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# THE SYNTHESIS AND REACTIVITY OF RHENOCENE

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## Summary

Oxidation of lithiodicyclopentadienylrhenium by organic carbonyl compounds gives the complex ($C_{20}H_{20}Re_2$). Spectroscopic data show that this complex consists of two rhenocene fragments, $\{(C_5H_5)_2Re\}$, linked by a metal–metal bond, and so that it must be represented as a dimer of rhenocene, $\{(C_5H_5)_2Re\}_2$. Reaction of the dimer with benzyl bromide gives $\{(C_5H_5)_2ReCH_2C_6H_5\}$ and $\{(C_5H_5)_2ReBr\}$, while thermolysis gives the new dimeric complex $\{(C_5H_5)_2(C_5H_4)_2Re_2\}$ and two equivalents of $\{(C_5H_5)_2ReH\}$ and photolysis ($\lambda \geqslant 410$ nm) gives $[\{\eta^4\text{-}(C_5H_6)(C_5H_5)Re\}\{\eta^5,\eta^1\text{-}(C_5H_4)(C_5H_5)Re\}]$.

## Introduction

Following the first synthesis of ferrocene [1] stable monomeric metallocenes have been obtained for all 3*d* transition metals except titanium [2]. Synthesis of the 4*d* and 5*d* metallocenes, on the other hand, has met with considerable difficulties, owing to the fact that the 4*d* and 5*d* elements have a much stronger tendency to complete the 18-electron configuration around the metal centre than do the 3*d* elements. Thus, although ruthenocene and osmocene are stable monomers [1], only dimeric complexes of the general formula $(C_{10}H_{10}M)_2$ have been obtained for most other metals at room temperature [3]. In some cases monomers were identified by spectroscopic means at low temperature, but they were never isolated [4].

The only transition metal for which no metallocene or metallocene dimer has been isolated is rhenium. Thus attempts to generate $\{(C_5H_5)_2Re\}$ from $ReCl_5$ and $NaC_5H_5$ gave $\{(C_5H_5)_2ReH\}$ instead [5]. Recently it was reported that the rhenium–hydrogen bond in the latter complex can be cleaved homolytically by UV light in an argon/CO matrix, and resonances which could be ascribed to $\{(C_5H_5)_2Re\}$ were identified in the IR spectrum at 4 K [4c].

We here describe the first synthesis of rhenocene, and report on its structure and reactivity.

TABLE 1

$^1$H NMR SPECTROSCOPIC DATA FOR COMPLEXES **1**–**5**, **7** AND **8** (25 °C, ppm rel. to TMS)

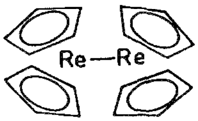
| Compound | Solvent | Shifts |
|---|---|---|
| **1** | THF-$d_8$ | 3.75(s,$C_5H_5$) |
| **2** | $CD_2Cl_2$ | 4.33(s,$C_5H_5$) |
| **3** | $C_6D_6$ | 7.10(5H,m,$C_6H_5$); 3.76(10H,s,$C_5H_5$); 2.70(2H,s,$CH_2$) |
| **4** | $C_6D_6$ | 3.80(s,$C_5H_5$) |
| **5** | THF-$d_8$ | 4.34(10H,s,$C_5H_5$); −13.3(1H,s,Re$H$) |
| **7** | $CD_2Cl_2$ | 4.46(5H,s,$C_5H_5$); 4.28(2H,$AA'$BB′), 4.05(2H,AA′$BB'$) |
| **8** | THF-$d_8$ | 5.06(5H,s,$C_5H_5$); 4.13(5H,s,$C_5H_5$)<br>4.93(1H,m); 4.55(1H,m), 4.26(1H,m); 3.94(1H,m) [a]<br>6.52(1H,d,$J$ 10 Hz); 6.09(1H,m), 5.15(1H,m); 3.62(1H,m),<br>3.17(1H,m); 3.03(1H,d.m., $J$ 10 Hz) [b] |

[a] All four protons are mutually coupled ($J \leq 1$ Hz). [b] All six protons are mutually coupled ($J \leq 1$ Hz)

## Results

### *Formation and reactions of* $\{(C_5H_5)_2Re\}_2$

When $\{(C_5H_5)_2Re\text{-}Li\}$, **1**, is treated with one equivalent of benzaldehyde at −78 °C in toluene/tetrahydrofuran (THF) and slowly allowed to warm to −50 °C, a dark purple red colour develops and purple-black powder is slowly deposited. The negative-ion-chemical-ionization-mass spectrum of this product indicates that the molecular formula is $C_{20}H_{20}Re_2$, as demonstrated by the appearance of a parent ion peak at $m/e = 632$ *. The $^1$H NMR spectrum in $CD_2Cl_2$ shows only one resonance: a singlet at $\delta$ 4.33 ppm (rel. to TMS); notably, no resonances due to hydridic protons are found in the region 0 to −40 ppm. This suggests that the complex contains four equivalent cyclopentadienyl ligands. Furthermore, the observed chemical shift is typical of a $(C_5H_5)_2ReR$ type of complex (cf. Table 1) and we therefore formulate the complex as dimeric dicyclopentadienylrhenium, **2**, in which the dimerization is effected by formation of a metal-to-metal bond, and in which the cyclopentadienyl ligands are tilted as in $\{(C_5H_5)_2ReH\}$ and related complexes.



2

The formation of **2** appears to be the result of a one-electron transfer from the dicyclopentadienyl anion to benzaldehyde, to produce monomeric rhenocene and the radical-anion of benzaldehyde, followed by dimerization of the former and decomposition of the latter. To demonstrate the initial one-electron-transfer reaction, we treated **1** with benzophenone and obtained a deep blue solution, typical of the formation of the radical-anion of benzophenone. Surprisingly, this solution was

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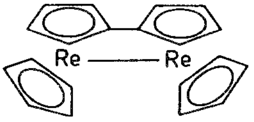
* Only the figure corresponding to $C_{20}H_{20}{}^{185}Re^{187}Re$ is given, but the observed isotopic pattern was identical with that produced by computer simulation for $C_{20}H_{20}Re_2$.

stable even at room temperature, and only after introduction of traces of oxygen did the blue colour disappear, leaving a dark red solution from which the dimer again separated. Clearly this behaviour reflects the difference in stability between the ion pairs that are intially formed: the rhenocene-benzaldehyde ion pair decomposes even at low temperature due to the instability of the benzaldehyde radical-anion, whereas the rhenocene-benzophenone pair is only decomposed when the thermally stable radical-anion of benzophenone is quenched with oxygen.

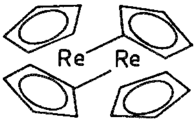
Additional $^1H$ NMR spectroscopic evidence for the structure of **2** is found in the reaction with benzyl bromide, which gives products containing the $(C_5H_5)_2Re$ fragment. Thus, when we monitored the reaction of **2** with benzyl bromide by $^1H$ NMR we observed that the original resonance of **2** at $\delta$ 4.33 ppm vanished and new resonances coinciding with those of $\{(C_5H_5)_2ReCH_2C_6H_5\}$, **3**, and $\{(C_5H_5)_2ReBr\}$, **4**, appeared in a 1/1 ratio (cf. Table 1).

### *Thermolysis of* $\{(C_5H_5)_2Re\}_2$

Solutions of **2** are not indefinitely stable at room temperature. At 60 °C decomposition is complete in a few minutes, and two products are formed in a 2/1 ratio: the first is $\{(C_5H_5)_2ReH\}$, **5**, and the second is, as evidenced by its mass spectrum, a dimeric complex of general formula $C_{20}H_{18}Re_2$. The $^1H$ NMR spectrum in dichloromethane shows a singlet at $\delta$ 4.46 ppm (relative intensity 5) and an AA′BB′ type resonance centered at $\delta$ 4.11 ppm (relative intensity 4). There are no resonances in the region 0 to −40 ppm, indicating that the dimer is not a metal hydride species. These data suggest that the dimer has either the fulvalene structure **6** or the doubly metallated structure **7**.



**6**



**7**

Comparison of the $^{13}C$ NMR spectrum in dichloromethane with literature data for complexes of known structure (cf. Table 2) suggests [3a] that $C_{20}H_{18}Re_2$ has the doubly metallated structure **7** since (i) the resonance of C(1) is found at higher field than those of C(2) and C(3), while in all fulvalene complexes this sequences is reversed; and (ii) there is a relatively large difference in chemical shift between the resonances of C(2) and C(3) in contrast to their virtual coincidence in the fulvalene complexes.

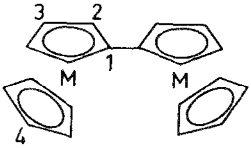
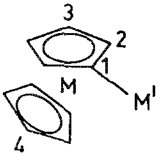
The new dimer can formally be regarded as the dehydrogenation product of $\{(C_5H_5)_2Re\}_2$. The hydrogen is quantitatively recovered as the hydridic proton in $\{(C_5H_5)_2ReH\}$, as was shown by independent runs in deuterated solvents which all gave **7** and $\{(C_5H_5)_2Re\mathit{H}\}$ in a 1/2 ratio.

### *Photochemical rearrangement of* $[(C_5H_5)_2Re]_2$

Irradiation of a solution of $[(C_5H_5)_2Re]_2$ with visible light ($\lambda > 400$ nm, sodium chromate filter) gives a product, which on the basis of its $^1H$ NMR spectrum is tentatively identified as **8**. Thus there are resonances due to two inequivalent $C_5H_5$ ligands, one $C_5H_6$ ligand in which all six protons are inequivalent, and one $C_5H_4$ ligand again with four inequivalent protons. The coordination around the metal

TABLE 2

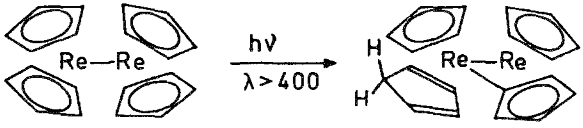
$^{13}C$ NMR SPECTROSCOPIC DATA FOR COMPLEX 7 AND FOR FULVALENE- AND $[(\eta^5\text{-}C_5H_5)(\eta^5,\eta^1\text{-}C_5H_4)]$-TYPE MODEL COMPLEXES

| Compound | | C(1) | C(2) [a] | C(3) [a] | C(4) | Δ(C(2)-C(3)) |
|---|---|---|---|---|---|---|
| 7 [c] | | 60.0 | 80.9(181) | 70.0(173) | 71.7(173) | 10.9 |
| Fulvalene complexes<br> | | | | | | |
| $(C_5H_5)_2(C_{10}H_8)Fe_2$ | [6a] | 84.6 | 67.6 | 66.5 | 69.1 | 1.1 |
| $(C_5H_5)_2(C_{10}H_8)Ti_2H_2$ | [3a] | 122.6 | 102.7 | 100.4 | 104.6 | 2.3 |
| $(C_5H_5)_2(C_{10}H_8)MoH_2$ | [3c] | 81.4 | 69.2 | 67.8 | 77.6 | 1.4 |
| $(C_{10}H_8)_2Co^{2+}$ | [6b] | 111.2 | 85.7 | 83.0 | – | 2.7 |
| $(\eta^5\text{-}C_5H_5)(\eta^5,\eta^1\text{-}C_5H_4)$<br>Metal complexes<br> | | | | | | |
| M = Mo(CO) $M^1 = Mn(CO)_4$ | [3a] | [b] | 104.5 | 86.0 | 82.9 | 18.5 |
| M = W(CO) $M^1 = Mn(CO_4)$ | [3a] | [b] | 100.8 | 81.3 | 78.7 | 19.5 |

[a] Assignment of C(2) and C(3) may be reversed. [b] Not observed. [c] Chemical shift in ppm rel. to TMS, $^1J(C,H)$ coupling constant in Hz given in parentheses.

bearing the $\eta^4$-$C_5H_6$ ligand strongly resembles that found [7] in $\{\eta^4\text{-}(C_5H_5Me)\text{-}\eta^5\text{-}(C_5H_5)ReMe_2\}$ whereas that of the other metal centre is very similar to that found in 7.

The product is not thermally stable in solution and is slowly converted into among other products, 5 and 7, the thermolysis products of 2.



8

The mechanisms by which dimers 7 and 8 are formed have not been elucidated. On the basis of ample evidence from related rhenium [4c,8] and molybdenum [9] chemistry it is likely that formation of 8 proceeds through an $\eta^5$ to $\eta^3$ ligand slip, which allows oxidative addition of one of the C–H bonds to give a metal-hydride intermediate, which rearranges to 8 via metal to ring hydrogen migration [4c]. The formation of 7 from 8 strongly resembles the dehydrogenation of $\{(C_5H_5)_2Mo\}_2$ [9], and a similar mechanism can readily be envisaged.

The thermolysis of 2 at room temperature, however, gives 7 and $\{(C_5H_5)_2ReH\}$, 5, as the sole products, and intermediate formation of 8 is not observed. It is unlikely that **8** is an intermediate in the thermolysis of **2**, since **8** and **2** have comparable lifetimes under these circumstances. The thermolysis apparently proceeds by a different mechanism, which might involve the formation of $\{(C_5H_5)_2ReH\}$ via a hydrogen abstraction in a dissociated dimer. Recombination of the resulting monomer fragments then directly produces **7**.

## Concluding remarks

We have shown that $(C_5H_5)_2ReLi$ is capable of transferring one electron to organic substrates, thus forming rhenocene. It shares this tendency with the only other isolable [10] anionic metallocene $(C_5Me_5)_2MnNa$, although the latter is a much more powerful reducing agent, as it reduces alkyl halides and $H_2O$, whereas $(C_5H_5)_2ReLi$ reacts with these substrates to give $(C_5H_5)_2ReR$ (R = alkyl) and $(C_5H_5)_2ReH$, respectively.

We have not been able to isolate or detect monomeric rhenocene, because of its great tendency to dimerize. The mode of dimerization is not unexpected in view of the fact that the monomer is a 17-electron species, which by simple metal-to-metal bond formation can generate a dimer in which both metals have an 18-electron count. The thermal instability of the rhenocene dimer is interesting, since it shows that earlier attempts to synthesize rhenocene may have been successful but that the high reaction temperatures used led to the isolation of $(C_5H_5)_2ReH$, the thermal decomposition product of the rhenocene dimer.

## Experimental

*Materials.* $(\eta^5\text{-}C_5H_5)_2ReH$ [5] and neopentyllithium [11] were prepared by literature procedures.

*Reactions.* All reactions were carried out under argon in rigorously dried solvents.

*Preparation of $(\eta^5\text{-}C_5H_5)_2ReLi$.* Solutions of $Cp_2ReLi$ were prepared by adding one equivalent of a solution of neopentyllithium in benzene or toluene (0.27 *M*) to a solution of $Cp_2ReH$ in THF (0.135 *M*) at room temperature.

*$[Cp_2Re]_2$.* Benzaldehyde (56 μl, 0.54 mmol) was added to a cold (−78 °C) solution of 0.54 mmol of $Cp_2ReLi$ in 4 ml of THF and 2 ml of benzene. The temperature was slowly raised until a purple colour was observed (approx. −40 °C). The mixture was stirred at this temperature for 30 min and then slowly allowed to warm to room temperature. The purple-black powder which separated was filtered off, washed with cold THF, and dried. Yield 50–75%.

*Thermal decomposition of $[Cp_2Re]_2$.* A suspension of 100 mg of $[Cp_2Re]_2$ in 4 ml of acetonitrile was refluxed until the red colour of the starting complex had disappeared, to give a bright yellow solution. Upon cooling crystalline **7** was isolated.

*Photochemical decomposition of $[Cp_2Re]_2$.* A solution of $[Cp_2Re]_2$ in THF or benzene was irradiated in a Pyrex vessel with visible light until the red colour of the starting complex had disappeared. The solution was analyzed by NMR spectrometry. The product was not isolated.

*Reaction of $[Cp_2Re]_2$ with benzyl bromide.* A solution of 3 mg of $[Cp_2Re]_2$ in 0.3 ml of benzene-$d_6$ was treated with a slight excess of benzyl bromide at room temperature in an NMR tube. The reaction was monitored by $^1H$ NMR. The products, $Cp_2ReCH_2C_6H_5$ and $Cp_2ReBr$, were identified by comparison with authentic samples made by reaction of $Cp_2ReLi$ and $Cp_2ReH$ with benzyl bromide [12].

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