

Preliminary communication

TRANSITION METAL—CARBENE COMPLEXES

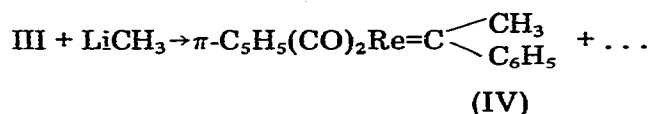
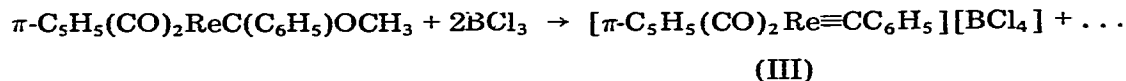
XCVII*. π -CYCLOPENTADIENYLDICARBONYLMETHYLPHENYL-CARBENERHENIUM

ERNST OTTO FISCHER*, ROGER L. CLOUGH and PETER STÜCKLER

Inorganic Chemistry Institute, Technical University, Munich (Germany)

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We recently submitted a report [2] of the first examples of transition metal—carbene complexes having aryl, alkyl or alkyl, alkyl substituents at the carbene carbon atom; π -cyclopentadienyldicarbonylmethylphenylcarbene-manganese (I) and π -cyclopentadienyldicarbonyldimethylcarbenemanganese (II). We now report the isolation of an aryl, alkyl carbene complex of rhenium, π -cyclopentadienyldicarbonylmethylphenylcarbenerrhenium (IV), which was obtained using the analogous preparative route: low temperature reaction of methyl lithium with a cationic carbyne complex, in this case π -cyclopentadienyldicarbonylphenylcarbynerhenium tetrachloroborate (III), which was itself synthesized by reaction of π -cyclopentadienyldicarbonylmethoxyphenylcarbenerrhenium with boron trichloride.



The carbyne complex III was obtained as yellow crystals, the carbene complex IV as orange crystals of relatively high thermal stability. The complex III is soluble in polar solvents only such as methylene chloride or acetonitrile, the complex IV is soluble in both polar and nonpolar organic solvents. The molecular compositions of III and IV were established by complete elemental analyses. The mass spectrum of IV showed the expected molecular peak (412, referred to ^{187}Re), as well as peaks corresponding to the successive loss of the two carbonyl ligands. The NMR spectra confirm the proposed structures of III and IV.

*For part XCVI see ref. 1.

TABLE 1

¹H NMR CHEMICAL SHIFTS (PPM) OF III AND IV(acetone-*d*₆ with TMS as internal standard, multiplicity, intensity in brackets)

	$\delta(\pi\text{-C}_6\text{H}_5)$	$\delta(\pi\text{-C}_5\text{H}_5)$	$\delta(\text{CH}_3)$	Temperature (°C)
III	8.10 m (5) ^a	6.76 s (5)	—	-60
IV	7.10 m (5)	5.67 s (5)	2.27 s (3)	20

^am = multiplet; s = singlet.

TABLE 2

¹³C SHIFT ASSIGNMENTS FOR III AND IV(acetone-*d*₆, ppm)

	$\delta(\text{Re}-\text{C})$	$\delta(\text{CO})$	$\delta(\text{C}_1)$ ^a	$\delta(\text{C}_{o,m,p})$	$\delta(\text{C}_5\text{H}_5)$	$\delta(\text{CH}_3)$	Temperature (°C)
III	317.7	186.8	145.3	136.7 132.9 128.8	94.1	—	-70
IV	306.0	206.5	168.7	127.4 126.0 118.5	92.9	57.9	-50

The very low field ¹³C resonance at δ 306.0 ppm in IV is characteristic of a carbene carbon atom. This carbene signal is actually shifted significantly downfield compared with other known rhenium carbene complexes which have an electron-donating α -oxygen atom (for example δ 290.9 ppm for $\pi\text{-C}_5\text{H}_5(\text{CO})_2\text{ReC}(\text{CH}_3)\text{OCH}_3$ and δ 289.0 ppm for $\pi\text{-C}_5\text{H}_5(\text{CO})_2\text{ReC}(\text{C}_6\text{H}_5)\text{OCH}_3$) [3]. This downfield shift has also been observed for the complexes I and II.

Experimental

All work was carried out under a nitrogen atmosphere, employing solvents free of water and oxygen.

 π -Cyclopentadienyldicarbonylphenylcarbynerhenium tetrachloroborate

Gaseous boron trichloride was passed through a solution of 250 mg (0.58 mmol) π -cyclopentadienyldicarbonylmethoxyphenylcarbenerhenium in 30 ml of pentane. The yellow precipitate thus formed was collected and washed twice with cold pentane (0°C). The residue was dissolved in 4 ml of methylene chloride. After filtration and evaporation of the solvent at 0°C yellow crystals of III were obtained. M.p. 78°C (dec.); yield 0.27 g (86% from $\pi\text{-C}_5\text{H}_5(\text{CO})_2\text{ReC}(\text{C}_6\text{H}_5)\text{OCH}_3$); IR in methylene chloride: 2089 vs, 2038 vs cm^{-1} (Found: C, 30.79; H, 1.95; B, 1.85; Cl, 25.05; O, 5.95; Re, 34.35. $\text{C}_{14}\text{H}_{10}\text{BCl}_4\text{O}_2\text{Re}$ calcd.: C, 30.62; H, 1.84; B, 1.97; Cl, 25.83; O, 5.83; Re, 33.91%. Mol. wt. 549.1.

 π -Cyclopentadienyldicarbonylmethylphenylcarbenerhenium

At -40°C 2.5 ml of a 1.4 molar solution of methyllithium in ether were

added to 0.9 g (1.6 mmol) of π -cyclopentadienyldicarbonylphenylcarbyne-rhenium tetrachloroborate. After stirring for 8 h at this temperature, the dark red solution was decanted. The solid residue was again treated with 2.5 ml of methyllithium solution at -40°C for 8 h and the organic layers combined and washed through a column containing a 5 cm layer of silica gel. The solvent was evaporated and the compound redissolved in a 2% solution of ether in pentane and submitted to column chromatography on silica gel at 12°C with 2% ether in pentane as eluent. The orange band eluted first was collected. Recrystallisation from pentane or ether/pentane gave orange crystals of analytically pure IV. M.p. $74-75^{\circ}\text{C}$; yield: 0.31 g (46% from III); IR in hexane: 1975 vs, 1901 vs cm^{-1} . (Found: C, 43.93; H, 3.17; O, 7.95; Re, 45.80. $\text{C}_{15}\text{H}_{13}\text{O}_2\text{Re}$ calcd.: C, 43.79; H, 3.18; O, 7.78; Re, 45.25%).

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