

Synthesis, characterisation and reactivity of $[\text{Re}(\eta^6\text{-C}_9\text{H}_8)(\eta^5\text{-C}_9\text{H}_7)]$, a precursor to $\mu_2\text{-}\eta^3\text{:}\eta^5\text{-indenyl derivatives}^*$

Malcolm L.H. Green, Nigel D. Lowe and Dermot O'Hare

Inorganic Chemistry laboratory, South Parks Road, Oxford, OX1 3QR (Great Britain)

(Received May 8th, 1988)

Abstract

The compounds $[\text{Re}(\eta^6\text{-C}_9\text{H}_8)(\eta^5\text{-C}_9\text{H}_7)]$ (major) and $[\text{Re}(\eta^6\text{-C}_9\text{H}_{10})(\eta^5\text{-C}_9\text{H}_7)]$ (minor) are formed by co-condensation of rhenium atoms with indene. $[\text{Re}(\eta^6\text{-C}_9\text{H}_8)(\eta^5\text{-C}_9\text{H}_7)]$ can be reversibly protonated giving $[\text{Re}(\eta^6\text{-C}_9\text{H}_8)(\eta^5\text{-C}_9\text{H}_7)\text{H}]\text{BF}_4$. $[\text{Re}(\eta^6\text{-C}_9\text{H}_8)(\eta^5\text{-C}_9\text{H}_7)]$ is deprotonated by KH giving the compound $\text{K}^+ [\text{Re}(\eta^6\text{-C}_9\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)]^-$, which reacts with $[\text{Rh}(\eta^3\text{-C}_8\text{H}_{12})\text{Cl}]_2$ to form $[\text{Re}(\eta^5\text{-C}_9\text{H}_7)(\mu_2\text{-}\eta^6\text{:}\eta^3\text{-C}_9\text{H}_7)\text{Rh}(\eta^4\text{-C}_8\text{H}_{12})]$; the first example of an $\eta^3\text{:}\eta^6\text{-indenyl}$ ligand.

$\eta^5\text{-Indenyl}$ complexes are known for most transition metals where the $\text{C}_5\text{-ring}$ is bonded to the metal in a manner analogous to the $\eta\text{-cyclopentadienyl}$ ligand [1]. Less commonly the indene ligand can act as an $\eta^6\text{-ligand}$ analogous to the $\eta^6\text{-benzene}$ ligand [2].

Here we describe the preparation and chemistry of $[\text{Re}(\eta^6\text{-C}_9\text{H}_8)(\eta^5\text{-C}_9\text{H}_7)]$ formed by co-condensation of rhenium atoms with indene. A preliminary account of part of this work has been published [3].

Results and discussion

Co-condensation of rhenium atoms (2–3 g) using the metal vapour synthesis technique (MVS) [4], with an excess of indene (ca. 120 cm³) at -195°C , yields after chromatography orange crystals of $[\text{Re}(\eta^6\text{-C}_9\text{H}_8)(\eta^5\text{-C}_9\text{H}_7)]$ (**1**).

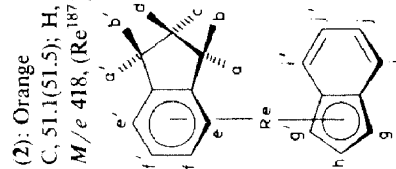
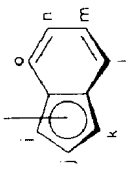
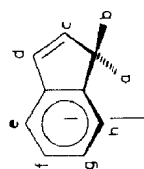
Fractional recrystallisation of the reaction mixture at low temperatures from pentane gave a second minor product namely the compound $[\text{Re}(\eta^6\text{-C}_9\text{H}_{10})(\eta^5\text{-C}_9\text{H}_7)]$ (**2**). **1** and **2** could not be separated by chromatography since **2** decomposed. The hydrogenation of double bonds during metal vapour cocondensation reactions is not uncommon, for example, co-condensation of benzene and cycloheptatriene

(Continued on p. 319)

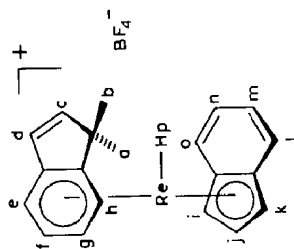
* Dedicated to Professor E.O. Fischer in recognition of his outstanding contribution to chemistry.

Table 1. Analytical and spectroscopic data

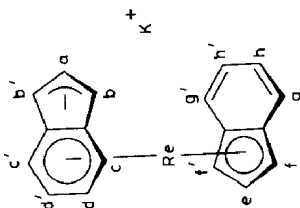
Compound	NMR data ^a		¹³ C ^c
	Found (calc)	¹ H ^b	
(1): Red C, 51.0(51.8); H, 3.7(3.6) M/e 418(Re ¹⁸⁷)(P ⁺)		6.91[1H, dq, J(H ₁ -H _m)7.5, J(H ₁ -H _n)] J(H ₁ -H _o)](H ₁ -H _k)1.0, H ₁], 6.75[1H, ddd, J(H _m -H _n)8.5, J(H _m -H ₁)7.5, J(H _m -H _o)1.0, H _m], 6.61[1H, dq, J(H _o -H _n)7.5, J(H _o -H _m)] J(H _o -H ₁)] J(H _o -H ₁)1.0, H _o], 6.58[1H, ddd, J(H _n -H _m)8.5, J(H _n -H _o)7.5, J(H _n -H ₁)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 -H _k)] J(H _j -H ₁)3, H _j], 5.23[1H, dd, J(H _g -H _h)5, J(H _g -H _e)1, H _g], 4.91[1H, dd, J(H _e -H _g)1, J(H _e -H _f)5, H _e], 4.72[1H, t, J(H _f -H _g)] J(H _f -H _e)5, H _f], 4.55[1H, t, J(H _h -H _g)] J(H _h -H _f)5, H _h], 1.81[1H, dt, J(H _{a/b} -H _{a/b})21, J(H _{a/b} -H _c)] J(H _{a/b} -H _d)1, H _a or H _b], 0.75[1H, dt, J(H _{a/b} -H _{a/b})21, J(H _{a/b} -H _c)] J(H _{a/b} -H _d)1, H _b or H _d]	131.6[ddq, J(CH)166, J(CH _a), J(CH _b), J(CH _c)3, C _d], 127.6[addt, J(CH)168, J(CH _a) J(CH _b)3, J(CH _c)1.5, C _d], 126.8[dd, J(CH)167, J(CH)3.7, C ₁], 126.4[dd, J(CH)170, J(CH)3.7, C _o], 121.2[dd, J(CH)168, C _n], 120.1[dd, J(CH)161, C _m], 92.7[s, C _j], 92.2[s, C _l], 84.4[s, C ₁], 79.4[s, C ₁], 74.9[dd, J(CH)176, C ₁], 66.6[dd, J(CH)177, C _k], 66.1[dd, J(CH)178, C ₁], 59.9[dd, J(CH)170, C _e], 58.9[dd, J(CH)165, C _f], 57.9[dd, J(CH)172, C _g], 57.6[dd, J(CH)169, C _h], 35.5[t, J(CH)129, C _{a/b}]
(2): Orange C, 51.3(51.5); H, 4.0(4.05) M/e 418, (Re ¹⁸⁷), [P ⁺ - 2]		7.16[2H, m, (4 lines), H _{ir} '], 6.68[2H, m, (4 lines), H _{jr} '], 5.49[2H, d, J(H _g -H _h)2.3, H _{gg} '], 5.17[1H, t, J(H _h -H _g)2.3, H _h], 4.75[2H, m, (4 lines), H _{ee} '], 4.53[2H, m, (4 lines), H _{ir} '] 2.73[2H, ddd, J(H _b -H _a)13.8, J(H _b -H _d)10.3, J(H _b -H _c)8, H _{bb} '], 1.95[2H, ddd, J(H _a -H _b)13.8, J(H _a -H _c)8.7, J(H _a -H _d)1.2, H _{aa} '], 1.56[1H, m, (18 lines)H _{da}], 1.14[1H, m, (16 lines), H _{ec} ']	128.0[dd, obscured by solvent, C _{1/1}], 122.0[dd, J(CH)150, C _{1/1}], 75.2[dd, J(CH)170, C _k], 67.0[dd, J(CH)169, C _g], 59.1[dd, J(CH)165, C _{f/e}], 58.7[dd, J(CH)165, C _{e/f}], 32.1[t, J(CH)130, C _{ab}], 23.6[t, J(CH)130, C _{cd}]



(3): Yellow
C, 42.6(42.7); H, 3.8(3.2)


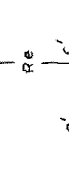
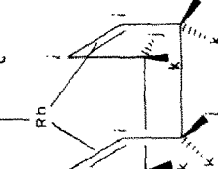


(4): Red^g



- 7.32[1H, dd, $J(\text{H}_1-\text{H}_m)$ 6.7, $J(\text{H}_1-\text{H}_n)$ 1.0, H_1],
 7.17[2H, m (6 lines), $\text{H}_m + \text{H}_n$],
 6.98[1H, dd $J(\text{H}_o-\text{H}_n)$ 8.5, $J(\text{H}_o-\text{H}_m)$ 1.0, H_o],
 6.61[1H, dt $J(\text{H}_c-\text{H}_d)$ 5.5, $J(\text{H}_c-\text{H}_a)$, $J(\text{H}_c-\text{H}_b)$ 2.0, H_c],
 6.33[1H, m (8 lines), H_d],
 5.93[1H, d $J(\text{H}_h-\text{H}_g)$ 10, H_h],
 5.84[1H, m (3 lines), H_i],
 5.70[1H, m (4 lines), H_k],
 5.57[1H, t, $J(\text{H}_j-\text{H}_i)$, $J(\text{H}_j-\text{H}_k)$ 3.2, H_j],
 5.41[1H, dd, $J(\text{H}_e-\text{H}_f)$ 5.5, $J(\text{H}_e-\text{H}_g)$ 1.9, H_e],
 5.32[1H, m, H_g],
 5.17[1H, t, $J(\text{H}_f-\text{H}_g)$, $J(\text{H}_f-\text{H}_e)$ 5.5, H_f],
 3.10[1H, dt, $J(\text{H}_{a/b}-\text{H}_{b/a})$ 23.2, $J(\text{H}_{a/b}-\text{H}_c)$, $J(\text{H}_{a/b}-\text{H}_d)$ 2.0, $\text{H}_{a/b}$],
 1.89[1H, dt, $J(\text{H}_{a/b}-\text{H}_{a/b})$ 23.2, $J(\text{H}_{a/b}-\text{H}_c)$, $J(\text{H}_{a/b}-\text{H}_d)$ 2.0, $\text{H}_{b/a}$],
 -5.14[1H, s, H_p]^e
- 6.87[1H, t, $J(\text{H}_a-\text{H}_b)$ 3.5, H_a],
 6.63[2H, m, (6 lines), $J(\text{H}_g-\text{H}_f)$ 1.0, $\text{H}_{gg'}$],
 6.40[2H, m, (4 lines), $\text{H}_{hh'}$],
 5.44[2H, m, (4 lines), $\text{H}_{cc'}$],
 4.85[2H, dd, $J(\text{H}_f-\text{H}_e)$ 1.9, $J(\text{H}_f-\text{H}_g)$ 1.0, $\text{H}_{ff'}$],
 4.72[2H, d, $J(\text{H}_b-\text{H}_a)$ 3.5, $\text{H}_{bb'}$],
 4.71[1H, t, $J(\text{H}_e-\text{H}_f)$ 1.9, H_e],
 4.64[2H, m, (4 lines), $\text{H}_{dd'}$]^f
- 125.3[d, $\nu(\text{CH})$ 162, C_g],
 121.2[d, $\nu(\text{CH})$ 147, C_a],
 118.6[d, $\nu(\text{CH})$ 162, C_h],
 91.5[s, C_j],
 90.3[d, $\nu(\text{CH})$ 164, C_b],
 86.2[s, C_l],
 63.8[d, $\nu(\text{CH})$ 176, C_e],
 61.6[d, $\nu(\text{CH})$ 167, C_d],
 59.2[d, $\nu(\text{CH})$ 176, C_f],
 52.0[d, $\nu(\text{CH})$ 167, C_c].

Table 1 (continuation)

Compound Analysis: Found (calc) (%)	NMR data ^a		¹³ C ^c
	¹ H ^b		
(5): Red-Orange C, 50.3(50.7); H, 4.0(4.22)	6.95[2H, m, (4 lines), H _{hh'}], 6.75[2H, m, (4 lines), H _{gg'}], 5.96[1H, q, J(H _b - ¹⁰³ Rh)J(H _b -H _a)2.2, H _b], 5.49[2H, d, J(H _e -H _f)2.1, H _{ee'}], 5.21[1H, t, J(H _f -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 -H _b)2.2, H _{aa'}], 1.95[4H, m, br, H _{l/k}], 1.87[4H, m, br, H _{l/k}] ^d	127.1[d, C _{g/h}], 121.4[d, C _{g/h}], 98.1[dd, J(C _b - ¹⁰³ Rh)4.5, C _b], 72.7[d, C _f], 71.7[dd, J(C _a - ¹⁰³ Rh)4.0, C _{aa}], 69.6[dd, J(C _i - 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}] ^{d,h}	
	  		

^a Given as: chemical shift δ (ppm) [relative intensity, multiplicity, J in Hz, assignment]. ^b Recorded at room temperature at 500 MHz. ^c Recorded at room temperature at 126 MHz. ^d In benzene- d_6 . ^e In dichloromethane- d_2 . ^f In tetrahydrofuran- d_2 . ^g No elemental analysis due to sensitivity to oxygen and moisture. ^h Quaternary carbon resonances were not observed.

with rhenium atoms gives both $[\text{Re}(\eta\text{-C}_6\text{H}_6)(\eta\text{-C}_7\text{H}_7)]$ and $[\text{Re}(\eta\text{-C}_6\text{H}_6)(\eta\text{-C}_7\text{H}_9)]$ [5]. A pure sample of **2** was isolated by treating the mixture of **1** and **2** with KH. Compound **1** reacted giving an ionic compound (vide infra) while **2** was inert. Subsequent extraction with pentane gave pure **2**.

Compound **1** has been characterised by elemental analysis, mass spectroscopy and by detailed 1- and 2-dimensional NMR spectroscopy. The assignments for **1** and the other new compounds **1**–**5** are given in Table 1. Discussion of the NMR data will be presented only where the interpretation is not straightforward.

The NMR spectra of **1** show the absence of any symmetry elements for **1** since there are 15 chemically unique hydrogens and 14 unique protonated carbon atoms which have all been assigned unambiguously. Several features of the ^1H NMR spectrum of **1** are worthy of note. The four hydrogens of the η^6 -indene ligand appear between δ 5.5 ($\text{H}_i\text{--H}_k$) and δ 4.5 (H_f) and the methylene hydrogens of the same ligand appear as doublets of triplets at δ 1.8 and 0.8. It is not possible to assign the latter resonances unambiguously to the *endo* and *exo* positions although the higher field signal is tentatively assigned to H_{endo} , on the assumption that the electron density on the metal would make a positive contribution to the shielding.

Transition metal indenyl complexes are well known to undergo ring shift [6] and "slip-fold" [7] distortions. However, high temperature ^1H magnetisation transfer NMR experiments on **1** showed no dynamic behaviour of the η^6 -indene or η^5 -indenyl ligands.

Compound **1** exhibits a one electron redox couple with $E_{1/2} = -235$ mV with respect to internal Fc^+/Fc ($\text{Fc} = \text{ferrocene}$), with $\Delta(E_a - E_c) = 90$ mV and $I_a/I_c = 0.99$ in thf. The heterogeneous rate constant, calculated from the kinetic analysis of the current–voltage curves indicates a diffusion controlled electron transfer reaction. Attempts to oxidise **1** with AgBF_4 were however unsuccessful.

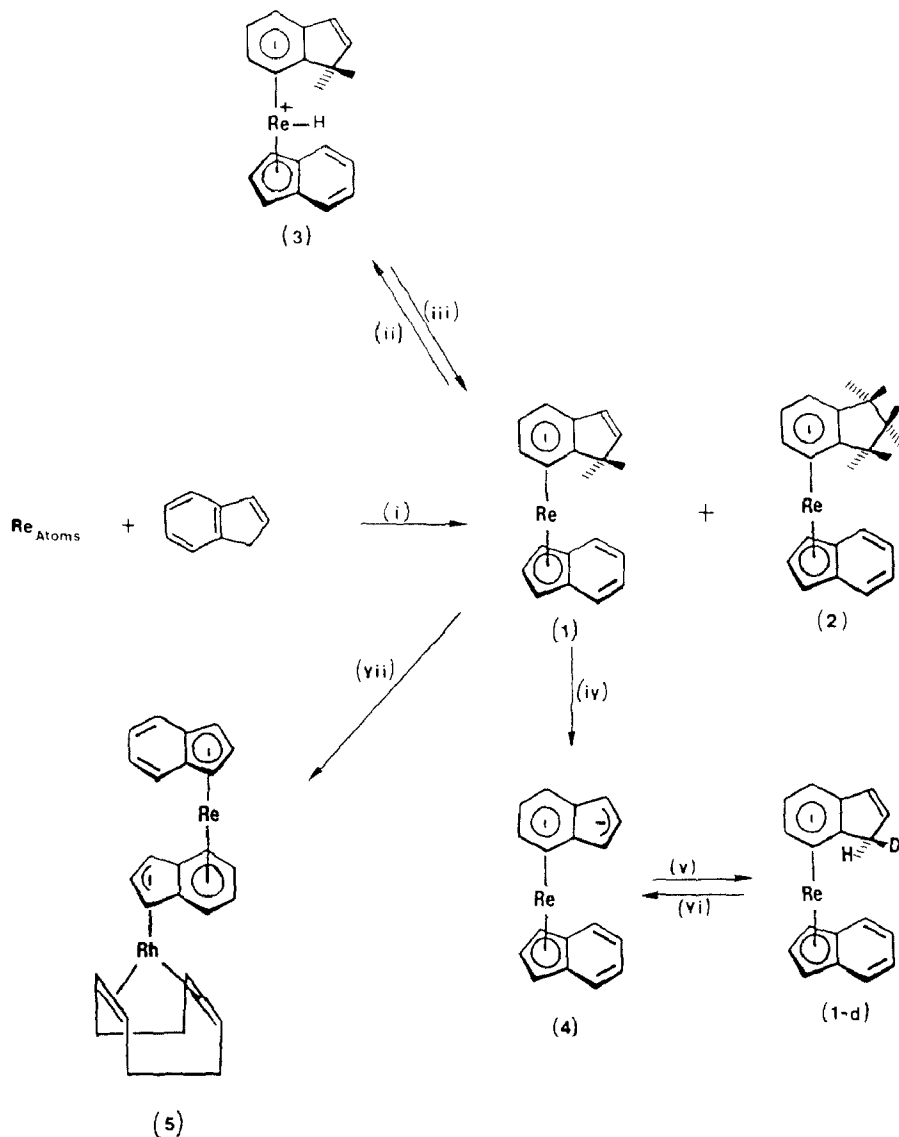
Treatment of **1** in diethyl ether with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in diethyl ether gave an instant precipitation of the highly air-sensitive bright yellow compound $[\text{Re}(\eta^6\text{-C}_9\text{H}_8)(\eta^5\text{-C}_9\text{H}_7)\text{H}]^+\text{BF}_4^-$ (**3**), in high yield. Compound **3** can be recrystallised from dichloromethane. The ^1H NMR spectrum of **3** shows a band at $\delta -5.1$ which may be assigned to a Re–H group. The spectrum is not consistent with alternative agostic structures [8]. Further there is a band in the infrared spectrum at 1950 cm^{-1} assignable to a terminal $\nu(\text{Re}\text{--H})$.

Compound **3** reacts with solvents such as acetone or methanol to reform (**1**). In contrast to bis(η^5 -indenyl)ruthenium which undergoes a ring shift on protonation with HBF_4 to form $[\text{Ru}(\eta^6\text{-indene})(\eta^5\text{-indenyl})]^+\text{BF}_4^-$ [9], there was no evidence for isomerisation of **3** to $[\text{Re}(\eta^6\text{-C}_9\text{H}_8)_2]\text{BF}_4^-$, even on heating.

Reaction of **1** with KH in tetrahydrofuran gave a deep red solution which was extremely sensitive to moisture. Attempts to isolate crystals resulted in recovery of **1**, due, presumably to hydrolysis by adventitious water. The reaction was carried out in tetrahydrofuran- d_8 and the ^1H , ^{13}C and 2-dimensional NMR spectra of the solution clearly indicate that KH had cleanly deprotonated the methylene group of the $\eta^6\text{-C}_9\text{H}_8$ ligand of **1** to give the anion $[\text{Re}(\eta^6\text{-C}_9\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)]^-$ (**4**). The ^1H and ^{13}C NMR spectra of **4** indicate that the negative charge is localised on the $\eta^6\text{-C}_9\text{H}_7$ ring since the ^{13}C chemical shifts of the C_5 ring are in close agreement with those found for $\text{Na}^+\text{C}_9\text{H}_7^-$. Compound **4** proved to be thermally stable and showed no evidence for isomerisation to $[\text{Re}(\eta^5\text{-C}_9\text{H}_7)_2]^-$, although $[\text{Re}(\eta\text{-C}_5\text{Me}_5)_2]^-$ has recently been isolated [10]. Solutions of **4** can be quenched with D_2O giving **1d** in

which the D^+ has added stereoselectively to the $\eta\text{-C}_9\text{H}_8$ ring at the position assigned as *exo*. Treatment of **1d** with KH removes D^+ selectively forming **4** and HD .

We were interested in determining whether **4** could act as an η^3 -ligand to other transition metal centres. Treatment of a solution of **4** with $[\text{Rh}(\eta^4\text{-C}_8\text{H}_{12})\text{Cl}]_2$ gave orange-red crystals of a benzene soluble complex characterised as $[\text{Re}(\eta^5\text{-C}_9\text{H}_7)(\mu_2\text{-}\eta^3\text{:}\eta^6\text{-C}_9\text{H}_7)\text{Rh}(\eta^4\text{-C}_8\text{H}_{12})]$ (**5**). In particular, we observed coupling of the ^{103}Rh nucleus (100%; $I = 1/2$) to the central allylic proton H_b of the $\mu_2\text{-}\eta^3\text{:}\eta^6\text{-C}_9\text{H}_7$ ring $\{^2J(^{103}\text{Rh}\text{-H}) 2.2 \text{ Hz}\}$. It is surprising that no coupling of the protons H_a and $\text{H}_{a'}$



Scheme 1. (i) Co-condensation at -195°C , **(1)**; 6%, **(2)** 0.6%. (ii) HBF_4 in diethyl ether at r.t., 77%. (iii) KOH in thf at r.t., 50%. (iv) KH in thf at r.t., 90%. (v) D_2O in thf at r.t., 80%. (vi) KH in thf at 50°C , 90%. (vii) $[\text{Rh}(\eta\text{-C}_8\text{H}_{12})\text{Cl}]_2$ in thf at r.t., 70%.

to ^{103}Rh is resolvable, a phenomenon which has been observed for the related complex $[\text{Rh}(\eta^5\text{-C}_9\text{H}_7)(\eta^2\text{-C}_2\text{H}_4)_2]$ [11]. The NMR data do not allow us to determine whether the $\text{Re}(\eta^5\text{-C}_9\text{H}_7)$ moiety lies on the same or opposite side of the $\mu_2\text{-}\eta^3\text{:}\eta^6\text{-C}_9\text{H}_7$ ligand to the $\text{Rh}(\eta^4\text{-C}_8\text{H}_{12})$ group. The NMR data indicates that **5** possesses mirror symmetry. On steric grounds we favour the structure shown in Scheme 1.

Conclusion

The structures of all the new compounds are shown in Scheme 1. Compound **5** contains the first example of an indene ligand simultaneously bonded to metal via both the C_6 and C_5 rings.

Experimental

General techniques

All preparations, manipulations and reactions were carried out under dinitrogen using standard Schlenk tube and vacuum-line techniques, or in an inert-atmosphere dry box. Dinitrogen was purified by passage through a column containing BTS catalyst and 5 Å molecular sieves.

All solvents were thoroughly deoxygenated before use by repeated evacuation followed by admission of dinitrogen. Solvents were pre-dried over activated molecular sieves and then distilled from potassium (tetrahydrofuran, thf), sodium (toluene), sodium–potassium alloy [light petroleum (b.p. 40–60 °C throughout), diethyl ether] or phosphorus pentoxide (dichloromethane), under an inert atmosphere of dinitrogen before use. Methanol was dried over activated molecular sieves and deoxygenated before use. Deuterated solvents for NMR samples were stored in Rotaflo ampoules over activated molecular sieves and transferred by vacuum distillation. Celite 545 filtration aid (Koch-Light) was pre-dried in an oven at 80 °C before use.

Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin–Elmer 1510 FT interferometer. ^1H and ^{13}C NMR spectra were determined at 500 MHz and 126 MHz respectively using a AM-500 spectrometer. Spectra were referenced internally using the residual solvent (^1H) and solvent (^{13}C) resonances relative to tetramethylsilane ($\delta = 0$ ppm). All chemical shifts are quoted in δ (ppm) and coupling constants are in Hertz (Hz).

Cyclic voltammetry measurements were recorded in thf saturated with $\text{Bu}_4^+\text{PF}_6^-$ between +1.0 and –1.0 V with respect to the reference electrode. The potential was controlled using an Oxford Electrodes potentiostat.

Metal vapour synthesis (MVS) experiments were performed using the 10 kW metal-atom reactor described previously [4], operating in the positive hearth mode.

$(\eta^6\text{-Indene})(\eta^5\text{-indenyl})\text{rhenium(I)}$ (**1**)

Rhenium atoms (3.1 g, 15.9 mmol) generated from a molten ingot (ca. 14.5 g) were co-condensed with freshly distilled indene (ca. 120 cm³, 1 mol) onto the liquid nitrogen cooled reactor wall for 4 h. The power input to the furnace was 2.7–3.0 kW. The reaction mixture was allowed to warm to r.t. and was washed from the reaction vessel with tetrahydrofuran (ca. 1 dm³). The dark red extract was filtered

through a Celite bed, to remove excess metal, and the solvent and excess ligand removed from the filtrate under reduced pressure. The dark solid residue was extracted into light petroleum ether (b.p. 40–60 °C, 200 cm³) over 12 h. The extract was filtered, concentrated to ca. 20 cm³, and placed on an alumina (grade III) chromatography column. Elution with petroleum ether (b.p. 40–60 °C) gave an initial yellow band (an organic oil) and a second yellow-orange band which was collected. Orange crystals were obtained from the eluate by concentration to ca. 10 cm³ and cooling to –80 °C overnight. The crystals were separated and dried in vacuo. Yield ca. 400 mg, 6%.

(η^6 -Indane)(η^5 -indenyl)rhenium(I) (2)

Rhenium atoms (4.5 g, 23 mmol) generated from a molten ingot (ca. 21 g) were co-condensed with freshly distilled indene (ca. 150 cm³, 1.3 mol) onto the reactor wall for 4 h. The power input to the furnace was 3 kW. The reaction mixture was allowed to warm to r.t. and was washed from the reactor with diethyl ether (ca. 1.2 dm³). The dark red extract was filtered through a Celite bed to remove excess metal. A saturated solution of tetrafluoroboric acid in Et₂O (ca. 3 M) was added dropwise to the stirred filtrate until no further precipitation was observed. The precipitate was separated and washed with Et₂O (2 × 50 cm³) then dissolved thf, filtered, and left stirring overnight in the presence of an excess of potassium hydride. The thf was removed at reduced pressure and the dark solid extracted into petroleum ether (b.pt. 40–60 °C, 50 cm³) to give an orange solution. The solution was concentrated to 10 cm³ and cooled to –80 °C overnight yielding orange crystals. The crystals were separated and dried in vacuo. Yield ca. 40 mg, 0.6%.

(η^6 -Indene)(η^5 -indenyl)hydridorhenium(II) tetrafluoroborate (3)

A dilute solution of tetrafluoroboric acid in Et₂O (ca. 1 cm³) was added dropwise to an orange solution of **1** (150 mg, 0.35 mmol) in Et₂O (10 cm³), with stirring. A bright yellow precipitate formed immediately and was collected by filtration and washed with two portions of Et₂O (2 × 10 cm³). The yellow solid was extracted into dichloromethane (2 × 10 cm³). The extract was filtered and cooled to –80 °C overnight giving a yellow microcrystalline solid. This was separated and dried in vacuo. Yield, ca. 140 mg, 77%.

Potassium (η^6 -indenyl)(η^5 -indenyl)rhenium(I)

Compound **1** (25 mg, 0.05 mmol), and an excess of KH (ca. 20 mg) were placed in a 10 mm NMR tube. Thf-*d*₈ (1.5 cm³) was vacuum distilled into the tube which was then sealed under vacuum. The mixture was shaken and after 5 h became dark red. After 12 h the NMR tube was centrifuged to separate the excess KH from the solution. Then product was characterised by NMR spectroscopy. (Yield 90% NMR).

Reaction of K⁺[Re(η^6 -indenyl)(η^5 -indenyl)][–] with D₂O

A red solution of K⁺[Re(η^6 -indenyl)(η^5 -indenyl)][–] (30 mg, 0.06 mmol) in thf was added to D₂O (1 cm³) and the solution turned yellow immediately. The excess D₂O was removed under reduced pressure and the yellow residue was dissolved in benzene (ca. 3 cm³) and the ²H NMR spectrum was recorded.

Reaction of (η^6 -indene)(η^5 -indenyl)rhenium(I)- d_1 with KH

Compound **1d** (25 mg, 0.06 mmol), and an excess of KH (ca. 20 mg) were placed in a NMR tube. Thf- d_8 (1.5 cm³) was vacuum distilled into the tube which was sealed under vacuum. The mixture was heated to 50 °C for 2 d. After 1 d the solution turned dark red. The product was characterised by NMR spectroscopy. (Yield 90% NMR).

[(η^5 -Indenyl)(μ_2 - η^3 : η^6 -indenyl)rhenium(I)(η^4 -cycloocta-1,4-diene)rhodium(I)] (5)

The compound [Rh(η^4 -C₈H₁₂)Cl]₂ (35 mg, 0.07 mmol), was dissolved in dry thf (ca. 10 cm³). A thf solution (10 cm³) of K⁺[Re(η^6 -indenyl)(η^5 -indenyl)]⁻ (ca. 30 mg, 0.07 mmol) was filtered into the orange solution. The orange solution darkened slightly and was allowed to stir at r.t. for 3 h. The solvent was removed under reduced pressure and the solid extracted into petroleum ether (b.p. 40–60 °C, 10 cm³) to give an orange solution. This was concentrated and cooled at –80 °C overnight giving orange crystals which were collected by filtration and dried in vacuo. Yield 30 mg; 70%.

Acknowledgements

We thank the Royal Commission of 1851 for a Fellowship (to D.O'H).

References

- 1 G. Wilkinson, E.W. Abel and F.G.A. Stone (Eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, Vol. 3, Ch. 19.
- 2 E.M. Van Dam, W.N. Brent, M.P. Silvon, and P.S. Skell, *J. Am. Chem. Soc.*, 97 (1975) 467.
- 3 M.L.H. Green, N.D. Lowe, and D. O'Hare, *J. Chem. Soc., Chem Commun.*, (1986) 1547.
- 4 (a) M.L.H. Green, *J. Organomet. Chem.*, 200 (1980) 199; and *Frontiers of Chemistry*, IUPAC, K.J. Laidler (Ed.) Pergamon Press, Oxford and New York, 1982; (b) J.R. Blackborrow and D. Young, *Metal Vapour Synthesis in Organometallic Chemistry*, Springer Verlag, Berlin, 1979; (c) M.L.H. Green and D. O'Hare, *ACS Symp Ser.*, 333 (1987) 126.
- 5 M.L.H. Green and D. O'Hare, *J. Chem. Soc., Chem. Commun.*, (1985) 332.
- 6 P.M. Treichel and J.W. Johnson, *J. Organomet. Chem.*, 88 (1975) 207.
- 7 R.T. Baker and T.H. Tulip, *Organometallics*, 5 (1986) 839.
- 8 M. Brookhart and M.L.H. Green, *J. Organomet. Chem.*, 250 (1983) 395.
- 9 G. Stringer, Personal communication, (1988).
- 10 F.G.N. Cloke and J.P. Day, *J. Chem. Soc., Chem. Commun.*, (1985) 967.
- 11 (a) H. Eshtiagh-Hosseini and J.F. Nixon, *J. Less Common Met.* 61 (1978) 107, (b) D.F. Shriver, *Acc. Chem. Res.*, 31 (1970) 231.