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# The reactivity of complexed carbocycles XII: mono- and dimetallic cyclooctatetraene complexes of manganese and rhenium: synthesis, structure and dynamic behaviour☆

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**Abstract**

On irradiation of $C_5Me_5Re(CO)_3$ in the presence of $C_8H_8$, complexes $C_5Me_5Re(CO)_2(\eta^2\text{-}C_8H_8)$ (**1**) as well as $C_5Me_5Re(\eta^6\text{-}C_8H_8)$ (**2**) are formed. The latter was characterised by a crystal structure analysis. The reaction of $K_2[C_8H_8]$ with $[ReBr(CO)_3(THF)_2]$ yields a dimetallic complex $(CO)_3Re(\mu\text{-}C_8H_8)Re(CO)_3$ (**3**), which has a *syn*-bridging structure and is fluxional in solution. The manganese complex $(\eta^5\text{-}C_8H_9)Mn(CO)_3$ can be deprotonated to give the anion $[\eta^4\text{-}C_8H_8)Mn(CO)_3]^-$, which is used as a building block for heterodimetallic complexes. It reacts with cationic 12-electron fragments $[L_nM]^+$ to give dimetallic compounds $[(CO)_3Mn(\mu\text{-}C_8H_8)ML_n]$. These complexes have either *syn*- or *anti*-bridging structures. Both structural types exhibit dynamic behaviour in solution. The carbonyl groups of complex $(CO)_3Mn(\mu\text{-}C_8H_8)Rh(CO)_2$ were labelled with $^{13}CO$ and shown to undergo very slow intermetallic scrambling. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Cyclooctatetraene; Manganese; Rhenium; Dimetallic complexes; Bridging ligands

## 1. Introduction

While the cyclopentadienyl ligand is by far the most ubiquitous π-complexed ligand in organometallic chemistry, cyclooctatetraene (COT) is certainly the most versatile. It can exhibit a surprising number of coordination modes in mono- as well as dimetallic complexes, the more simple ones being $\eta^2$, $\eta^4$, $\eta^6$ and $\eta^8$ in monometallic complexes [1,2]. In dimetallic complexes, other coordination modes such as $\eta^3$–$\eta^3$, or $\eta^3$–$\eta^5$ or $\eta^5$–$\eta^5$ among others have been observed, both *cisoid* and *transoid* complexes being possible. In addition, COT complexes show a wide variety of fluxional behaviour in both monomeric as well as dimeric compounds [1–6]. These complexes also sometimes have unique electrochemical properties [7,8].

The family of dimetallic complexes of general composition $[C_5H_5M_1(\mu\text{-}C_8H_8)M_2C_5H_5]^{x+}$ ($x = 0, 1, 2$) is quite extensive, incorporating metals from vanadium to rhodium. In the neutral homodimetallic series $C_5H_5M(\mu\text{-}C_8H_8)MC_5H_5$ (M = V, Cr, Ru, Co, Rh), the number of valence electrons ranges from 28 to 36, with both variants of *syn*- and *anti*-bridging being known. Decreasing number of valence electrons leads to more closed structures. This trend is noticeable already from the structural changes which accompany the oxidation of $C_5H_5Rh(\mu\text{-}C_8H_8)RhC_5H_5$, for which both *syn* and *anti* isomers are known [5] and continues with dramatic results in the oxidation of $C_5H_5Ru(\mu\text{-}C_8H_8)RuC_5H_5$, with an unprecedented ring-opening and concurrent formation of a metal–metal bond [8]. A further increase in electron deficiency, as in the chromium and

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

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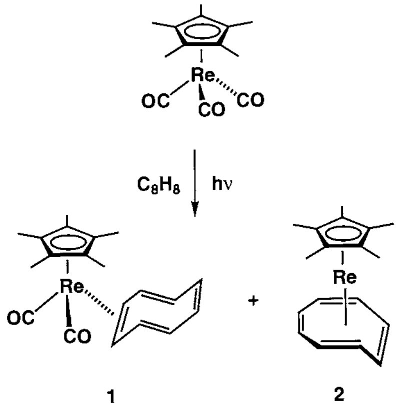
vanadium complexes, completes the change from *anti*- to *syn*-coordination of the two $C_5H_5M$ units. The only missing homodimetallic compounds in this series are those of manganese and rhenium. Their isoelectronic heterodimetallic analogue $C_5H_5Cr(\mu\text{-}C_8H_8)FeC_5H_5$ exhibits a *syn*-structure with a $\eta^4$–$\eta^4$-coordination of the bridging ring [9].

Interestingly enough, very little in general is known about COT complexes of the group 7 metals, not even in monomeric form. We therefore explored several synthetic routes for the synthesis of dimetallic complexes with bridging cyclooctatetraene, starting from various monometallic precursors.

## 2. Results and discussion

A possible route into the chemistry of $C_5R_5M(\mu\text{-}C_8H_8)MC_5R_5$ (M = Mn, Re) consists in the irradiation of $C_5R_5M(CO)_3$ in the presence of cyclooctatetraene. A survey of the literature reveals that irradiation of $C_5H_5Mn(CO)_3$ with $C_8H_8$ gives the highly unstable product $C_5H_5MnC_8H_8$, which could only be characterized at very low temperatures [10]. No evidence for formation of a dimetallic compound is given. A similar irradiation of $C_5Me_5Mn(CO)_3$ produces $C_5Me_5MnC_8H_8$, a compound that is stable at room temperature and could be characterised by a crystal structure analysis [11]. Again, no evidence is presented for the possible formation of a dimetallic compound. Both authors state that similar irradiation experiments with $C_5H_5Re(CO)_3$ or $C_5Me_5Re(CO)_3$ were unsuccessful, in contrast to the observation of Orpen that irradiation of $C_5Me_5Re(CO)_3$ in benzene produced low yields of $C_5Me_5ReC_6H_6$ as well as a dimetallic product $C_5Me_5Re(C_6H_6)ReC_5Me_5$, with an unusal $\mu$–$\eta^2$–$\eta^2$-bridging mode for benzene [12].

We therefore attempted irradiation of $C_5Me_5Re(CO)_3$ with UV light in the presence of COT. The solution slowly evolved carbon monoxide and the colour changed from colourless to yellow, then orange. After chromatographic workup, we were able to isolate two products, identified as $C_5Me_5Re(CO)_2(\eta^2\text{-}C_8H_8)$ (**1**) and $C_5Me_5Re(\eta^6\text{-}C_8H_8)$ (**2**) as yellow and orange crystals, respectively (Scheme 1).



Scheme 1.

On using a 125 W lamp, the predominant product is **1**, while irradiation with a 150 W lamp produced **2** as the major product. Both products are stable at room temperature. The $^{13}C$-NMR spectrum of **2** showed sharp signals with three resonances for coordinated olefins ($\delta = 56.9$, 79.6 and 88.5) and one for an uncoordinated double bond ($\delta = 137.7$), as expected for a non-fluxional $\eta^6$-structure, while the signals in the $^1H$-NMR were already broadened slightly at room temperature and became broader on further heating. Compound **2** therefore appears to behave very similarly to its manganese analogue in that it undergoes a very slow ring rotation that is also found in other $\eta^6$-coordinated COT-complexes [2,13]. This is in contrast to the very low barriers for rotation for $\eta^4$-COT complexes. These differences in rearrangement mechanisms and barriers of rotation have been discussed extensively by Mann [14].

To further confirm the geometry of **2**, we grew single crystals from toluene solution and performed an X-ray structural analysis. A displacement ellipsoid plot of a molecule is represented in Fig. 1. Crystal data, data collection parameters and refinement results are given in Table 1, atomic coordinates in Tables 2 and 3.

Compound **2** is isostructural to its manganese analogue, with two carbons of the eight-membered ring being non-coordinated and bent away from the plane of the other six ring carbons by a dihedral angle of 67.5(4)° (Fig. 1). The bond distances between rhenium and the six coordinated carbons average between 212(1) and 221(1) pm.

**2** appears to be the first structurally characterized rhenium complex with an $\eta^6$-coordinated triolefin and the ease of its preparation and good yields are some-

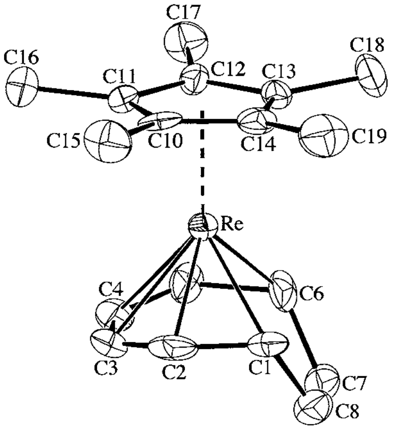


Fig. 1. The molecular structure (ORTEP) of $C_5Me_5Re(\eta^6\text{-}C_8H_8)$ (**2**).

Table 1
Crystal data, data collection parameters, and convergence results for **2**

| | |
|---|---|
| Empirical formula | $C_{18}H_{23}Re$ |
| Crystal colour and shape | Orange, translucent rod |
| Crystal size (mm) | $0.8 \times 0.16 \times 0.14$ |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | |
| $a$ (Å) | 2.201(6) |
| $b$ (Å) | 9.304(3) |
| $c$ (Å) | 13.519(8) |
| $\beta$ (°) | 98.48(5) |
| Volume, molecules per unit cell | $V = 1518(1)$, $Z = 4$ |
| $D_{calc.}$ (g $cm^{-3}$) | $\rho = 1.86$ |
| Absorption coefficient ($cm^{-1}$) | $\mu = 81.0$ |
| $F(000)$ | 824 |
| Wavelength (monochromator) | Mo–$K_{\alpha}$, $\lambda = 0.7107$ Å (graphite) |
| Data collection temperature | 263 K |
| Scan type and range | ω, $3 < \theta < 25°$ |
| Reflections collected | 2787 |
| Independent reflections | 2657 |
| Independent reflections observed $[I > \sigma(I)]$ | 2151 |
| Variables refined on $F$ | 172 |
| Agreement factors for observed data | $R = 0.043$<br>$R_w = 0.049$,<br>$w^{-1} = \sigma^2(F_o)$ |
| Residual electron density | 1.5 e$Å^{-3}$ close to Re |

what surprising, considering that several similar reactions have been attempted before. We have, however, not been able to detect any evidence for the formation of a dimetallic complex, so that other routes will have to be developed for the possible synthesis of $C_5Me_5Re(\mu\text{-}C_8H_8)ReC_5Me_5$.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for non-hydrogen atoms in **2**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Re | 0.23033(3) | 0.14599(4) | 0.22178(3) | 0.03345(9) |
| C1 | 0.0792(8) | 0.171(1) | 0.1115(9) | 0.057(3) |
| C2 | 0.0516(8) | 0.120(1) | 0.204(1) | 0.063(4) |
| C3 | 0.0855(9) | 0.189(1) | 0.2978(9) | 0.064(4) |
| C4 | 0.1672(9) | 0.293(1) | 0.3309(9) | 0.058(3) |
| C5 | 0.240(1) | 0.359(1) | 0.2798(8) | 0.053(3) |
| C6 | 0.235(1) | 0.370(1) | 0.1703(8) | 0.054(3) |
| C7 | 0.130(1) | 0.421(1) | 0.1065(9) | 0.070(4) |
| C8 | 0.055(1) | 0.323(1) | 0.0802(9) | 0.063(4) |
| C10 | 0.2776(7) | −0.091(1) | 0.2430(9) | 0.040(3) |
| C11 | 0.3414(8) | −0.009(1) | 0.3157(8) | 0.039(3) |
| C12 | 0.4091(8) | 0.085(1) | 0.2691(7) | 0.039(3) |
| C13 | 0.3818(7) | 0.067(1) | 0.1646(7) | 0.039(3) |
| C14 | 0.3009(8) | −0.039(1) | 0.1471(8) | 0.046(3) |
| C15 | 0.200(1) | −0.209(1) | 0.261(1) | 0.071(4) |
| C16 | 0.348(1) | −0.030(2) | 0.4284(8) | 0.064(4) |
| C17 | 0.4999(9) | 0.180(1) | 0.319(1) | 0.063(4) |
| C18 | 0.440(1) | 0.141(1) | 0.0849(9) | 0.068(4) |
| C19 | 0.254(1) | −0.106(2) | 0.047(1) | 0.080(5) |

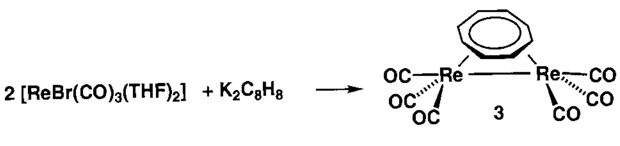
Table 3
Selected interatomic distances (Å) and angles (°) in **2**

| | | | |
|---|---|---|---|
| *Bond length* (Å) | | | |
| Re–C1 | 2.206(9) | C1–C2 | 1.43(2) |
| Re–C2 | 2.172(9) | C1–C8 | 1.50(1) |
| Re–C3 | 2.21(1) | C2–C3 | 1.43(2) |
| Re–C4 | 2.23(1) | C3–C4 | 1.42(2) |
| Re–C5 | 2.12(1) | C4–C5 | 1.34(1) |
| Re–C6 | 2.20(1) | C5–C6 | 1.48(1) |
| Re–C10 | 2.286(9) | C6–C7 | 1.51(2) |
| Re–C11 | 2.240(8) | C7–C8 | 1.30(2) |
| Re–C12 | 2.252(8) | | |
| Re–C13 | 2.230(8) | | |
| Re–C14 | 2.235(9) | | |
| *Bond angles* (°) | | | |
| C1–C2–C3 | 124.(1) | C4–C5–C6 | 128.(1) |
| C2–C1–C8 | 120(1) | C5–C6–C7 | 119.9(9) |
| C2–C3–C4 | 133.(1) | C6–C7–C8 | 116.(1) |
| C3–C4–C5 | 129.(1) | C1–C8–C7 | 119(1) |

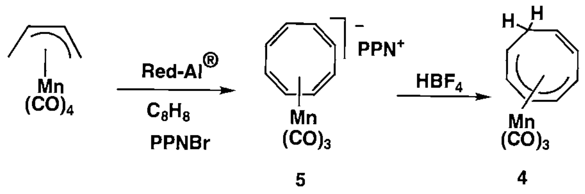
Another yet unknown dimetallic complex of rhenium is $(CO)_3Re(\mu\text{-}C_8H_8)Re(CO)_3$. Both *syn*- and *anti*-structures are again possible. The manganese analogue had been prepared by reaction of $[HMn(CO)_4]_3$ with COT as a minor product and had been shown to have a *cis*-structure with a μ–$\eta^4$–$\eta^4$-bridging mode [15].

Reaction of two equivalents of $[ReBr(CO)_3(THF)_2]$ with $K_2COT$ at −30°C gave good yields of $(CO)_3Re(\mu\text{-}C_8H_8)Re(CO)_3$ (**3**) as lemon–yellow crystals (Scheme 2). Its $^1H$-NMR spectrum shows only one sharp singlet at 5.06 ppm and the $^{13}C$-NMR spectrum likewise shows one signal only for the $C_8H_8$-ring at 65.85 ppm, with no change observed on cooling down to −80°C. This clearly indicates that **3** has the same *cis*-structure as its manganese analogue, with the two rhenium centres being linked to one 'butadiene' moiety each with the high fluxionality normally associated with this bonding mode [5]. The synthetic route employed here, which joins two organometallic fragments in one step to the dianion of $C_8H_8$, appears to be quite versatile and useful; we had successfully employed it before for the synthesis of $C_5H_5Ru(\mu\text{-}C_8H_8)RuC_5H_5$ [8].

The other product formed from the reaction of $[HMn(CO)_4]_3$ with COT in 10% yield was shown to be monomeric $(\eta^5\text{-}C_8H_9)Mn(CO)_3$ (**4**) [15]. An alternate and high-yield route to this complex was presented by Brookhart, who prepared **4** by protonation of the anion $[\eta^4\text{-}C_8H_8Mn(CO)_3]^-$ (**5**) [16]. Anion **5** was isolated as



Scheme 2.



Scheme 3.

the PPN salt from (methallyl)Mn$(CO)_4$ by the following route (Scheme 3):

Complexes **4** and **5** show fluxional behaviour in solution as shown in Scheme 4.

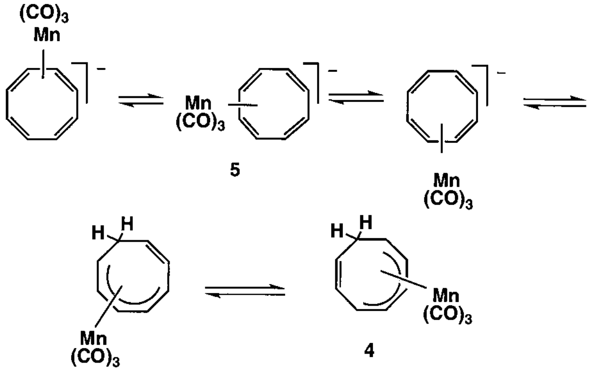
The rapid rotation of the cyclooctatetraene ring in **5** is analogous to the dynamic behaviour of the well-known $C_8H_8Fe(CO)_3$ and $[C_7H_7Fe(CO)_3]^-$ complexes and is typical for $\eta^4$-coordinated conjugated polyolefins [2,14].

We had employed previously both iron compounds successfully as components for the synthesis of dimetallic compounds and it therefore seemed worthwhile to establish that **5** could also act as an 18 + 4 building block [4,17].

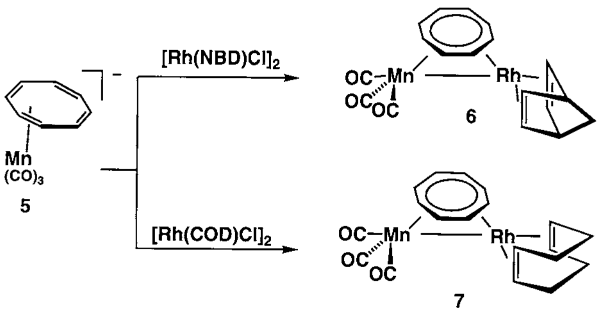
Reaction of **5** as its PPN salt with 12 $e^-$ organometallic fragments did not give any isolable dimetallic compounds. When we prepared the anion **5**, however, as the lithium salt by deprotonation of **4** isolated previously with BuLi and treated this solution at low temperatures with the complex $[Rh(NBD)Cl]_2$ (NBD = nor-$C_7H_8$), we were able to isolate the dimetallic compound $(CO)_3Mn(C_8H_8)Rh(C_7H_8)$ (**6**) in almost quantitative yields as bright-red, hexane-soluble crystals (Scheme 5).

Compound **6** shows one signal in the $^{13}$C-NMR at $\delta = 68.1$ for COT and three signals for coordinated NBD at 57.5 (d, 6.3 Hz), 47.3 (d, 8.2 Hz) and 47.1. The carbonyl groups give rise to one broad signal at $\delta =$ 227.6.

By the same method, we also prepared $(CO)_3Mn(C_8H_8)Rh(C_8H_{12})$ (**7**) (Scheme 5).



Scheme 4.



Scheme 5.

The spectra of **6** and **7** are similar in that they show only one signal for the fluxional COT-ring and also an apparently symmetrical bonding mode for the NBD and the 1,5-$C_8H_{12}$ (COD) ligand. On cooling a d$^6$-acetone solution of **7** to − 90°C, however, the signals for the coordinated olefins of COD appear now as two doublets ($J_{Rh-C} = 11-12$ Hz) and the aliphatic carbons also split into two signals. Complexes **6** and **7** therefore have *syn*-bridging structures similar to $(CO)_3Fe(\mu$-COT)Rh(NBD) and $(CO)_3Fe(\mu$-$C_7H_7)$Rh(NBD), where the overall geometry of symmetry $C_s$ had been confirmed by X-ray structural analyses [5,18]. While the rotation of the bridging COT ligand cannot be sufficiently slowed down on the NMR time scale, the rotation of the NBD and COD ligands becomes slow enough at − 90°C to observe the lower limiting spectrum.

By similar methods, we also prepared $(CO)_3Mn(C_8H_8)Rh(CO)_2$ (**8**) and $(CO)_3Mn(C_8H_8)Rh$-$(P[OMe]_3)_2$ (**9**) as red, crystalline material.

We had shown previously that $(CO)_3Fe(\mu$-$C_7H_7)$Rh(COD) could react very readily with both carbon monoxide as well as phospites by displacement of the diolefinic ligand [17]. Takats et al. had also prepared $(CO)_3Fe(\mu$-$C_7H_7)Rh(CO)_2$ and shown that this compound could very quickly and indiscriminately be enriched in $^{13}$CO at both metals [18a]. This facile ligand exchange was explained by ring slippage of the $C_7H_7$ ring similar to the indenyl ligand from a $\mu-\eta^7$ to an $\mu-\eta^5$ bonding mode with one uncoordinated double bond, allowing an associate mechanism of ligand exchange. This complex also exchanged one or two carbonyl groups at rhodium for various phosphines [18b].

We expected that **6** and **7** would show similar behaviour to these rhodium–iron dimers. However, this was not the case. No exchange of the diolefinic ligands in **6** or **7** for carbon monoxide was observable under ambient pressure; at higher pressures (50 bar) we found only decomposition products, but no trace of **8**. Similarly, the reaction with trimethylphosphite did not lead to the formation of **9** at room temperature or under reflux condition. Only the reaction of the carbonyl compound **8** with trimethylphosphite yielded moderate amounts of **9** in ca. 40% yield together with unidentifiable products. This showed that the reactivity of the $C_8H_8$-bridged dimer was different from ist $C_7H_7$ analogue, possibly because ring slippage was not equally facile.

To determine whether intermetallic CO scrambling would also be possible in **8**, we prepared isotopically enriched $[Rh(^{13}CO)_2Cl]_2$ and reacted it with $Li[C_8H_8Mn(CO)_3]$. The labelled compound **8** after workup and recrystallisation (ca. 1 day) showed a very intense dublet ($J^{13}C,^{103}Rh = 77.7$ Hz) in the $^{13}C$-NMR for the $^{13}C$-enriched carbonyl groups attached to rhodium and an enhanced signal for the carbonyl groups attached to manganese (Fig. 2). These spectra were recorded at −60°C to minimize quadrupole broadening due to $^{55}Mn$. After 3 more days the same solution showed a further increase in the intensity of the $Mn(CO)_3$ signal, suggesting that a very slow intermetallic equilibration of carbonyl groups is taking place (Fig. 2). As we observe only one signal for the three carbonyl groups at manganese even at −60°C, there is still rapid carbonyl scrambling within the tricarbonyl group.

We conclude from these results that the *cisoid* dimetallic complexes with bridging $C_7H_7$ and $C_8H_8$ ligands, while similar structurally, nevertheless differ considerably in their chemical behaviour, especially in their tendency for ligand exchange. One reason for this may be the fact that $C_7H_7$ as a bridging ligand in a dimetallic carbonyl compound can more easily assume an $\mu-\eta^5$ bonding mode, thus allowing a new ligand to enter the coordination sphere as well as a more increased tendency to form carbonyl-bridged species. Similar structural changes for **8** seem to be less favourable, although both $\mu-\eta^4-\eta^4$ and $\mu-\eta^3-\eta^5$ coordination modes have been structurally characterised by us for dimetallic species of $C_8H_8$ as has been the $\mu-\eta^6$ bonding mode [5].

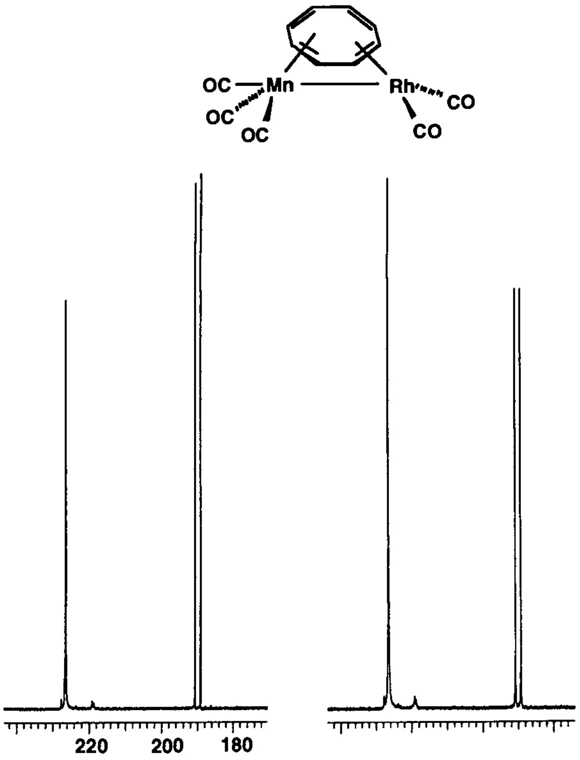
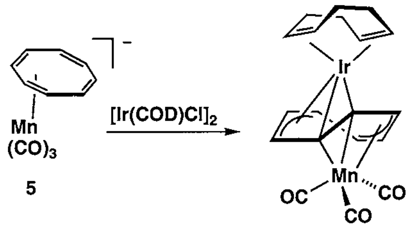


Fig. 2. $^{13}C$-NMR of $^{13}CO$-enriched $(CO)_3Mn(C_8H_8)Rh(CO)_2$ (**8**) after 1 day (left) and after 4 days (right) at −60°C.



5

10

Scheme 6.

The anion **5** did not only react with 12e⁻ fragments of rhodium, but also with similar compounds of iridium and ruthenium. Treatment of **5** with $[Ir(COD)Cl]_2$ produced a light-brown crystalline solid of analytical composition $(CO)_3MnC_8H_8Ir(COD)$ (**10**) in 50% yield. This compound at room temperature showed only two signals in the $^{13}C$-NMR at 33.7 and 60.1 ppm, which we assigned to the aliphatic and olefinic carbons of cyclooctadiene. At −40°C, five additional signals appeared, three of which disappeared again at −60°C. At −114°C, the lowest temperature we could reach in a mixture of $CD_2Cl_2/CDCl_3$, the lower limiting spectrum was reached, which now showed eight signals for bridging cyclooctatetraene, eight signals for cyclooctadiene as well as three signals for carbonyl groups. This NMR spectrum was only compatible with a completely unsymmetrical structure. **10** therefore must have a slipped tripledecker structure, similar to compounds we and others have described before [5,6]. This is very surprising, as the analogous rhodium complex **7** has the *cis*-bridging structure. In contrast to compounds such as $C_5H_5Ru(\mu-C_8H_8)RuC_5H_5$, which have a symmetrical slipped tripledecker structure of symmetry $C_2$, **10** lacks any element of symmetry due to the two different metal moieties (Scheme 6).

Similar compounds could be prepared from **5** and $[C_5H_5Ru(CH_3CN)_3]PF_6$ and $[C_5Me_5Ru(CH_3CN)_3]PF_6$. $C_5H_5Ru(\mu-C_8H_8)Mn(CO)_3$ (**11**) and $C_5Me_5Ru(\mu-C_8H_8)$-$Mn(CO)_3$ (**12**) were isolated as orange crystals in 60–50% yield, respectively. Their NMR spectra were quite similar to **10**. The temperature-dependent NMR spectra of these complexes were studied in detail. For **11** and **12**, the sequence of all $^1H$ as well as $^{13}C$ signals was assigned by selective decoupling experiments of the lower-limiting spectra (Fig. 3). The assignment of manganese and ruthenium bonding is tentative and based on chemical shift analogies by comparison to the compounds $C_8H_9Mn(CO)_3$ [16] as well as $C_5H_5Ru(\mu\text{-}C_8H_8)RuC_5H_5$ [5,8].

At 30°C, complex **11** showed, apart from two resonances assigned to $C_5H_5$ and CO, five resonances for coordinated $C_8H_8$ (Fig. 4). On cooling, three signals collapsed consecutively, while the resonances attributed to carbon atoms 4 and 8 remain sharp throughout. The lower limiting sprectrum was reached at $-100$°C. This now showed eight resonances for the coordinated $C_8H_8$-ring and three resonances for the carbonyl groups. This proves that **11** has an unsymmetrical ground state, consistent only with a slipped tripledecker structure.

The dynamic behaviour of slipped tripledecker compounds has been described in detail by Geiger et al. [6,8]. The behaviour of compounds such as **10**–**12** is, however, even more complex than that of compounds described previously, as **10**, **11** and **12** are the first heterodimetallic examples for this type of bonding, which therefore lack any element of symmetry.

There are in principle four distinct 1,$n$-shifts ($n=2$–5) available for each metal. This rearrangement process could occur by unidirectional motion of both metals or by movement in opposite directions [6,8], or, as seems to be the case for the complexes discussed here, by two completely independent rearrangement processes of both metals with different activation energies. **11** has an unsymmetrical ground state at $T < -90$°C. Analysis of the temperature-dependent spectrum of **11** shows that at $T > -90$°C, one of the metals undergoes a 1,3 shift. The number 3 refers to the position of the carbon atom of the C–C bond to which the metal has moved relative to its original position ('screen-wiper movement'). This would be analogous to the fluxional behaviour of monomeric $C_8H_9Mn(CO)_3$ [16] (Scheme 4). Carbons 4 and 8 do not change their chemical environment during this process (Fig. 4), so their signals remain sharp and unchanged, while all other carbons undergo a two-site exchange (3↔5, 2↔6, 1↔7). This observation allows us to exclude all other possible 1,$n$-shifts, as they would lead to complete exchange and broadening of all signals at some stage. If the assignments of chemical shifts are correct, the fluxional entity must be CpRu and not $Mn(CO)_3$, as only then carbon atoms 4 and 8 are the ones not changing their chemical environment throughout the fluxional process. As the molecule is chiral, this process can also be described as the interconversion of the two enantiomers of **11**.

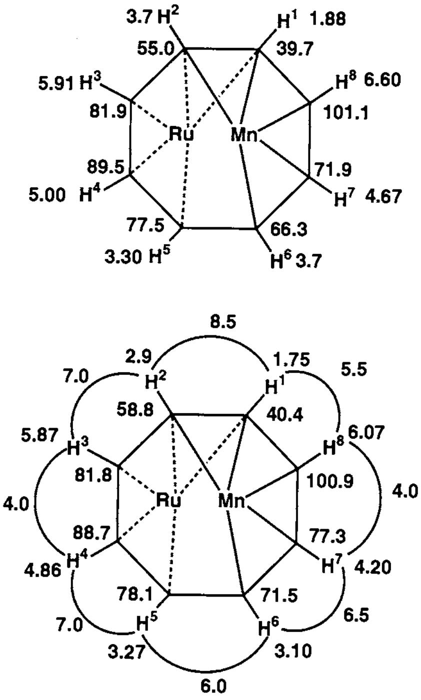


Fig. 3. $^1H$- and $^{13}C$-NMR chemical shifts and assignments of $(CO)_3Mn(C_8H_8)RuC_5H_5$ (**11**) (top) and of $(CO)_3Mn(C_8H_8)RuC_5Me_5$ (**12**) (bottom), at $-100$°C, coupling constants in Hz.

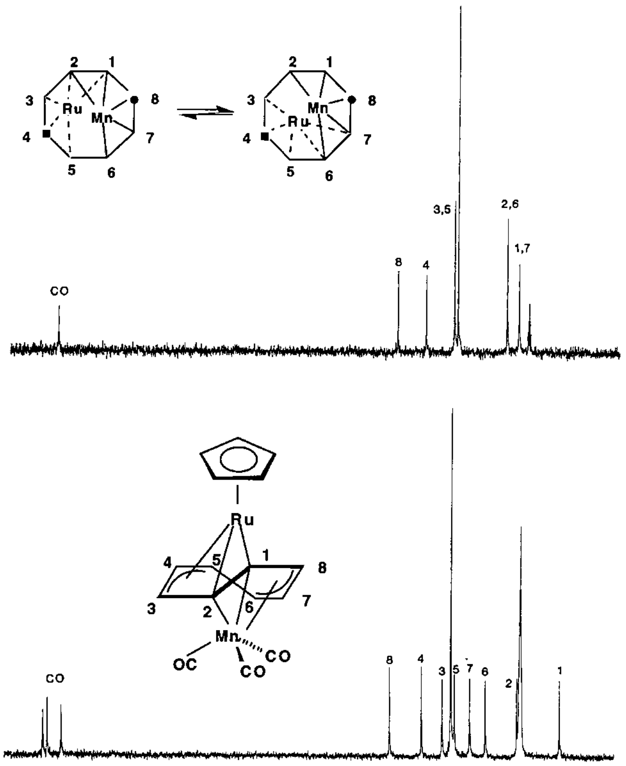


Fig. 4. $^{13}C$-NMR spectra of $(CO)_3Mn(C_8H_8)RuC_5H_5$ (**11**) at $+30$°C (top) and $-100$°C (bottom) and the proposed 'screenwiper movement' mechanism for the fluxional behaviour of **11**.

The fluxional behaviour of complex **12**, while similar to **11** at lower temperatures, is different at room temperature. All signals for coordinated $C_8H_8$ become broadened at temperatures above 0°C, indicating that the $Mn(CO)_3$ moiety now also begins to undergo 1,*n*-metal shifts. We have not been able to observe the fast-exchange spectrum, as slight decomposition sets in at temperatures $>50°C$, a temperature at which the only visible resonances of **12** are those of the $C_5Me_5$-ring and one resonance for all carbonyl groups. In this, the compounds behave completely similar to the slipped tripledecker complexes of ruthenium [5,8], cobalt and rhodium [6]], which also become fully fluxional at elevated temperatures.

Compounds **10**–**12** represent the first examples of heterodimetallic slipped tripledecker compounds displaying this unique type of consecutive fluxionality around the perimeter of a *trans*-coordinated polyolefin.

## 3. Summary

In conclusion, it can be said that the synthesis of mono- and dimetallic complexes of manganese and rhenium with a bridging cyclooctaetrene ligand has yielded a surprising wealth of new compounds and unusual structures, most notably *syn*-and *anti*-bridged heterodimetallic species. It confirms our previous observations that both structural variants are very similar in energy for $34e^-$ compounds and a preference for one or the other cannot be predicted. Our results also show that cyclooctatetraene is certainly the most versatile π-coordinating ligand in offering an unrivalled number of different bonding modes.Further research will focus on establishing quantitative kinetic data of the fluxional processes described here as well as studying the electrochemistry of slipped-tripledecker compounds.

## 4. Experimental

### 4.1. General

All reactions and manipulations were performed under nitrogen using standard vacuum line and Schlenk tube techniques. All solvents were degassed before use. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride and stored over molecular sieves. Hexane and toluene were dried over molecular sieves. Aluminiumoxide (Merck N 90, Activity grade II–III) was further deactivated by addition of 4% of water. $C_5Me_5Re(CO)_3$ [19]; $[ReBr(CO)_3(THF)_2]$ [20]; $[MnBr(CO)_5]$ [21]; methallyl$Mn(CO)_4$ [22], $[C_8H_8$-$Mn(CO)_3]PPN$ [16] and $C_8H_9Mn(CO)_3$ [16] were prepared as described in the literature. $[Rh(CO)_2Cl]_2$ and $[Rh\{P(OCH_3)_3\}_2Cl]_2$ were prepared by ligand exchange from $[Rh(C_2H_4)_2Cl]_2$ [23]. Carbon monoxide (99% $^{13}C$) was purchased from Aldrich. $[Rh(COD)Cl]_2$, $[Rh(NBD)Cl]_2$ was synthesized according to Schrock and Osborn [24], $[Ir(COD)Cl]_2$ according to [25], $[CpRu(CH_3CN)_3]PF_6$ and $C_5Me_5Ru(CH_3CN)_3]PF_6$ following the procedure by Mann [26,27].

$^1H$ and $^{13}C$-NMR spectra were recorded on a Varian Gemini 200, Varian VXR 300 and a Bruker AM 400 spectrometer, and referenced to tetramethylsilane (TMS) or using internal solvent peaks. IR Spectra were recorded on a Bio-Rad FTS 45 FT and a Perkin–Elmer FT-IR 1720 X spectrometer. The EI mass spectra were obtained on a Finnagan MAT 8230 spectrometer. Photochemical reactions were performed in a Mangels reaction vessel using either a Philips 125 W or a Hanau 150 W high-pressure mercury lamp with quartz immersion wells.

The X-ray structure determination was performed on an ENRAF-Nonius CAD4 diffractometer. Experimental details are given in Table 1. Before averaging over symmetry related parts of the reciprocal lattice a numerical absorption correction [28] was applied. The structure was solved by Patterson methods and refined on structure factors with the SDP [29] program system. Non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms wer included as riding on their carbon atoms with $C–H=98$ pm, $U_{iso}(H)=1.3\ U_{eq}(C)$. Crystallographic data (excluding structure factors) for the structure of **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-104611. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

### 4.2. Preparation of $C_5Me_5Re(CO)_2(\eta^2$-$C_8H_8)$ (**1**) and $C_5Me_5Re(\eta^6$-$C_8H_8)$ (**2**)

A total of 2.19 g (5.39 mmol) of $C_5Me_5Re(CO)_3$ and 6.2 ml (53.9 mmol) of freshly distilled $C_8H_8$ were photolysed in 400 ml of toluene under $N_2$ for 20 h with a 150 W high-pressure mercury lamp. Under gas evolution, the initially pale yellow solution turned orange. After evaporation of the solvent under reduced pressure, the residue was extracted with hot hexane and the solution quickly filtered, while hot. The solvent was evaporated and the residue taken up in hexane/$CH_2Cl_2$ (1:1).This solution was transferred to a chromatography column (Alumina, activity grade IV) and eluted with hexane. The first orange fraction was collected and, after recrystallisation at $-30°C$, furnished pure orange crystals of **2**, 0.8 g (35%). A second yellow fraction from the column was obtained by elution with hexane/$CH_2Cl_2$ (1:1). After evaporation of the solvent, this gave pure **1** as a yellow solid, 0.64 g (25%). The yield of **1** can be improved to 65% by irradiation with a 125 W mercury lamp under otherwise identical conditions.

(**1**) IR (hexane, cm$^{-1}$): $\nu$(CO) 1962 (s), 1893 (s). $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$ 10.1 ($CH_3$), 40.8 (2C), 97.8 (5, $C_5$), 126.6 (4 C), 135.6 (2 C), 207.3 (CO). Anal. Found: C, 49.54, H, 4.72%. $C_{20}H_{23}O_2Re$ (481.6) Calc.: C, 49.87, H, 4.81%.

(**2**) $^{13}$C-NMR (75 MHz, $C_6D_6$): $\delta$ 10.8 ($CH_3$), 56.9, 79.6 ($C_5$), 88.5, 93.4, 137.7 Anal. Found: C, 50.58, H, 5.22%. $C_{18}H_{23}Re$ (425.6) Calc.: C, 50.80, H, 5.44%.

### *4.3. Preparation of $(CO)_3Re(\mu\text{-}C_8H_8)Re(CO)_3$ (**3**)*

A total of 190 mg (4.92 mmol) of potassium were suspended in 50 ml of THF and, by stirring vigorously under reflux conditions, dispersed into little globules. The suspension was then cooled to −30°C and treated with freshly distilled $C_8H_8$ (0.28 ml, 2.46 mmol). The solution turned brown and stirring was continued until all potassium sand had dissolved. The temperature should not rise above 0°C. A solution of $[ReBr(CO)_3(THF)_2]$, prepared by refluxing 2 g (4.92 mmol) of $[Re(CO)_5Br]$ in THF for 12 h, was added at −30°C. The solution was warmed to room temperature, giving a clear orange solution. The solution was evaporated and the residue extracted with warm toluene. The solution was filtered over Celite and cooled to −80°C. Lemon–yellow crystals were collected by filtration and washed with cold hexane. Yield: 0.96 g (60.5%). IR (toluene, cm$^{-1}$): $\nu$(CO) 2022, 1924. $^1$H-NMR (300 MHz, d$^6$-acetone): $\delta$ 5.06 (s).$^{13}$C-NMR (75 MHz, d$^6$-acetone): $\delta$ 65.85 (COT), 191 (CO). Anal. Found: C, 25.85, H, 1.20%. $C_{14}H_8O_6Re_2$ (644.6) Calc.: C, 26.08, H, 1.25%.

### *4.4. Preparation of $(CO)_3Mn(C_8H_8)Rh(C_7H_8)$ (**6**), $(CO)_3Mn(C_8H_8)Rh(C_8H_{12})$ (**7**), $(CO)_3Mn(C_8H_8)Rh(CO)_2$ (**8**), $(CO)_3Mn(C_8H_8)Rh[(POMe)_3]_2$ (**9**)*

250 mg of **4** (1.02. mmol) in THF were treated at −80°C with 0.7 ml (1.02 mmol) of butyllithium (1.5 molar in hexane). A dark-red solution formed immediately and was reacted with 240 mg (0.52 mol) of $[Rh(NBD)Cl]_2$. The solution was slowly warmed to room temperature and then evaporated. The residue in a small volume of toluene was filtered over LiChroPrep. Recrystallisation from toluene/hexane afforded scarlet-red crystals, yield 420 mg (93%).

IR (hexane, cm$^{-1}$): $\nu$(CO) 1989, 1912. $^1$H-NMR (200 MHz, $CDCl_3$: $\delta$ 4.21 (s), 3.65 (m), 3.46 (b) 0.95 (t). $^{13}$C-NMR (50 MHz, $CDCl_3$): $\delta$ 68.1 (COT), 47.3 (d, 8.2 Hz), 47,1 (s), 57.5 (d, 6.3 Hz) 227.6 (b, CO). Anal. Found: C, 49.55, H, 3.71%. $C_{18}H_{16}O_3MnRh$ (438.2) Calc.: C, 49.34, H, 3.68%.

**7** was prepared similar to **6**, from 280 mg of **4** and 290 mg of $[Rh(COD)Cl]_2$, yield 340 mg, 65% as brown-red crystals. IR (hexane, cm$^{-1}$): $\nu$(CO) 1990, 1915. $^1$H-NMR (400 MHz, $CD_2Cl_2$, 21°C): $\delta$ 2.19 (m, 4H, $CH_2$), 2.44 (m, 4H, $CH_2$), 4.06 (s, 4H, CH) 4.14 (s, 8H, COT); $^{13}$C-NMR (100 MHz, $CDCl_3$, +20°C): $\delta$ 31.7, 68.4, 80.7; (100 MHz, acetone-d$^6$, −90°C): $\delta$ 30.1, 32.9 ($CH_2$, COD), 69.2 (CH, COT), 76.8 (d, $J_{\text{Rh-C}} = 10.3$, CH, COD), 85.0 (d, $J_{\text{Rh-C}} = 11.2$, CH, COD), 229.3 (CO). Anal. Found: C, 50.47, H, 4.47, Mn, 11.90%. $C_{19}H_{20}O_3MnRh$ (438.16) Calc.: C, 50.24, H, 4.44, Mn, 12.10%.

**8** was prepared similar to **6**, starting from 250 mg of **4** (1.02 mmol) and 202 mg (0.51 mmol) of $[Rh(CO)_2Cl]_2$, yield 184 mg (45%) as red crystals. IR (hexane, cm$^{-1}$): $\nu$(CO) 2060 (vs), 2023 (w), 2010 (s), 1997 (vs), 1961 (w), 1936 (m), 1928 (m). $^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ 4.56 (d, $J_{\text{Rh-H}} = 0.4$ Hz), $^{13}$C-NMR (50 MHz, $CDCl_3$): $\delta$ 68.2 (d, $J_{\text{Rh-C}} = 1.5$ Hz), 190.0 (d, $J_{\text{Rh-C}} = 77.7$ Hz), 226.2. Anal. Found: C, 38.65, H, 2.23%. $C_{13}H_8O_5MnRh$ (402.04) Calc.: C, 38.84, H, 2.01%.

**9** was prepared similar to **6**, starting from 250 mg of **4** (1.02 mmol) and 394 mg (0.51 mmol) of $[RhCl\{P(OCH_3)_3\}_2]_2$, recrystallisation from toluene/hexane at −80°C, yield 497 mg as a dark-red powder. IR (hexane, cm$^{-1}$): $\nu$(CO) 1993, 1901. $^1$H-NMR (200 MHz, $C_6D_6$): $\delta$ 3.33 (m, 9H, $OCH_3$), 4.33 (s, 8H, COT). $^{13}$C-NMR (50 MHz, $C_6D_6$) $\delta$ 51.2 ($OCH_3$), 68.0 (d, $J_{\text{Rh-C}} = 1.9$ Hz, COT), 229.6 (CO). Anal. Found: C, 34.46, H, 4.36%. $C_{17}H_{26}MnO_9P_2Rh$ (594.2) Calc.: C, 34.36, H, 4.41.

### *4.5. Preparation of $(CO)_3Mn(C_8H_8)Ir(COD)$ (**10**), $(CO)_3Mn(C_8H_8)RuC_5H_5$ (**11**) and $(CO)_3Mn(C_8H_8)Ru(C_5Me_5)$ (**12**)*

350 mg (1.43 mmol) of **4** were dissolved in 50 ml of THF, cooled to −80°C and treated with an equivalent amount of BuLi/hexane. After stirring for 30 min, this solution was treated with 480 mg (0.71 mmol) of $[Ir(COD)Cl]_2$. The solution was warmed slowly to room temperature and was then evaporated to dryness under vacuum. The residue was taken up in toluene, filtered over $Al_2O_3$ and reduced in volume. Recrystallisation from touene/hexane afforded **10** as a brown, microcrystalline solid, 400 mg (51%). IR (hexane cm$^{-1}$): $\nu$(CO) 2014, 1946, 1931. $^1$H-NMR (200 MHz, $CDCl_3$, 20°C): $\delta$ 2.07 (s, 8 H), 3.4 (b, 4H), 4.6 (vb, 8 H). $^{13}$C-NMR (50 MHz, $CDCl_3$, 20°C): $\delta$ 33.7 ($CH_2$), 60.2 (CH), 77 (b, CH), 223.5 (CO); (100 MHz, $CD_2Cl_2/CDCl_3$, −114°C): $\delta$ 25.8, 28.9, 37.0, 40.4 ($CH_2$, COD), 51.0, 51.9, 67.6, 77.0, CH, COD), 52.3, 56.6, 63.3, 69.6, 79.8, 80.2, 86.4, 96.0 (COT), 220.0, 223.3, 227.4 (CO). Anal. Found: C, 42.47, H, 3.82, Mn, 10.01%. $C_{19}H_{20}IrMnO_3$ (543.49) Calc.: C, 41.99, H, 3.71, Mn, 10.11%.

**11** was synthesized similar to **10** from 290 mg (1.19 mmol) of **4** and 520 mg (1.2 mmol) of $[CpRu(CH_3CN)_3]PF_6$. Recrystallisation from hexane afforded red needles at −30°C, 290 mg (60%). IR (hexane, $cm^{-1}$): $\nu$(CO) 2012, 1939, 1923. $^1$H-NMR (400 MHz, $CD_2Cl_2$) and $^{13}$C-NMR (100 MHz, $CD_2Cl_2$) at −100°C see Fig. 3. EI-MS ($^{102}$Ru): 410 ($M^+$), 382 ($M^+$–CO), 354 ($M^+$–2CO), 326 ($M^+$–3CO); 271 ($M^+$–$Mn(CO)_3$); 167 ($C_5H_5Ru^+$). Anal. Found: C, 47.00, H, 3.20, Mn, 13.42%. $C_{16}H_{13}MnO_3Ru$ (409.27) Calc.: C, 46.95, H, 3.20, Mn, 13.42%.

**12** was synthesized similar to **10** from 290 mg (1.19 mmol) of **4** and 605 mg (1.2 mmol) of $[C_5Me_5Ru(CH_3CN)_3]PF_6$. Yield 287 mg (50%). IR (hexane, $cm^{-1}$): $\nu$(CO) 2009, 1935, 1918. $^1$H-NMR (400 MHz, $CD_2Cl_2$ −100°C) and $^{13}$C-NMR (100 MHz, $CD_2Cl_2$, −100°C) see Fig. 3. EI-MS ($^{102}$Ru): 480 ($M^+$) 452 ($M^+$–CO), 424 ($M^+$–2CO), 396 ($M^+$–3CO), 341 ($M^+$–$Mn(CO)_3$), 237 ($RuC_5Me_5$). Anal. Found: C, 52.29, H, 4.76, Mn, 11.46%. $C_{21}H_{23}MnO_3Ru$ (479.4) Calc.: C, 52.61, H, 4.84, Mn, 11.46%.

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