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Preliminary communication

VINYLIDENE COMPLEXES OF TRANSITION METALS

IV*. THE TRANSFER OF THE PHENYLVINYLIDENE LIGAND FROM MANGANESE TO RHENIUM. THE NOVEL BINUCLEAR COMPLEX $Cp_2MnRe(\mu\text{-}C{=}CHPh)(CO)_4$

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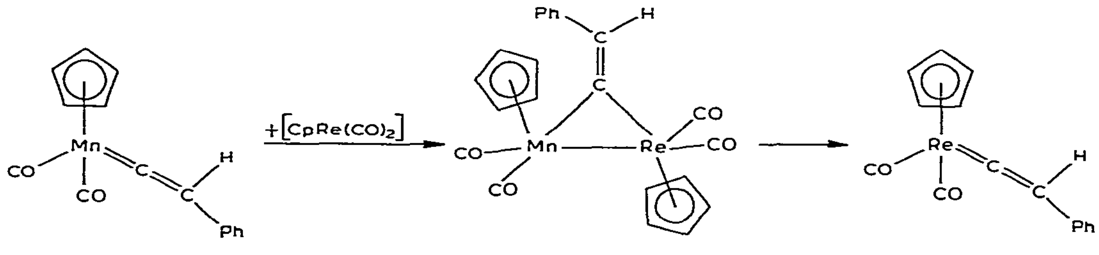
Summary

The novel complex $Cp_2MnRe(\mu\text{-}C{=}CHPh)(CO)_4$ (I) containing the bridging phenylvinylidene ligand and Mn—Re bond was obtained in the reaction of $CpMn(C{=}CHPh)(CO)_2$ with $CpRe(CO)_2\cdot THF$. Complex I turns into $CpRe(C{=}CHPh)(CO)_2$ under normal conditions. This is the first example of the transfer of the vinylidene ligand from one transition metal to another.

Previously [1,2] we obtained the complexes of type $CpM(C{=}CHPh)(CO)_2$ and $Cp_2M_2(\mu\text{-}C{=}CHPh)(CO)_4$, where M = Mn or Re, with a terminal and a bridging phenylvinylidene ligand respectively.

This paper is concerned with the transfer of the phenylvinylidene ligand from manganese to rhenium through intermediate formation of the binuclear complex $Cp_2MnRe(\mu\text{-}C{=}CHPh)(CO)_4$ (I):



(I)

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*For part III see ref. 2.

The reaction was carried out in THF at 20°C within 4 h. Complex I was isolated by chromatography in 4% yield, and small amounts of Cp_2Mn_2-(μ-C=CHPh)$(CO)_4$ and Cp_2Re_2(μ-C=CHPh)$(CO)_4$ were also obtained and identified by IR spectra and TLC.

Complex I represents dark orange crystals with m.p. 161—163°C, readily soluble in common organic solvents. Analysis: Found: C, 45.23; H, 2.93; Re, 31.07; Mn, 9.16. $C_{22}H_{16}O_4MnRe$ calcd.: C, 45.13; H, 2.76; Re, 31.82; Mn, 9.38%.

Complex I is only slightly stable and transforms into CpRe(C=CHPh)$(CO)_2$ both under normal conditions and at low temperature (—78°C). This transformation is well observed in IR spectra. The IR spectrum of solid I (KBr) contains the intensive ν(C=C) band of the bridging vinylidene ligand at 1552 cm^{-1}. This band is close to the ν(C=C) of Cp_2Mn_2 (μ-C=CHPh)$(CO)_4$ at 1548 cm^{-1} [1] and Cp_2Re_2(μ-C=CHPh)$(CO)_4$ at 1555 cm^{-1} [2]. The IR spectrum of the solution of I in cyclohexane contains the ν(C≡O) bands at 2003w, 1981w, 1952s, 1938w and 1920m cm^{-1}. The ν(C≡O) bands at 1981, 1952 and 1920 cm^{-1}, attributable to the complex I, gradually disappear and after 20 h at room temperature only the two ν(C≡O) bands at 2003s and 1938s cm^{-1} of equal intensity remain. The spectrum of the obtained product of transformation is identical to that of CpRe(C=CHPh)$(CO)_2$ [2].

Complex I was obtained also by the independent synthesis in the reaction of CpRe(C=CHPh)$(CO)_2$ with CpMn$(CO)_2$·THF under analogous conditions.

References

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