Synthesis, Characterisation, and Reactivity of $(\eta^6$-Indene$)(\eta^5$-indenyl$)$rhenium: a Precursor to Hetero-bimetallic $(\mu$-$\eta^3:\eta^6$-Indenyl$)$ Derivatives

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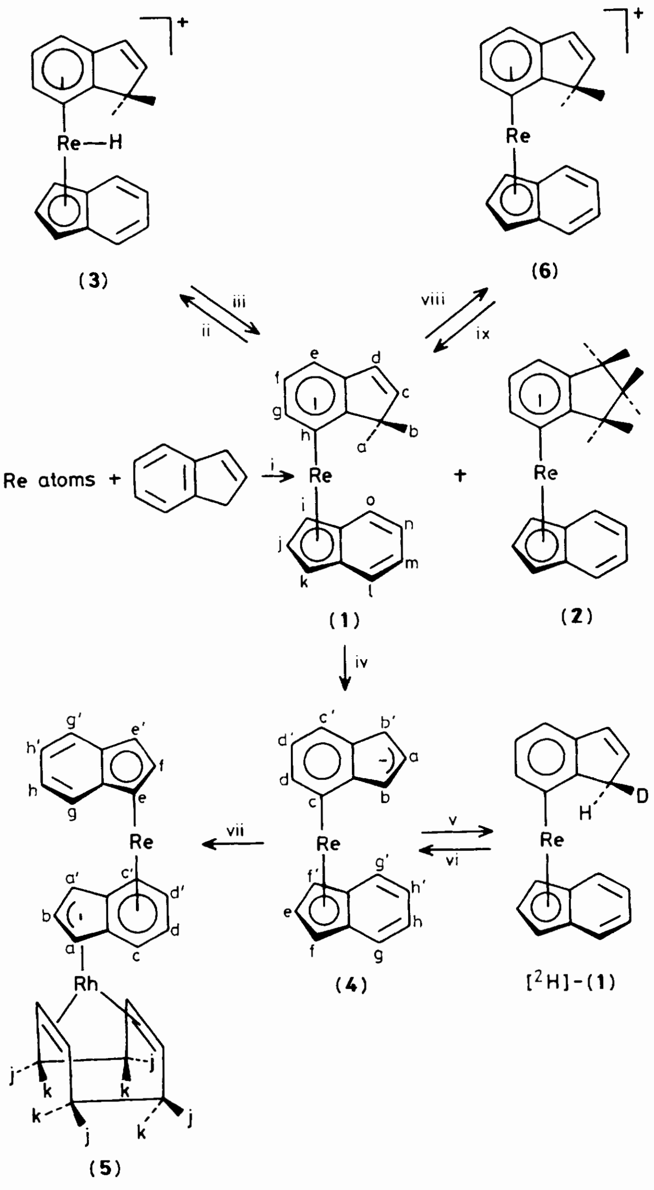
The compound $[Re(\eta^6\text{-}C_9H_8)(\eta^5\text{-}C_9H_7)]$ formed by co-condensation of rhenium atoms with indene deprotonates with KH giving the ionic compound $K^+[Re(\eta^6\text{-}C_9H_7)(\eta^5\text{-}C_9H_7)]^-$ which reacts with $[Rh(\eta\text{-}C_8H_{12})Cl]_2$ to form $[Re(\eta^5\text{-}C_9H_7)(\mu\text{-}\eta^6:\eta^3\text{-}C_9H_7)Rh(\eta^4\text{-}C_8H_{12})]$.

η^5-Indenyl complexes are known for most transition metals and normally they are bonded to the metal *via* the C_5-ring in a manner analogous to the η-cyclopentadienyl ligand. Less commonly the η^6-indene ligand can act as a substituted benzene ligand *i.e.* as $\eta^6\text{-}C_9H_8$. Here we describe the first example of an indenyl ligand acting as an η^6-ligand and also as a bridging ligand, to two transition metals, in the $(\mu\text{-}\eta^3:\eta^6\text{-}C_9H_7)^-$ mode.

Co-condensation of rhenium atoms (2—3 g) using the metal vapour synthesis technique[1,2] with an excess of pure indene (*ca.* 120 cm^3) yields orange, air-sensitive crystals of $[Re(\eta^6\text{-}C_9H_8)(\eta^5\text{-}C_9H_7)]$ (**1**)† (*ca.* 400 mg, 5%). During larger scale syntheses of (**1**) we also isolated as a second product, $[Re(\eta^6\text{-}C_9H_{10})(\eta^5\text{-}C_9H_7)]$ (**2**) (typically 1—2% of total product).

Cyclic voltammetry studies show that (**1**) undergoes a reversible one-electron oxidation in tetrahydrofuran with $E_{1/2}$ of -235 mV with respect to the Fc^+/Fc couple $\{Fc = [Fe(\eta\text{-}C_5H_5)_2]\}$ with a peak-to-peak separation of 95 mV.



Scheme 1. i, Co-condensation at -195 °C [(**1**); 5%]; ii, HBF_4 in diethyl ether (room temp.; 90%); iii, KOH in thf (room temp.; 50%); iv, KH in thf (room temp.; 90%); v, D_2O in thf (room temp.; 90%); vi, KH in thf (60 °C; 90%); vii, $[Rh(\eta\text{-}C_8H_{12})Cl]_2$ in thf, (room temp.; 80%); vii and ix, cyclic voltammetry experiment in thf (supporting electrolyte $NBu^n_4PF_6$).

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† *Selected spectroscopic data:* (*J* in Hz).

Compound (**1**), ^1H n.m.r. data ([$^2H_6$]-benzene at 500 MHz): 6.91 [1H, dq, $J(H_l\text{–}H_m)$ 7.5, $J(H_l\text{–}H_n)$ $J(H_l\text{–}H_o)$ $J(H_l\text{–}H_k)$ 1.0, H_l], 6.75 [1H, ddd, $J(H_m\text{–}H_n)$ 8.5, $J(H_m\text{–}H_l)$ 7.5, $J(H_m\text{–}H_o)$ 1.0, H_m], 6.61 [1H, dq, $J(H_o\text{–}H_n)$ 7.5, $J(H_o\text{–}H_m)$ $J(H_o\text{–}H_l)$ $J(H_o\text{–}H_i)$ 1.0, H_o], 6.58 [1H, ddd, $J(H_n\text{–}H_m)$ 8.5, $J(H_n\text{–}H_o)$ 7.5, $J(H_n\text{–}H_l)$ 1.0, H_n], 5.84 [2H, m (16 lines), $H_c + H_d$], 5.53 [1H, m (4 lines), H_i], 5.40 [1H, m (4 lines), H_k], 5.25 [1H, t, $J(H_j\text{–}H_k)$ $J(H_j\text{–}H_i)$ 3, H_j], 5.23 [1H, dd, $J(H_g\text{–}H_h)$ 5, $J(H_g\text{–}H_e)$ 1, H_g], 4.91 [1H, dd, $J(H_e\text{–}H_g)$ 1, $J(H_e\text{–}H_f)$ 5, H_e], 4.72 [1H, t, $J(H_f\text{–}H_g)$ $J(H_f\text{–}H_e)$ 5, H_f], 4.55 [1H, t, $J(H_h\text{–}H_g)$ $J(H_h\text{–}H_f)$ 5, H_h], 1.81 [1H, dt, $J(H_{a/b}\text{–}H_{a/b})$ 21, $J(H_{a/b}\text{–}H_c)$ $J(H_{a/b}\text{–}H_d)$ 1, H_a or H_b], 0.75 [1H, dt, $J(H_{a/b}\text{–}H_{a/b})$ 21, $J(H_{a/b}\text{–}H_c)$ $J(H_{a/b}\text{–}H_d)$ 1, H_b or H_a].

^{13}C n.m.r. data ([$^2H_6$]benzene at 125.6 MHz): 131.6 [dq, $^1J(C\text{–}H)$ 166, $^2J(C\text{–}H_a)$ $^2J(C\text{–}H_b)$ $^3J(C\text{–}H_d)$ 3, C_c], 127.6 [ddt, $^1J(C\text{–}H)$ 168, $^3J(C\text{–}H_a)$ $^3J(C\text{–}H_b)$ 3, $^2J(C\text{–}H_c)$ 1.5, C_d], 126.8 [dd, $^1J(C\text{–}H)$ 167, $^3J(C\text{–}H)$ 3.7, C_l], 126.4 [dd, $^1J(C\text{–}H)$ 170, $^3J(C\text{–}H)$ 3.7, C_o], 121.2 [d, $^1J(C\text{–}H)$ 168, C_n], 120.1 [d, $^1J(C\text{–}H)$ 161, C_m], 92.7 [s, C_p], 92.2 [s, C], 84.4 [s, C], 79.4 [s, C], 74.9 [d, $^1J(C\text{–}H)$ 176, C_j], 66.6 [d, $^1J(C\text{–}H)$ 177, C_k], 66.1 [d, $^1J(C\text{–}H)$ 178, C_i], 59.9 [d, $^1J(C\text{–}H)$ 170, C_e], 58.9 [d, $^1J(C\text{–}H)$ 165, C_f], 57.9 [d, $^1J(C\text{–}H)$ 172, C_g], 57.6 [d, $^1J(C\text{–}H)$ 169, C_h], 35.5 [t, $^1J(C\text{–}H)$ 129, $C_{a/b}$].

Compound (**3**), partial ^1H n.m.r. data: ([$^2H_2$]dichloromethane, room temp., 500 MHz): -5.14 [1H, s, H_p].

Compound (**4**), ^1H n.m.r. data: ([$^2H_8$]tetrahydrofuran, room temp., 500 MHz): 6.87 [1H, t, $J(H_a\text{–}H_b)$ 3.5, H_a], 6.63 [2H, m, (6 lines), $J(H_g\text{–}H_f)$ 1.0, $H_{gg'}$], 6.40 [2H, m, (4 lines), $H_{hh'}$], 5.44 [2H, m, (4 lines), $H_{cc'}$], 4.85 [2H, dd, $J(H_f\text{–}H_e)$ 1.9, $J(H_f\text{–}H_g)$ 1.0, $H_{ff'}$], 4.72 [2H, d, $J(H_b\text{–}H_a)$ 3.5, $H_{bb'}$], 4.71 [1H, t, $J(H_e\text{–}H_f)$ 1.9, H_e], 4.64 [2H, m, (4 lines), $H_{dd'}$].

^{13}C n.m.r. data: ([$^2H_8$]tetrahydrofuran, room temp., 125.6 MHz): 125.3 [d, $^1J(C\text{–}H)$ 162, C_g], 121.2 [d, $^1J(C\text{–}H)$ 147, C_a], 118.6 [d, $^1J(C\text{–}H)$ 162, C_h], 91.5 [s, C], 90.3 [d, $^1J(CH)$ 164, C_b], 86.2 [s, C], 63.8 [d, $^1J(CH)$ 176, C_e], 61.6 [d, $^1J(CH)$ 167, C_d], 59.2 [d, $^1J(CH)$ 176, C_f], 52.0 [d, $^1J(CH)$ 167, C_c].

Compound (**5**): ^1H n.m.r. data: ([$^2H_6$]benzene, room temp., 500 MHz): 6.95 [2H, m, (4 lines), $H_{hh'}$], 6.75 [2H, m, (4 lines), $H_{gg'}$], 5.96 [1H, q, $J(H_b\text{–}^{103}Rh)$ $J(H_b\text{–}H_a)$ 2.2, H_b], 5.49 [2H, d, $J(H_e\text{–}H_f)$ 2.1, $H_{ee'}$], 5.21 [1H, t, $J(H_f\text{–}H_e)$ 2.1, H_f], 5.14 [2H, m, (4 lines), $H_{cc'}$], 4.59 [2H, m, (6 lines), $H_{dd'}$], 4.25 [4H, s, br., H_i], 4.06 [2H, d, $J(H_a\text{–}H_b)$ 2.2, $H_{aa'}$], 1.95 [4H, m, br., $H_{j/k}$], 1.87 [4H, m, br., $H_{j/k}$].

^{13}C n.m.r. data: ([$^2H_6$]benzene, room temp., 125.6 MHz): 127.1 [d, $C_{g/h}$], 121.4 [d, $C_{g/h}$], 98.1 [dd, $J(C_b\text{–}^{103}Rh)$ 4.5, C_b], 72.7 [d, C_f], 71.7 [dd, $J(C_a\text{–}^{103}Rh)$ 4.0, $C_{aa'}$], 69.6 [dd, $J(C_i\text{–}^{103}Rh)$ 13.5, C_i], 65.8 [d, $C_{ee'}$], 60.4 [d, $C_{d/c}$], 49.2 [d, $C_{d/c}$], 32.0 [t, C_{jk}].

Treatment of (**1**) with $HBF_4{\cdot}Et_2O$ in diethyl ether at room temp. gives the hydrido cation $[Re(\eta^6\text{-}C_9H_8)(\eta^5\text{-}C_9H_7)H]^+BF_4^-$ (**3**).† Compound (**1**) reacts with a suspension of KH in tetrahydrofuran (thf) giving a deep-red, highly air- and moisture-sensitive complex characterised by n.m.r. spectroscopy and its reactivity (*vide infra*) as $K^+[Re(\eta^6\text{-}C_9H_7)(\eta^5\text{-}C_9H_7)]^-$ (**4**).† The ^1H and ^{13}C n.m.r. spectra of (**4**) indicate that the negative charge is primarily localised on the $\eta^6\text{-}C_9H_7$ ring since the ^1H and ^{13}C chemical shifts for this ring are in close agreement with those found for $Na^+C_9H_7^-$. The compound (**4**) proved to be thermally stable and showed no evidence of an isomerisation to the di-(η^5-indenyl) anion, although the analogous $[Re(\eta\text{-}C_5Me_5)_2]^-$ has recently been isolated.[3] Treatment of (**4**) with D_2O forms $[Re(\eta^6\text{-}C_9H_7D)(\eta^5\text{-}C_9H_7)]$ [^2H]-(**1**). The ^2H n.m.r. spectrum of [^2H]-(**1**) indicated that D^+ had added regioselectively to the position assigned as *exo*-CH_2. In addition treatment of [^2H]-(**1**) with KH results in regioselective removal of the D^+ with concomitant formation of (**1**) and HD (n.m.r.).

We were interested to discover if (**4**) could act as a 'ligand' to other transition metal centres. Treatment of (**4**) with $[Rh(\eta\text{-}C_8H_{12})Cl]_2$ yields orange-red crystals of a benzene-soluble $[Re(\eta^5\text{-}C_9H_7)(\eta^3:\eta^6\text{-}C_9H_7)Rh(\eta^4\text{-}C_8H_{12})]$ (**5**).† In particular, we observed coupling of the ^{103}Rh (100%; $I = 1/2$) nucleus to the central 'allylic' proton H_b of the $\eta^3:\eta^6$-indenyl ring [$^1J(^{103}Rh\text{–}^1H)$ 2.2 Hz]. Surprisingly no coupling of the protons H_a and $H_{a'}$ to ^{103}Rh was resolvable, a phenomenon which has been observed for the related complex $[Rh(\eta^5\text{-}C_9H_7)(\eta^2\text{-}C_2H_4)_2]$.[4] However, we were able to resolve $^1J(^{103}Rh\text{–}^{13}C)$ coupling to $C_{aa'}$ (J 4.0 Hz) and C_b (J 4.5 Hz). The spectroscopic data do not allow distinction between possible isomers: on steric grounds we favour the *trans*-isomer shown in Scheme 1.

Compounds (**1**)—(**5**) have been characterised by microanalysis, mass spectrometry, and by detailed one- and two-dimensional n.m.r. spectroscopy. For example, the absence of any symmetry operators for (**1**) results in 15 chemically unique hydrogens and 14 protonated carbon atoms which have all been unambiguously assigned. Interestingly, high temperature ^1H magnetisation transfer n.m.r. experiments indicated no evidence for any dynamic behaviour of the η-indene or η-indenyl rings. The compound (**5**) is the first example of $\eta^3:\eta^6$ co-ordination for an indenyl ligand.

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