

Reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ReH}$ with Organic Electrophiles: Preparation of New Biscyclopentadienyl Rhenium Compounds

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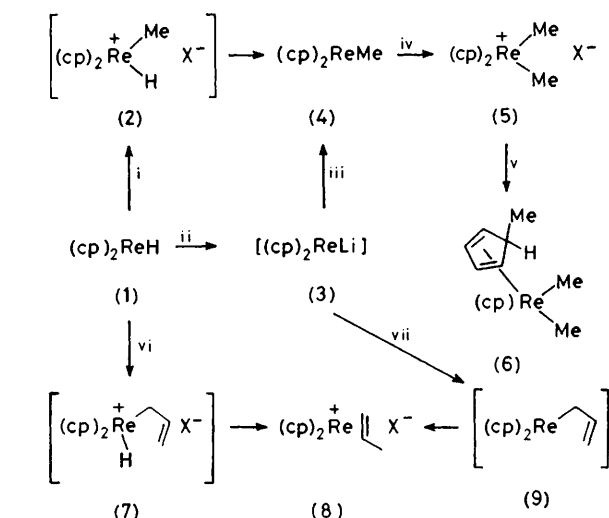
Summary The title compound (**1**) reacts with methyl iodide and allyl bromide to give $[(\text{cp})_2\text{ReMe}_2]^+$ (**5**) ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$) and $[(\text{cp})_2\text{Re}(\text{C}_3\text{H}_5)]^+$ (**8**) respectively; the dihydrido cation $[(\text{cp})_2\text{ReH}_2]^+$ (**10**) reacts with diazomethane and excess of RCN to give the metallocarbene cations $[(\text{cp})_2\text{Re}=\text{C}(\text{NHMe})\text{R}]$ (**11**).

An extensive chemistry of biscyclopentadienyl transition metal compounds is known.¹ However, biscyclopentadienyl rhenium compounds are rare and for this reason we have explored the potential of the hydride $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ReH}]$ (**1**)² as a precursor of such derivatives. Compound (**1**) is known to have donor properties; it can be protonated² and it gives complexes with Lewis acids.³ Here we report unusual reactions of the hydride (**1**) with organic electrophiles to give new biscyclopentadienyl rhenium compounds.

Compound (**1**) reacts with an excess of methyl iodide in the presence of di-isopropylethylamine to give the dimethyl cation **5** $\{\delta[(\text{CD}_3)_2\text{CO}] 5.65 (10\text{H}, \text{s}, \text{cp}) \text{ and } 1.05 (6\text{H}, \text{s}, \text{Me})\}$ in 80% yield. The rhenium iodide $(\text{cp})_2\text{ReI}$ is obtained as a by-product (*ca.* 40%) when the base is not present. It is clear that the role of the amine is deprotonation of the intermediate (**2**) to give the neutral methyl compound (**4**) which then reacts with another molecule of methyl iodide (Scheme 1) giving (**5**).

The hydride (**1**) reacts with an excess of butyl-lithium to give an intermediate lithio derivative, which we formulate as (**3**) by analogy with the same reactions in tungsten and molybdenum systems.⁴ The reaction of (**3**) with methyl tosylate gives the methyl compound (**4**) [oil; $\delta(\text{C}_6\text{D}_6) 4.0 (10\text{H}, \text{s}, \text{cp})$ and $0.75 (3\text{H}, \text{s}, \text{Me})$] (80% yield). Treatment of (**4**) with methyl iodide generates the cation (**5**) (90%).

The reaction of (**5**) with methyl-lithium gives the neutral complex (**6**) which has been previously obtained⁵ from the reaction of (**1**) with a large excess of methyl iodide and butyl-lithium. It is now possible to write a mechanism for this unusual reaction: $(1) \rightarrow (3) \rightarrow (4) \rightarrow (5) \rightarrow (6)$ (Scheme 1).

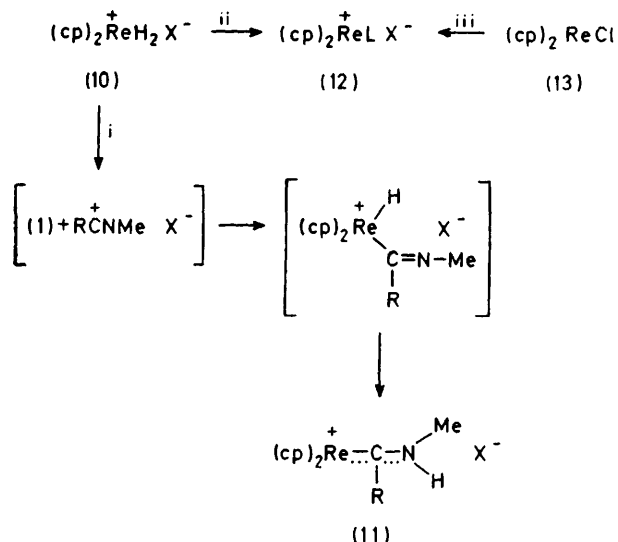


SCHEME 1. ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{X} = \text{PF}_6$) i, MeI, di-isopropylethylamine, acetone, 1 h, then NH_4PF_6 ; ii, $\text{BuLi-Et}_2\text{O}$, 15 min; iii, $\text{MeOSO}_2\text{C}_6\text{H}_4\text{OMe-}p$, 30 min; iv, $\text{MeI-Me}_2\text{CO}$, 15 min, then NH_4PF_6 ; v, $\text{MeLi-Et}_2\text{O}$, 30 min; vi, allyl bromide, acetone, 30 min, then NH_4PF_6 ; vii, allyl bromide then HPF_6 in toluene.

Compound (**1**) reacts with an excess of allyl bromide to give the π -olefin complex (**8**) (70%) $\{\delta[(\text{CD}_3)_2\text{CO}] 5.4 (10\text{H}, \text{s}, \text{cp}), 2.4 (3\text{H}, \text{m}, \text{CH}=\text{CH}_2), \text{ and } 1.85 (3\text{H}, \text{d}, J 6 \text{ Hz}, \text{Me})\}$. This complex presumably arises from rearrangement of the intermediate σ -allyl cation (**7**). Protonation of the neutral σ -allyl complex (**9**), generated from the lithio derivative (**3**), also gives the π -complex (**8**) (Scheme 1).

Treatment of the dihydrido cation (**10**) dissolved in acetonitrile with diazomethane leads to the formation of the metallocarbene (**11**) ($\text{R} = \text{Me}$) (60%) $\{\delta[(\text{CD}_3)_2\text{CO}] 12 (1\text{H},$

vbr, N-H), 4·85 (10H, s, cp), 3·65 (3H, d, *J* 6 Hz, N-Me), and 3·1 (3H, s, C-Me). The signal at 3·65 becomes a singlet when 1,4-diazabicyclo[2.2.2]octane is added to the n.m.r. tube or when the N-H proton is irradiated}. We assume



SCHEME 2. (cp = $\eta^5\text{-C}_5\text{H}_5$; R = Me, Ph; X = PF₆; L = PPh₃, PMePh₂, PMe₂Ph, or pyridine) i: CH₂N₂ in RCN, 20 °C, 30 min; ii: L in Me₂SO, 100 °C, 3 h; iii: L, AgSbF₆ in CH₂Cl₂ then NH₄PF₆.

that this reaction involves nucleophilic attack of (1) on the cation [MeCNMe]⁺, formed by reaction of diazomethane with acetonitrile in the presence of the acid (10), followed by rearrangement (Scheme 2). The metallocarbene (11) (R = Ph) is similarly obtained when benzonitrile is used instead of acetonitrile.

The cation (10) reacts with two-electron ligands L to generate the compounds (12) (L = phosphines, pyridine) which can also be made by reaction of the chloro derivative (13) with silver ion in the presence of L. Compound (13) may be prepared by the reaction of (1) with CCl₄ in acetone (excess of CCl₄ gives insoluble material).²

The above results show that the hydride (1) is a precursor of an extensive (cp)₂Re chemistry. It is interesting to contrast these reactions of (1) with organic halides to give new compounds containing Re-C bonds, with the results obtained with the analogous molybdenum and tungsten systems in which only hydrogen replacement by halogen and reduction of the organic halide have so far been observed.⁶

All the new cationic compounds gave satisfactory elemental analyses. The mass spectra of the neutral compounds (4) and (13) (*m/e* 332 and 352, respectively for Re = 187) were consistent with the structures assigned to them.

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¹ J. C. Green and M. L. H. Green in 'Comprehensive Inorganic Chemistry,' Pergamon, Oxford, 1973, Vol. 4, p. 418.

² M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1958, 3916.

³ M. P. Johnson and D. F. Shriver, *J. Amer. Chem. Soc.*, 1966, **88**, 301.

⁴ B. R. Francis, M. L. H. Green, Tuyet Luong-Thi, and G. A. Moser, *J.C.S. Dalton*, 1976, 1339. Compound (3) was initially formulated as a dithiated derivative (see ref. 5) but this was later found to be incorrect (M. L. H. Green, personal communication.)

⁵ R. L. Cooper, M. L. H. Green, and J. T. Moelwyn-Hughes, *J. Organometallic Chem.*, 1965, **3**, 261.

⁶ Akira Nakamura, *J. Organometallic Chem.*, 1978, **164**, 183; M. L. H. Green and P. J. Knowles, *J.C.S. Perkin I*, 1973, 989.