# Synthesis of Re($\eta^6$-$C_6H_6$)($\eta^5$-$C_7H_7$) and Re($\eta^6$-$C_6H_6$)($\eta^5$-$C_7H_9$) and Characterization using 2D N.M.R. Spectroscopy

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The compounds Re($\eta^6$-$C_6H_6$)($\eta^5$-$C_7H_7$) and Re($\eta^6$-$C_6H_6$)($\eta^5$-$C_7H_9$) have been prepared by co-condensation of rhenium atoms with a benzene–cycloheptatriene mixture and characterized by 2D n.m.r. spectroscopic methods.

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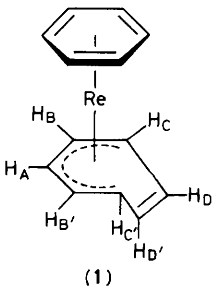
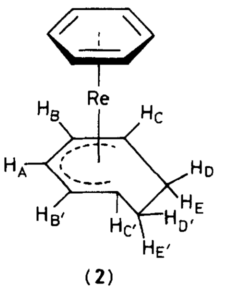
Co-condensation of metal atoms with binary ligand mixtures can lead to quite specific reactions even when separate co-condensation with pure constituent ligands fails to give tractable products. For example, chromium with benzene–$PF_3$ gives Cr($\eta$-$C_6H_6$)($PF_3$)$_3$,[1] and benzene–$PMe_3$ mixtures with Zr, Hf, Re, or Fe form M($\eta$-$C_6H_6$)$_2$($PMe_3$), M = Zr or Hf,[2] [Re($\eta$-$C_6H_6$)($PMe_3$)$_2$]$_2$,[3] or Fe($\eta$-$C_6H_6$)($PMe_3$)$_2$,[4] respectively. Co-condensation of rhenium with either pure benzene or cycloheptatriene gave no tractable products.

However, co-condensation of rhenium atoms (1.0 g) with a benzene–cycloheptatriene mixture (1 : 1; 70 cm$^3$) gave the compounds Re($\eta^6$-$C_6H_6$)($\eta^5$-$C_7H_7$) (**1**) and Re($\eta^6$-$C_6H_6$)($\eta^5$-$C_7H_9$) (**2**) in approximately equimolar quantities (0.3 g, 20%).

Compounds (**1**) and (**2**) are red, air-sensitive, volatile crystals. Chromatography on alumina (6% $H_2O$) isolates (**1**) in high purity, but destroys (**2**). We were unable to obtain (**2**) free from (**1**).



(1)



(2)

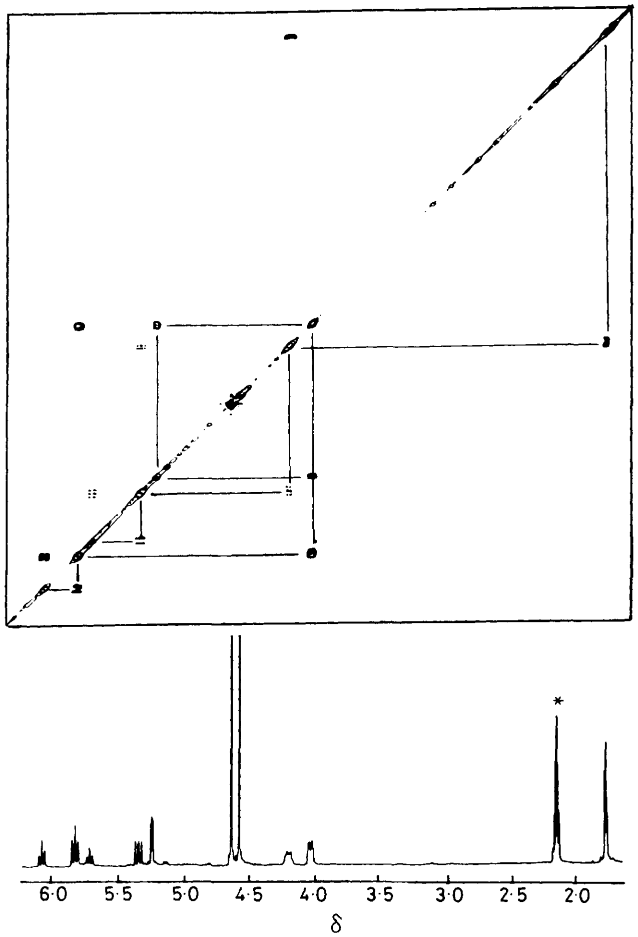


**Figure 1.** 250 MHz 2D Jeener spectrum (contour plot) run on a Bruker AM-250 instrument. A $90_x^\circ$–$t_1$–45° free induction decay (FID) pulse sequence was used with a delay of 1.0 s before each acquisition: 256 FIDs of 512 data points were accumulated at 256 $t_1$ values, using quadrature detection. The spectral width in both dimensions was 1500 Hz and the acquisition time was 0.65 s. Sine-bell multiplication and zero filling precede Fourier transformation in both dimensions. Symmetrized absolute-value spectra are shown. Total acquisition time 2.5 h. (Asterisk denotes solvent $C_6D_5CD_3$.)

Compounds (**1**) and (**2**) have been characterized by mass spectroscopy, microanalysis [for (**1**)], and especially n.m.r. spectroscopy.†

The 1D $^1H$ n.m.r. spectrum of the mixture of (**1**) and (**2**) was complex and the partial second-order nature of the spectrum limited a simple analysis. However, the 2D Jeener[5] spectrum allowed straightforward assignment of two independent

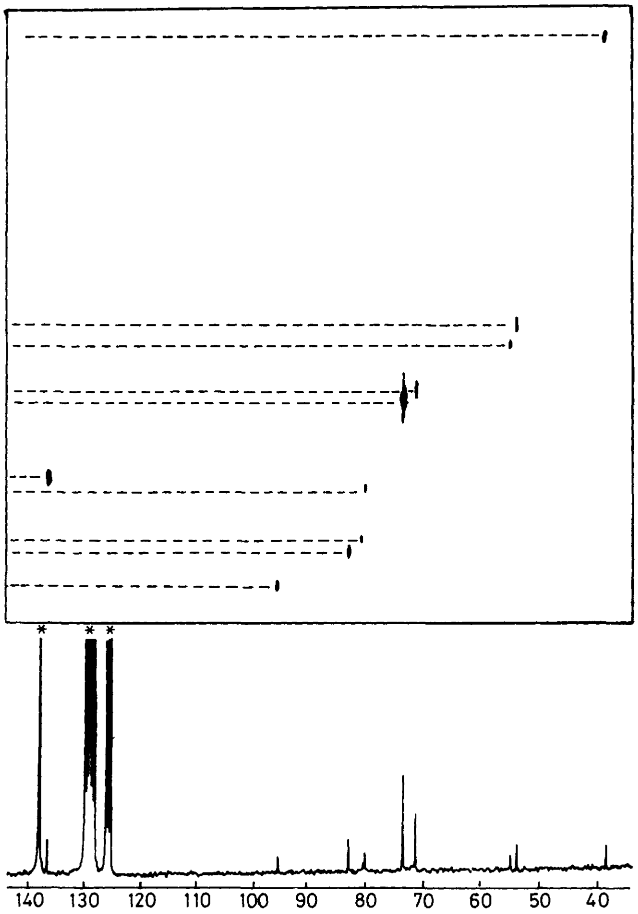


**Figure 2.** 2D $^{13}C$–$^1H$ shift correlation spectrum (contour plot) run on a Bruker AM-250 instrument.

$$\mathrm{A}\left(\begin{array}{llll} {}^{1}\mathrm{H}: & -90^\circ - t_1 - & -t_1 - \mathrm{D3} - 90^\circ & \mathrm{BB} \\ {}^{13}\mathrm{C}:\mathrm{D1} & & 180^\circ & 90^\circ - \mathrm{D4} - \mathrm{FID} \end{array}\right)$$

pulse sequence was used with delays D1 = 3.0 s, D3 = 3 ms, D4 = 2 ms. 256 FIDs of 2K data points were accumulated at 256 $t_1$ values, using quadrature detection. The spectral width was 1500 Hz in the $^1H$ dimension ($f_1$) and 8900 Hz in the $^{13}C$ dimension ($f_2$). Sine-bell squared multiplication was applied to the $f_1$ dimension and Gaussian weighting to the $f_2$ dimension prior to Fourier transformation in both dimensions. Total acquisition time 14 h. (Asterisk denotes solvent $C_6D_5CD_3$.)

coupling networks, one corresponding to a $\eta^5$-$C_7H_7$ ligand and the other to a $\eta^5$-$C_7H_9$ ligand (Figure 1). This assignment was confirmed by examining the $^{13}C$–$^1H$ 2D shift-correlation spectrum (Figure 2), and the combination of these two techniques allowed determination of the C–C connectivity.[6] $^{13}C$ N.m.r. methods, for example the INADEQUATE sequences,[7] would require both larger quantities of material and substantially longer acquisition times.

Surprisingly, high-temperature $^1H$ magnetization transfer experiments have shown that the $\eta^5$-$C_7H_7$ ring in (**1**) does not undergo ring-shift processes at temperatures up to 90 °C which puts a lower limit on $\Delta G^\ddagger$ of *ca.* 75 kJ $mol^{-1}$.

This work demonstrates the value of 2D n.m.r. methods for structural assignment; these methods are available for all Fourier transform n.m.r. instruments with adequate data handling facilities.

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† Compound (**1**), $^1H$ n.m.r. in $C_6D_5CD_3$ (*J* in Hz): 6.05 [1 H, tt, $J(H_A–H_B)$ 5.3, $J(H_A–H_C)$ 0.5, $H_A$], 5.8 [2 H, ddd, $J(H_B–H_A)$ 5.3, $J(H_B–H_C)$ 6.0, $J(H_B–H_D)$ 1.0, $H_B$], 5.3 [2 H, m(6 lines), $H_D$], 4.6 (6 H, s, $\eta$-$C_6H_6$), and 3.9 [2 H, m(15 lines), $H_C$]; $^{13}C$ n.m.r. in $C_6D_5CD_3$: 135.5 [d, $J$(C–H) obscured by solvent, $C_D$], 95.3 [d, $J$(C–H) 161, $C_A$], 82.6 [d, $J$(C–H) 162, $C_B$], 73.0 [d, $J$(C–H) 172, $\eta$-$C_6H_6$], and 52.8 [d, $J$(C–H) 152, $C_C$]; $M^+$, *m/z*, 356($Re^{187}$).

Compound (**2**), $^1H$ n.m.r. in $C_6D_5CD_3$ (*J* in Hz): 5.7 [1 H, t, $J(H_A–H_B)$ 5.1, $H_A$], 5.3 [2 H, dd, $J(H_B–H_A)$ 5.1, $J(H_B–H_C)$ 6.4, $H_B$], 4.54 [6 H, s, $\eta$-$C_6H_6$], 4.16 [2 H, m(13 lines), $H_C$], and 1.71 [4 H, d, $J(H_{D,E}–H_C)$ 2.2, $H_D + H_E$]; $^{13}C$ n.m.r. in $C_6H_5CD_3$: 92.8 [d, $J$(C–H) 163, $H_A$], 80.0 [d, $J$(C–H) 160, $H_B$], 70.7 [d, $J$(C–H) 173, $\eta$-$C_6H_6$], 54.0 [d, $J$(C–H) 143, $H_c$], and 37.0 [t, $J$(C–H) 130, $C_{D/E}$]; $M^+$, *m/z* 358($Re^{187}$).

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