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New bimetallic hydrocarbon-bridged complexes by nucleophilic attack of carbonylmetallates to coordinated unsaturated hydrocarbons

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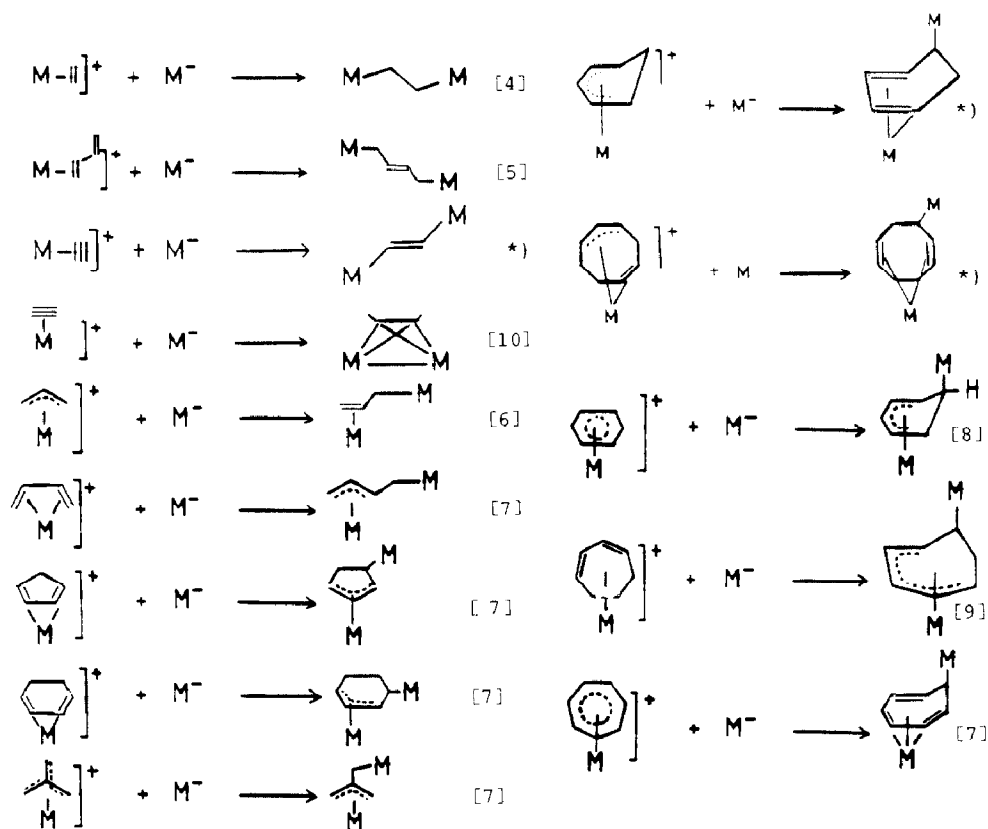
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Abstract

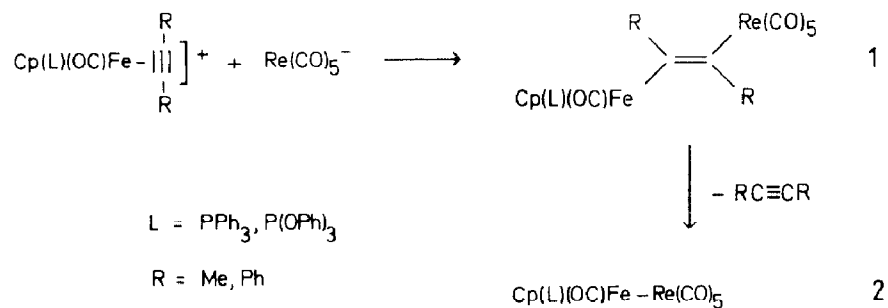
Nucleophilic attack of carbonyl metallates on unsaturated hydrocarbon in cationic complexes provides a directed synthesis of a series of bimetallic hydrocarbon bridged compounds. This method gives new classes of bimetallic complexes: $\text{Cp}(\text{OC})(\text{L})\text{Fe}(\mu\text{-}\eta^1 : \eta^1\text{-RC=CR})\text{Re}(\text{CO})_5$ ($\text{R} = \text{Me, Ph}$; $\text{L} = \text{PPh}_3, \text{P}(\text{OPh})_3$), $(\text{OC})_3\text{M}(\mu\text{-}\eta^1 : \eta^4\text{-C}_6\text{H}_7)\text{M}'(\text{CO})_5$ ($\text{M} = \text{Fe, Ru}$; $\text{M}' = \text{Re, Mn}$), $(\text{OC})_3\text{Fe}(\mu\text{-}\eta^1 : \eta^4\text{-C}_6\text{H}_7)\text{W}(\text{CO})_3\text{Cp}$, $(\text{OC})_3\text{Ru}(\mu\text{-}\eta^1 : \eta^4\text{-C}_8\text{H}_{11})\text{Re}(\text{CO})_5$, $(\text{OC})_3\text{M}(\mu\text{-}\eta^1 : \eta^5\text{-C}_6\text{H}_4\text{R}_2)\text{Re}(\text{CO})_5$ ($\text{M} = \text{Mn, Re}$; $\text{R} = \text{H, Me, Cl}$), $(\text{OC})_3\text{Mn}(\mu\text{-thiophene})\text{Re}(\text{CO})_5$. A comparison of the structural data of the C_2 -bridged complexes $(\text{OC})_5\text{ReCH}_2\text{CH}_2\text{Re}(\text{CO})_5$, $(\text{OC})_5\text{ReC}(\text{CO})=\text{C}(\text{CO})\text{Re}(\text{CO})_5$, $(\text{OC})_5\text{ReC}\equiv\text{CRE}(\text{CO})_5$ is given.

Walter Hieber laid the foundations of carbonylrhenium chemistry [1] in addition to his many other important achievements. Pentacarbonyl rhenate, $\text{Re}(\text{CO})_5^-$ [2], has been found to be an excellent reagent for the directed synthesis of hydrocarbon-bridged complexes [3] owing to its high nucleophilicity and to the formation of a strong $\text{Re}-\text{C}$ σ -bond. Pentacarbonylrhenium anion adds to cationic complexes of olefin [4], η^2 -butadiene [5], allyl [6], η^4 -diene and cyclopentadiene [7], trimethylenemethane [7], benzene [8], cycloheptatriene [9] and tropylium [7] ligands to give the bimetallic complexes with ethylene, butenediyl and σ, π -hydrocarbon bridges, respectively (Scheme 1). As also shown in Scheme 1, addition of carbonylmetallates to a four-electron donating alkyne ligand has led to a rational synthesis of dimetallatetrahedranes [10].

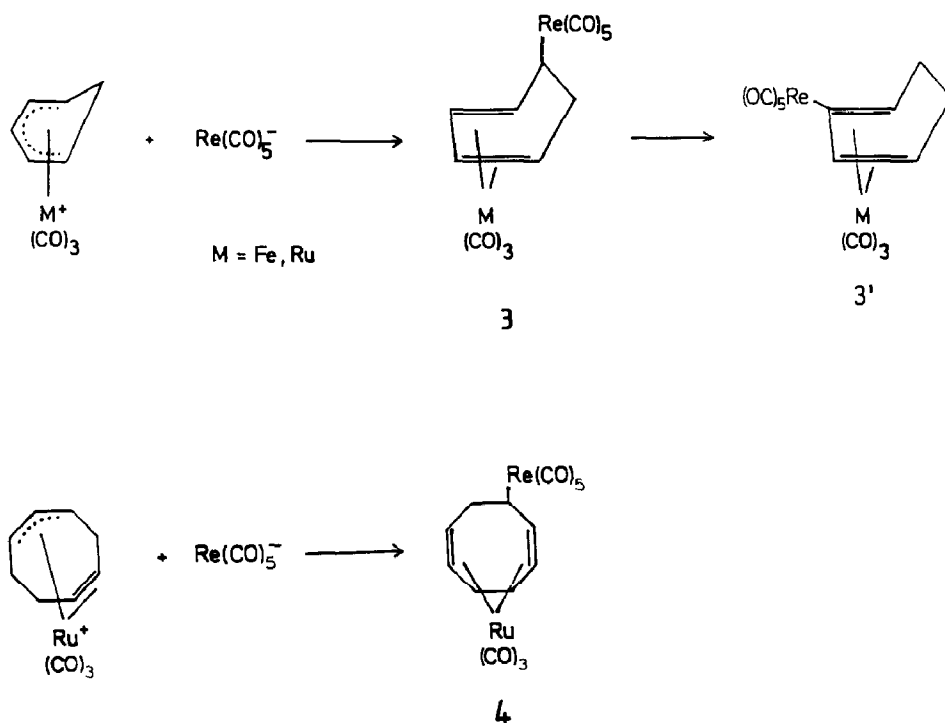
We have recently discovered new examples of such complexes. The addition of $\text{Re}(\text{CO})_5^-$ to the two-electron donating alkyne ligand of $[\text{Cp}(\text{L})(\text{OC})\text{Fe}(\text{RC}_2\text{R})]^+$ yields the σ, σ -alkyne bridged complexes **1**. These thermolabile compounds easily



Scheme 1. ★ this work.



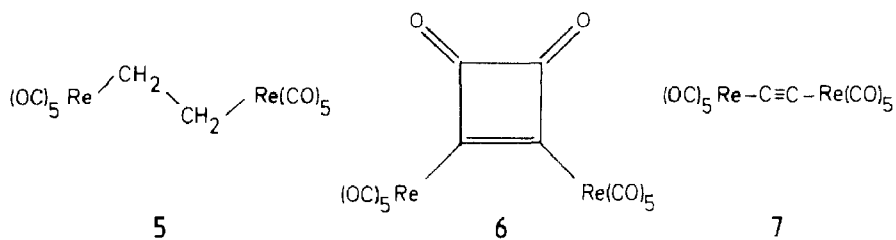
lose the alkyne bridge to give the metal-metal bonded dimers **2**, which are also accessible by other routes [11]; the stability of complexes decreases with $\text{L} = \text{PPh}_3 > \text{P(OPh)}_3 \gg \text{CO}$. With $\text{L} = \text{CO}$ the exclusive formation of the metal-metal bonded dimers has been observed. More stable is complex **1** with $\text{L} = \text{PPh}_3$, $\text{R} = \text{Me}$ which decomposes slowly at $\sim 20^\circ\text{C}$ in the solid state and quickly at $\sim -30^\circ\text{C}$ in solution. The most stable compounds of type **1** proved to be $\text{Cp}(\text{Me}_3\text{P})_2\text{Ru}(\mu\text{-}\eta^1: \eta^1\text{-MeO}_2\text{C}=\text{CCO}_2\text{Me})\text{Re}(\text{CO})_5$ and $\text{Cp}(\text{Me}_3\text{P})_2\text{Ru}(\mu\text{-}\eta^1: \eta^1\text{-MeO}_2\text{C}=\text{CCO}_2\text{Me})\text{Ru}(\text{CO})_2\text{Cp}$ which we have synthesized by addition of $\text{Re}(\text{CO})_5^-$ or $[\text{Ru}(\text{CO})_2\text{Cp}]^-$ to $[\text{Cp}(\text{Me}_3\text{P})_2\text{Ru}(\text{MeO}_2\text{C}\equiv\text{CCO}_2\text{Me})]^+ \text{PF}_6^-$ [12]. In this connection, we should



mention that the addition of organic nucleophiles to $[\text{Cp}(\text{CO})\text{LFe}(\text{alkyne})]^+$ has been extensively studied by Reger [13].

The σ, π -cyclic diene-bridged complexes **3** or **4** are formed from the addition of $\text{Re}(\text{CO})_5^-$ to $[(\eta^5\text{-C}_6\text{H}_7)\text{M}(\text{CO})_3]^+$ ($M = \text{Fe, Ru}$) or $[(\eta^2 : \eta^3\text{-C}_8\text{H}_{11})\text{Ru}(\text{CO})_3]^+$, respectively. NMR spectroscopic data indicate the structure of the first formed adduct **3**. However, a solution rearrangement occurs giving the final product **3'** in which the $\text{Re}(\text{CO})_5$ group is bonded to a sp^2 carbon atom; this must involve a H shift [15a]. Products **3'** ($M = \text{Ru}$) and **4** have been characterized by X-ray diffraction [14]. The anions $\text{Mn}(\text{CO})_5^-$ and $\text{Cp}(\text{OC})_3\text{W}^-$ also can be added to $[(\eta^5\text{-C}_6\text{H}_7)\text{Fe}(\text{CO})_3]^+$; the products are less thermostable, particularly in solution. Pearson, Lewis and Kane-Maguire [15] have examined attack of common nucleophiles to cyclohexa- and cycloocta-dienyl complexes of iron and ruthenium.

The coordinated benzene of $[(\text{OC})_3\text{Mn}(\eta^6\text{-C}_6\text{H}_6)]^+$ undergoes nucleophilic attack with $\text{Re}(\text{CO})_5^-$ to give the σ, π -cyclohexadienyl-bridged complex $(\text{OC})_3\text{Mn}(\eta^1 : \eta^5\text{-C}_6\text{H}_6)\text{Re}(\text{CO})_5$ which shows fluxional behaviour in solution [8]. Other examples of this class of compounds that we have prepared are $(\text{OC})_3\text{Mn}(\mu\text{-}\eta^1 : \eta^5\text{-C}_6\text{H}_5\text{Cl})\text{Re}(\text{CO})_5$, $(\text{OC})_3\text{Mn}(\mu\text{-}\eta^1 : \eta^5\text{-C}_6\text{H}_5\text{Me})\text{Re}(\text{CO})_5$, $(\text{OC})_3\text{Mn}(\mu\text{-}\eta^1 : \eta^5\text{-C}_6\text{H}_4\text{ClMe})\text{Re}(\text{CO})_5$, $(\text{OC})_3\text{Re}(\mu\text{-}\eta^1 : \eta^5\text{-C}_6\text{H}_6)\text{Re}(\text{CO})_5$ and $(\text{OC})_3\text{Re}(\mu\text{-}\eta^1 : \eta^5\text{-C}_6\text{H}_5\text{Me})\text{Re}(\text{CO})_5$. In the reactions of the cationic chlorobenzenemanganese complexes, chlorine displacement by $\text{Re}(\text{CO})_5^-$ also occurs producing $[(\text{OC})_3\text{Mn}(\eta^6\text{-C}_6\text{H}_5\text{Re}(\text{CO})_5)]^+$ as a by-product. Reaction between $[\text{CpFe}(\eta^6\text{-C}_6\text{H}_5\text{Cl})]^+$ and $\text{Re}(\text{CO})_5^-$ results in the exclusive formation of the chlorine substitution product $[\text{CpFe}(\eta^6\text{-C}_6\text{H}_5\text{Re}(\text{CO})_5)]^+$. Recently Heppert et al. have obtained various σ, π -



Re - C	2.30(1)	2.18(1)	2.14(2)
C - C	1.52(2)	1.37(1)	1.20(3)
C - C	1.53 C ₂ H ₆	1.34 C ₂ H ₄	1.21 C ₂ H ₂

benzene-bridged complexes by substitution of halide in $(\eta^6\text{-haloarene})\text{Cr}(\text{CO})_3$ by carbonyl metallates [16].

Angelici et al. have studied the addition of nucleophiles to π -thiophene complexes as models for the hydrodesulfurisation (HDS) reactions [17]. The use of $\text{Re}(\text{CO})_5^-$ as nucleophile has led us to the bimetallic complex $(\text{OC})_3\text{Mn}(\text{C}_4\text{H}_4\text{S})\text{Re}(\text{CO})_5$, whose structure still needs to be solved.

The recent synthesis [18] and X-ray structural determination [19] of **7** allow the comparison of dirhenated ethane [4], ethene [20] and ethyne. The carbon-carbon bond lengths of **5-7** parallel those in ethane, ethene and ethyne, as shown below. The significant shortening of the rhenium carbon distance in **7** compared to **5** reflects an increasing *s* character of carbon as observed for organic derivatives. Notably, the two $\text{Re}(\text{CO})_5$ groups of **7** are arranged in the eclipsed conformation (Fig. 1), whereas in $\text{Re}_2(\text{CO})_{10}$ the two $\text{Re}(\text{CO})_5$ groups are staggered in the solid state [21]. As in $\text{Re}_2(\text{CO})_{10}$, the equatorial carbonyl groups are bent away from the axial carbonyl group. The chemistry of **7** is under study in our laboratory.

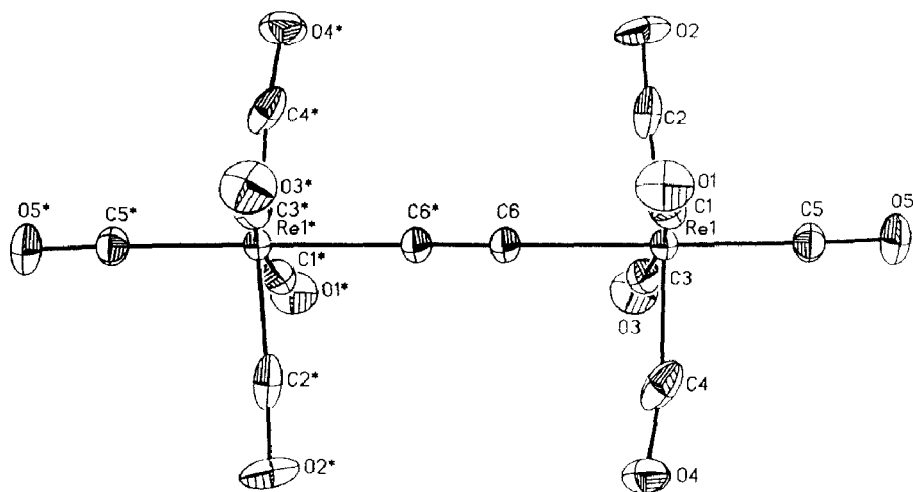


Fig. 1. Structure of $(\text{OC})_5\text{ReC}\equiv\text{CRe}(\text{CO})_5$.

The synthesis of hydrocarbon-bridged complexes may then be used to prepare a wide variety of heterobimetallic derivatives. Such compounds may be precursors to mixed metal clusters or to mixed metal particles on inorganic supports which at present find much interest in catalysis [22].

Acknowledgements

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