parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0135/0.0343. R_1/wR_2 (all reflections): 0.0136/0.0343. S = 1.130. Flack parameter[79] x = –0.004(5). Residual electron density between –0.81 and 0.94 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[48]

Compound 13a: $C_{32}H_{21}O_4Re$, Fw = 655.69, colorless needle, 0.54 × 0.26 × 0.09 mm, monoclinic, $P2_1/c$ (no. 14), a = 24.2037(6), b = 9.7144(3), c = 24.4980(7) Å, β = 118.953(1)°, V = 5040.2(2) Å^3, Z = 8, $D_{calcd.}$ = 1.728 g/cm^3, μ = 4.86 mm^{-1}. 190906 reflections were measured with a Bruker Kappa ApexII diffractometer with a sealed tube and a Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.81 Å^{-1}. The intensity data were integrated with the Eval15 software.[75] Analytical absorption correction and scaling were performed with SADABS[81] (correction range 0.21–0.66). 22188 reflections were unique (R_{int} = 0.022), of which 19198 were observed [$I > 2\sigma(I)$]. The structure was solved by Patterson methods with the program DIRDIF-08.[73] Least-squares refinement against F^2 for all reflections was performed with SHELXL-97.[74] Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps. Hydrogen atoms H1 and H2 of the hydroxy groups were refined freely with isotropic displacement parameters. The phenyl hydrogen atoms were refined with a riding model. 675 parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0202/0.0407. R_1/wR_2 (all reflections): 0.0271/0.0419. S = 1.066. Residual electron density between –1.07 and 2.33 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[48]

Compound 14a: $C_{32}H_{19}O_4Re\cdot CH_2Cl_2$, Fw = 738.60, colorless plate, 0.40 × 0.36 × 0.09 mm, triclinic, $P\bar{1}$ (no. 2), a = 9.6823(3), b = 9.7837(3), c = 16.5718(6) Å, α = 88.296(2), β = 74.297(2), γ = 68.637(2)°, V = 1403.25(8) Å^3, Z = 2, $D_{calcd.}$ = 1.748 g/cm^3, μ =

4.56 mm^{-1}. 24805 reflections were measured with a Bruker Kappa ApexII diffractometer with a sealed tube and a Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.64 Å^{-1}. The crystal was cracked into three fragments. Consequently, three orientation matrices were used for the integration of the intensity data with the Eval15 software.[75] Multiscan absorption correction and scaling were performed with TWINABS[81] (correction range 0.30–0.43) to produce an HKLF5 file.[80] 6438 reflections were unique (R_{int} = 0.018), of which 6172 were observed [$I > 2\sigma(I)$]. The structure was solved with the program SHELXT.[76] Least-squares refinement against F^2 for all reflections was performed with SHELXL-97.[74] Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. 363 parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0142/0.0339. R_1/wR_2 (all reflections): 0.0152/0.0342. S = 1.050. Batch scale factors for the second and third crystal fragment BASF = 0.197(4), 0.062(3). Residual electron density between –1.26 and 0.81 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[48]

CCDC 1455202 (for **2a**), 1455203 (for **7a**), 1455204 (for **9a**), 1455205 (for **11a**), 1455206 (for **12a**), 1455207 (for **13a**), and 1455208 (for **14a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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