# Synthesis of Bis(η-pentamethylcyclopentadienyl)rhenium Hydride and its Photochemical Conversion into Decamethylrhenocene

**F. Geoffrey N. Cloke* and Jeremy P. Day**

*School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.*

Cocondensation of rhenium vapour with 1,2,3,4,5-pentamethylcyclopentadiene gives bis(η-pentamethylcyclopentadienyl)rhenium hydride; photolysis of the hydride yields monomeric bis(η-pentamethylcyclopentadienyl)rhenium, and reduction of the latter gives a stable anion which may be readily converted into bis(η-pentamethylcyclopentadienyl)methylrhenium.

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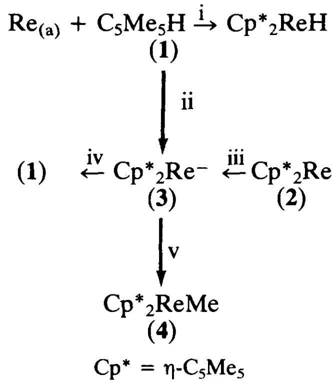
Elegant matrix isolation studies[1] have demonstrated the existence at low temperature of rhenocene, $(\eta\text{-}C_5H_5)_2Re$, generated by *in situ* photolysis of bis(η-cyclopentadienyl)rhenium hydride. Recent work has also resulted in the preparation of a stable rhenocene dimer, $[(\eta\text{-}C_5H_5)_2Re]_2$, containing a metal–metal bond.[2] We were interested to see if the pentamethylcyclopentadienyl analogues could be prepared, and whether the use of the bulky $C_5Me_5$ ligand would lead to a thermally stable monomeric rhenocene. Recently we described the synthesis of $(\eta\text{-}C_5Me_5)_2WH_2$ *via* tungsten atoms;[3] we now report that metal vapour synthesis can also be used to prepare $(\eta\text{-}C_5Me_5)_2ReH$.

Rhenium vapour (*ca.* 1.0 g) from a positive hearth electron-beam furnace[4] operating at 3200 °C was cocondensed with an excess of 1,2,3,4,5-pentamethylcyclopentadiene at 77 K. Work-up of the reaction mixture and finally purification by sublimation afforded air-sensitive pale yellow crystals of bis(η-pentamethylcyclopentadienyl)rhenium hydride, (η-C$_5$-



**Scheme 1.** *Reagents:* i, cocondensation at 77 K; ii, u.v. photolysis in pentane; iii, K mirror, 1,2-dimethoxyethane; iv, $H_2O$; v, MeI, 1.0 equivalent.

$Me_5)_2ReH$, (**1**), in 15% yield (based on rhenium). Compound (**1**)†‡ is highly soluble in hydrocarbon solvents and sublimes readily (40 °C/$10^{-3}$ mbar). The hydride ligand is characterised by a weak i.r. band at 2061 $cm^{-1}$ (Nujol mull) and a $^1H$ n.m.r. resonance at $\delta$ −13.24.§

Photolysis of (**1**) in n-pentane (125 W medium pressure Hg arc, 60 h) produced a deep red-purple solution from which could be isolated air-sensitive deep purple crystals of decamethylrhenocene, ($\eta$-$C_5Me_5)_2Re$, (**2**) in essentially quantitative yield. Compound (**2**) is paramagnetic with $\mu_{eff.} = 1.95$ $\mu_B$ (Evans method[5]) but is e.s.r. silent down to 150 K; this is in accord with magnetic circular dichroism measurements made on matrix isolated $(C_5H_5)_2Re$[6] which show the ground state to be $^2E_{2g}$, in which the large $g$ value anisotropy would be expected to make an e.s.r. signal hard to detect. Molecular weight measurements (vapour pressure equilibration method) show that (**2**) is monomeric in pentane.

The identity of (**2**) has been further confirmed by its ready conversion into a deep orange diamagnetic anion, ($\eta$-$C_5Me_5)_2Re^-$, (**3**),§ by potassium mirror reduction (see Scheme 1). Compound (**3**) reacts instantly with traces of water to form the hydride (**1**); reaction with 1 equivalent of extremely dry methyl iodide affords the methyl complex ($\eta$-$C_5Me_5)_2ReMe$, (**4**), in high yield. Compound (**4**) may be isolated as red crystals from pentane.†§ A similar route has been used to prepare $(C_5H_5)_2ReMe$ from $(C_5H_5)_2ReLi$.[7,8]

The results described represent the first entry into the bis($\eta$-pentamethylcyclopentadienyl)rhenium system, one which should prove to have an extensive chemistry. In particular the synthesis of the monomeric metallocene (**2**) (osmocene is the only other third row metallocene which has been isolated) is a further illustration of the role of the $C_5Me_5$ ligand in stabilising highly reactive and co-ordinatively unsaturated complexes. This has also previously been demonstrated by the use of the ligand to stabilise the open shell metallocene ($\eta$-$C_5Me_5)_2Ti$.[9]

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† Satisfactory microanalysis has been obtained.

‡ A parent ion was observed in the mass spectrum with the appropriate rhenium isotope pattern.

§ $^1H$ N.m.r. data ($\delta$) for (**1**), (**3**), and (**4**); spectra were run on a Bruker WP80 instrument; $\delta$ is relative to internal solvent. (**1**) ($C_6D_6$): 1.93 (30H, s, $C_5Me_5$), −13.24 (1 H, s, Re–H); (**3**) ($C_4D_8O$): 1.89 (30 H, s, $C_5Me_5$); (**4**) ($C_6D_6$): 1.67 (30 H, s, $C_5Me_5$), 0.24 (3 H, s, Re–$CH_3$).

## References

1 J. Chetwynd-Talbot, P. Grebenik, and R. N. Perutz, *J. Chem. Soc., Chem. Commun.*, 1981, 452.
2 P. Pasman and J. J. M. Snel, *J. Organomet. Chem.*, 1984, **276**, 387.
3 F. G. N. Cloke, J. C. Green, M. L. H. Green, and C. P. Morley, *J. Chem. Soc., Chem. Commun.*, in the press.
4 F. G. N. Cloke and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1981, 1938; F. G. N. Cloke, manuscript in preparation.
5 D. F. Evans, *J. Chem. Soc.*, 1959, 2005.
6 P. A. Cox, P. Grebenik, R. N. Perutz, R. G. Graham, and R. Grinter, *Chem. Phys. Lett.*, 1984, **109**, 5, 415.
7 D. Baundry and M. Ephritikine, *J. Chem. Soc., Chem. Commun.*, 1979, 895.
8 R. I. Mink, J. J. Wetter, P. R. Young, and G. D. Stucky, *J. Am. Chem. Soc.*, 1979, **101**, 6928.
9 J. E. Bercaw, *J. Am. Chem. Soc.*, 1974, **96**, 5087.