

Preliminary communication

TRANSITION METAL HYDRIDE ABSTRACTION BY TROPYLIUM CATION: A NEW ROUTE TO *monohapto*-CYCLOHEPTATRIENYL COMPLEXES

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Summary

Reaction of $(\eta\text{-C}_5\text{H}_5)(\text{ON})(\text{OC})\text{ReH}$ with tropylium tetrafluoroborate forms $[(\eta\text{-C}_5\text{H}_5)(\text{ON})(\text{OC})\text{Re}(1,2\text{-}\eta^2\text{-C}_7\text{H}_8)] [\text{BF}_4]$, which is deprotonated by $(\text{C}_2\text{H}_5)_3\text{N}$ to afford the thermally stable *monohapto* derivative $(\eta\text{-C}_5\text{H}_5)(\text{ON})(\text{OC})\text{Re}(\eta^1\text{-C}_7\text{H}_7)$.

The only *monohapto*-cycloheptatrienyl* complex of a transition metal thus far reported is $(\eta^1\text{-C}_7\text{H}_7)\text{Re}(\text{CO})_5$ (1) [1]. Its synthesis involved reaction of $\text{Na}^+\text{Re}(\text{CO})_5^-$ with $\text{C}_7\text{H}_7^+\text{BF}_4^-$, or with 7-cycloheptatrienylacyl chloride and subsequent decarbonylation. The rarity of these interesting derivatives is due in part to the stability of the C_7H_7 radical [2], which weakens the metal—metal bond by some 21–24 kcal mol⁻¹ relative to ordinary alkyl derivatives.

The high thermal stability [3] of $(\eta\text{-C}_5\text{H}_5)(\text{ON})(\text{OC})\text{ReH}$ (2) suggested that this transition metal moiety might form stable *monohapto*-cycloheptatrienyl complexes. Since our efforts to form the corresponding anion had been unsuccessful, an alternative synthetic approach was required. We have found that the hydride 2 reacts with tropylium tetrafluoroborate to form the yellow, air-stable salt 3 ($\nu(\text{CO})$ 2050, $\nu(\text{NO})$ 1774 cm⁻¹ in CH_2Cl_2) in which cycloheptatriene is coordinated in 1,2- η^2 fashion. Complex 3 is then readily deprotonated by triethylamine, forming the desired derivative 4 as dark red, air-stable crystals ($\nu(\text{CO})$ 1967, $\nu(\text{NO})$ 1712 cm⁻¹ in n-hexane). Both reactions proceed in high yield, and both new compounds give a satisfactory elemental analysis.

*We mean this term to denote specifically the $\eta^1\text{-C}_7\text{H}_7$ form, in which the metal atom replaces a methylene hydrogen of cycloheptatriene. The numbering system is shown in Fig. 1.

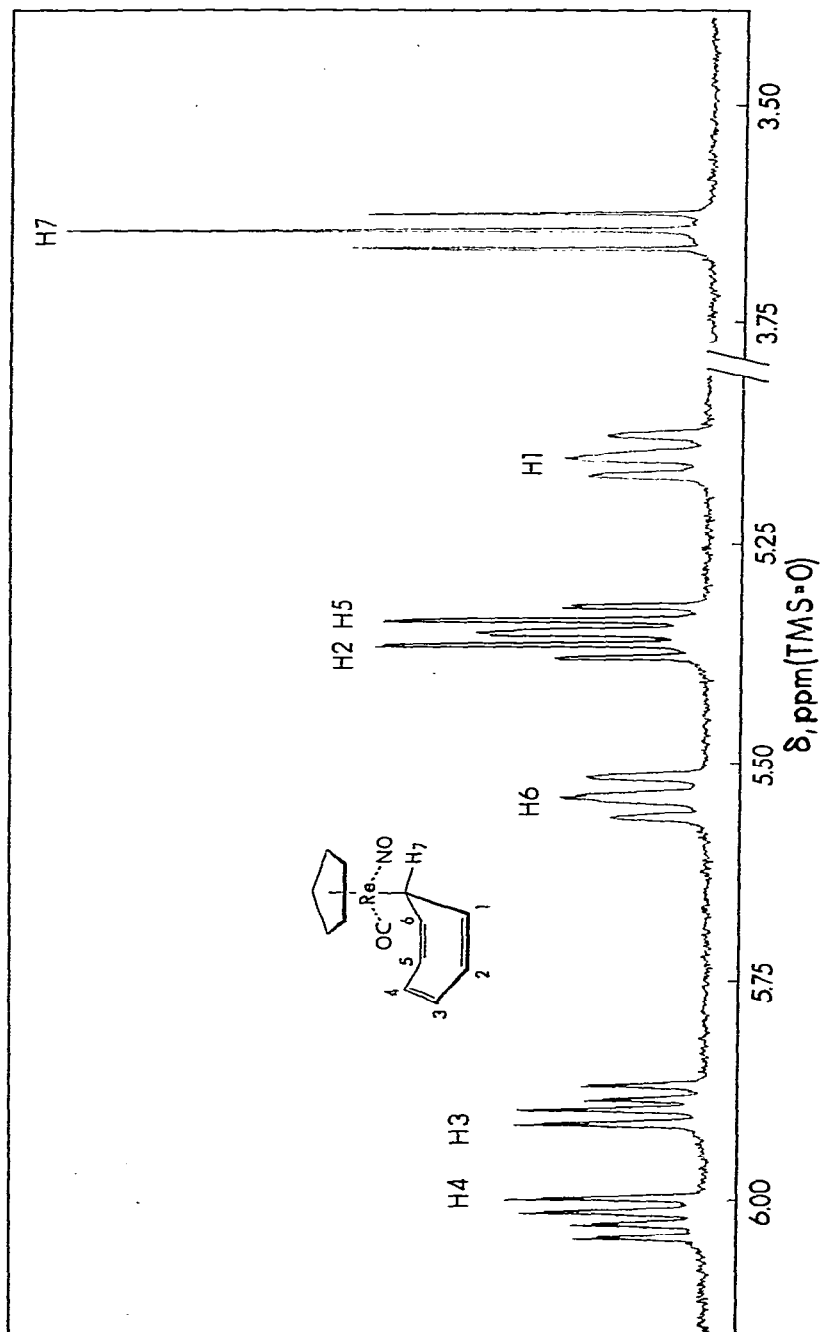
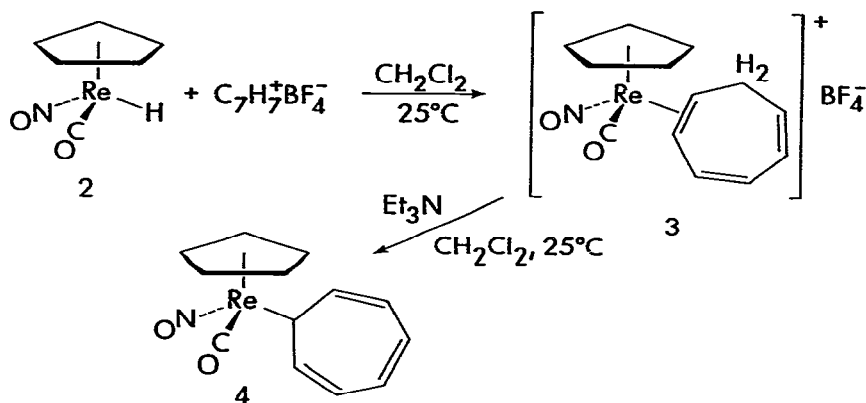


Fig. 1. Proton NMR spectrum of compound 4.



The proton NMR spectrum of 4 is of considerable interest. Since rhenium is a chiral center, the two sides of the ring are nonequivalent. Figure 1 shows the spectrum and assignments for the seven observed signals, as determined by selective decoupling. A boat conformation with rhenium in the quasi-axial position is suggested by the coupling constants, $J(\text{H}(1)-\text{H}(7)) \cong J(\text{H}(6)-\text{H}(7)) = 8 \text{ Hz}$, a value close to that observed in 1 [1]; the quasi-axial position of the metal in crystalline 1 has now been confirmed by X-ray crystallography [4]. Such a geometry is consistent with chemical shift differences between diastereotopic proton pairs ($|\delta(\text{H}(1)) - \delta(\text{H}(6))| > |\delta(\text{H}(3)) - \delta(\text{H}(4))| > |\delta(\text{H}(2)) - \delta(\text{H}(5))|$) if the trend reflects increasing distance from the chiral center.

Compound 4 is surprisingly stable thermally, decomposing only slowly (half life $\cong 76$ minutes) at 130°C (sealed NMR tube, dimethylsulfoxide- d_6) to form ditropyl and the new dimer $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CO})]_2$. No lineshape changes could be detected at 130°C , nor did attempted spin saturation transfer experiments indicate any fluxional behaviour. Thus the activation energies for both homolytic dissociation and metal migration are higher than in $(7\text{-}\eta^1\text{-C}_7\text{H}_7)\text{Re}(\text{CO})_5$ [1]. These observations also show that the chiral rhenium centre is configurationally stable on the NMR time scale at this temperature.

We presume that the olefin cation 3 is generated by hydride abstraction (compare the reported hydride abstractions by trityl cation [5,6]), with coordination of the triene produced. The assigned $1,2\text{-}\eta^2$ structure is based on the proton NMR spectrum. The two $(\eta^5\text{-C}_5\text{H}_5)$ signals (δ 6.29 and 6.25 ppm, 2:1 intensity ratio) and two sets of eight C_7H_8 resonances have been completely assigned to the expected two diastereomers. It is striking that the $\text{p}K_a$ of the notoriously unacidic free cycloheptatriene (estimated to be 36 [7]) has been lowered upon coordination to < 3.4 (i.e., $\text{p}K_a$ for Et_3NH^+).

We are currently exploring the applicability of this new route in the synthesis of further examples of *monohapto*-cycloheptatrienyl transition metal compounds.

Acknowledgments

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