Synthesis of [Re(η-C_6H_6)(η^5-C_8H_{11})], [Re(η-C_6H_6)(η^5-C_8H_{11})H]BF_4, and [Re(η-C_6H_6)(η^4-C_8H_{12})Ph] using Rhenium Atoms: Characterization by Application of a Modified Heteronuclear ^{13}C–^1H *J*-Resolved Two-dimensional Nuclear Magnetic Resonance Experiment

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Co-condensation of rhenium atoms and a mixture of benzene and cyclo-octa-1,5-diene gives the compounds [Re(η-C_6H_6)(η^5-C_8H_{11})] or [Re(η-C_6H_6)(η^4-C_8H_{12})Ph], whereas co-condensation of rhenium atoms and a mixture of benzene and cyclo-octa-1,3-diene gives only [Re(η-C_6H_6)(η^5-C_8H_{11})]. A heteronuclear ^{13}C–^1H *J*-resolved two-dimensional n.m.r. experiment is described.

Until recently, relatively few mono-η-arene rhenium complexes were known, the majority of these being members of the class of cations [Re(η-arene)$(CO)_3$]$^+$,[1] and the only reported neutral η-arene compound being [Re(η-C_6H_6)$(PPh_3)_2$H].[2] We have demonstrated that rhenium atoms react with a high degree of selectivity in low-temperature matrices, as exemplifed by the reactions of rhenium atoms with mixtures of benzene and an alkane.[3] We have also reported briefly the synthesis of new (η-benzene)bis(trimethylphosphine)rhenium derivatives using rhenium atoms.[4] Here we describe the study of the reactions of rhenium atoms with a mixture of benzene and cyclo-octa-1,3- or -1,5-diene.

Results and Discussion

Co-condensation of rhenium atoms (*ca.* 0.7 g) and a benzene–cyclo-octa-1,3-diene mixture (1:1, 70 cm^3) gives, after sublimation and recrystallization of the sublimate from cold pentane, orange crystals of the compound [Re(η-C_6H_6)(η^5-C_8H_{11})] (1) (0.2 g, 15% based on rhenium evaporated from the furnace). Compound (1) can be protonated by $HBF_4 \cdot Et_2O$ in diethyl ether giving the orange salt [Re(η-C_6H_6)(η^5-C_8H_{11})H]BF_4 (2). Compound (2) is unstable in solution decomposing with $T_{\frac{1}{2}}$ *ca.* 15 min at room temperature.

Co-condensation of rhenium atoms (*ca.* 1.0 g) and a mixture of benzene and cyclo-octa-1,5-diene (1:1, 80 cm^3) gives, after removal of the excess ligand under reduced pressure and sublimation of the more volatile products, a mixture of compounds [Re(η-C_6H_6)(η^5-C_8H_{11})] (1) and [Re(η-C_6H_6)(η^4-C_8H_{12})Ph] (3) (in the ratio 2:3). Chromatography of the sublimed product mixture on alumina and elution with toluene gives yellow crystals of (3) (0.15 g, 7%), see the Scheme.

The new compounds (1) and (3) have been characterized by microanalysis, mass spectroscopy, and especially by their n.m.r. spectra. Compound (2) has not been isolated pure.

The ^1H n.m.r. spectra of compounds (1)—(3) are complex (Table); assignments and connectivity patterns were made possible by ^1H–^1H COSY-45° spectra,[5] see Figure 1. In particular, the ^1H–^1H COSY-45 spectrum of (3) enables us to distinguish between two possible conformations of the η^4-cyclo-octadiene ligand.

We observe that the hydrogens attached to each end of the coordinated olefins are chemically inequivalent, which is consistent with the structure (**A**) whereas (**B**) possesses a mirror plane bisecting each double bond as a result of rapid rotation of the σ-phenyl group on the n.m.r. time-scale.

Assignment of the ^{13}C-{^1H} n.m.r. spectra of (1)—(3) was aided only by examination of the ^{13}C–^1H *J*-resolved two-dimensional (2-D) n.m.r. spectra (Figure 2). A modification of the method devised by Keeler[6] was used, which employed eight t_1 increments. This leads to a truncated time-domain signal which produces artefacts in the frequency-domain often called 'sinc-wiggles'. However, acceptable reduction of 'sinc-wiggles' of highly truncated signals can be achieved by multiplication with an appropriate weighting function.

We have found signal/noise improvement factors of 7—8 compared to a standard one-dimensional ^{13}C gated decoupled experiment. In addition, the methods of multiplicity selection based on spin echo[7] or polarization transfer sequences[8] all require setting of some experimental delay which depends on one-bond J_{CH} coupling, and calibration of the decoupler flip angles which often proves difficult or impossible for weak samples.

We were particularly interested to examine whether the C_8H_{11} ligand of (2) showed any evidence for equilibrium between the isomers (**C**) and (**D**). Brookhart *et al.*[9] have shown the related complex tricarbonyl(η^4-cyclohexenyl)manganese (**E**) to be in equilibrium with the diene hydride (**F**).

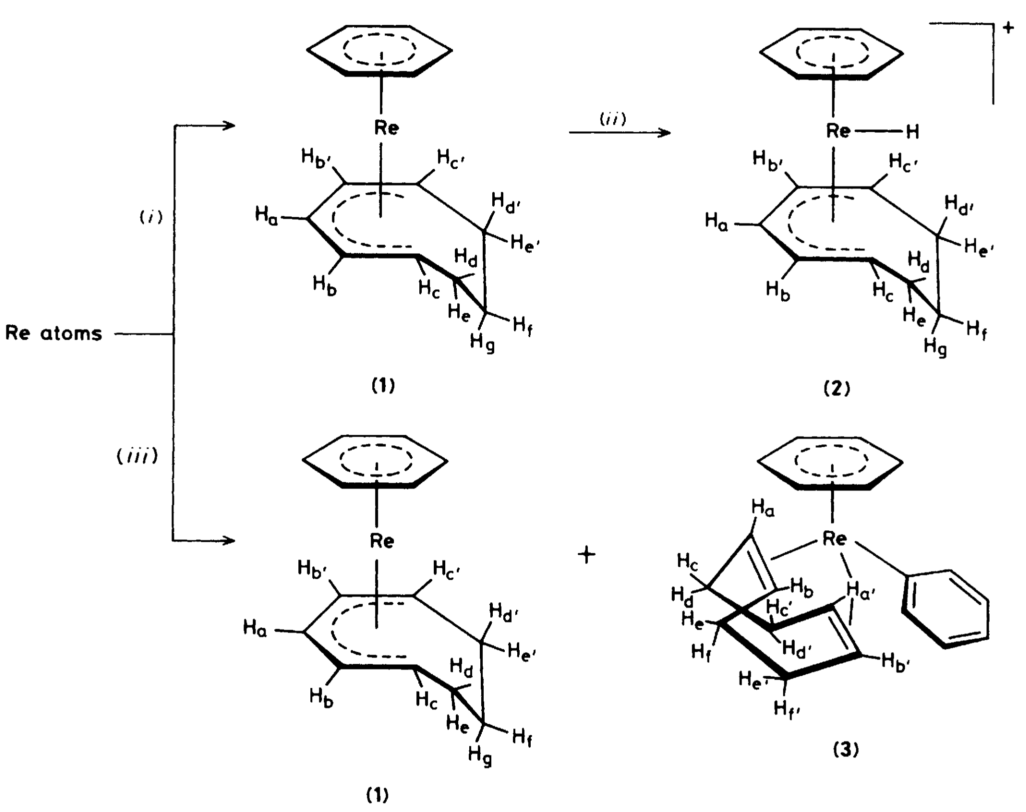
There is a medium strength absorption at 2 078 cm^{-1} in the i.r. spectrum of (2) assignable to ν(Re–H) and the n.m.r. spectra are entirely consistent with the structure (**D**). The absence of equilibrium between (**C**) and (**D**) provides further evidence for the thesis that agostic M←H–C interactions are generally less favoured in the sequence $5d < 4d < 3d$.[10]

Experimental

All reactions and manipulations were carried out under dinitrogen or *in vacuo*. All hydrocarbon solvents were dried by refluxing over potassium metal, sodium–potassium alloy or sodium metal under dinitrogen, and were distilled immediately before use. Microanalyses were carried out by the Microanalytical Laboratory of this department. I.r. spectra were determined using mulls on a Perkin-Elmer 1710 Fourier transform instrument. Mass spectra were determined using an M.S. 902 instrument upgraded with a console supplied by Mass Spectroscopy Services Ltd. Chromatography was carried out using alumina (100—200 mesh) supplied by East Anglia Chemicals and was deactivated by the addition of 6 wt.% of water before use. N.m.r. spectra were recorded on Bruker WH-300, AM-250, and AM-500 spectrometers.

Rhenium ingots were prepared by melting rhenium powder.

(η-*Benzene*)(η^5-*cyclo-octadienyl*)*rhenium*(I), (**1**).—Rhenium atoms (0.7 g, 3.6 mmol), generated from a molten ingot (*ca.* 5.0 g)



Scheme. (*i*) Co-condensation with cyclo-octa-1,3-diene–benzene (1 : 1) at −196 °C; (*ii*) $HBF_4 \cdot Et_2O$, −78 °C; (*iii*) co-condensation with cyclo-octa-1,5-diene–benzene (1 : 1) at −196 °C

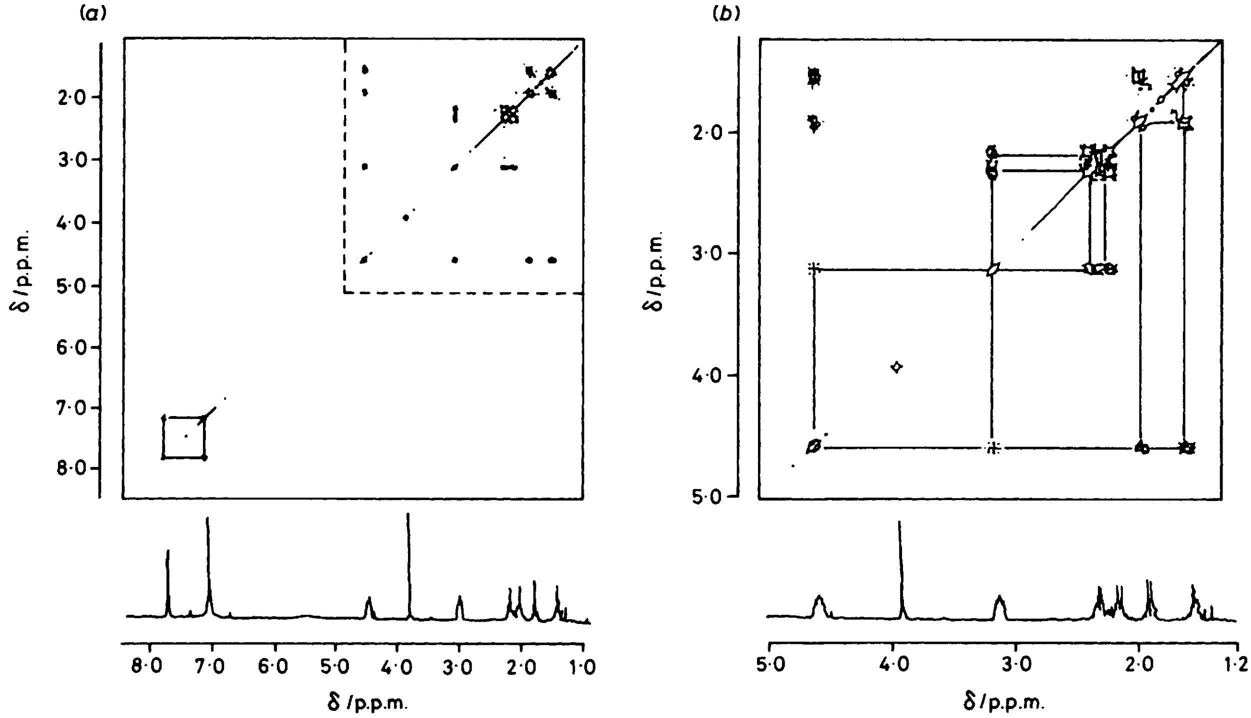
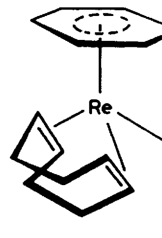
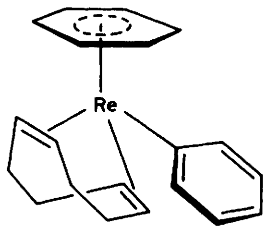


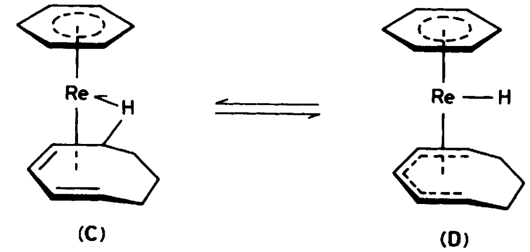
Figure 1. (*a*) Two-dimensional ^1H–^1H COSY spectrum (250 MHz) of (**1**) (contour plot) run on a Bruker AM-250 instrument. A (90°–t_1–45°–free induction decay) pulse sequence was used with delay of 1.5 s before each acquisition: 512 t_1 values each of 2k data points were accumulated, using quadrature detection. The spectral width in both dimensions was 1 850 Hz and the acquisition time in t_2 was 0.3 s. Sine-bell apodization and zero filling precede Fourier transformation in both dimensions. Symmetrized absolute-value spectra are shown. (*b*) Contour plot of expanded region δ 1.2—5.0



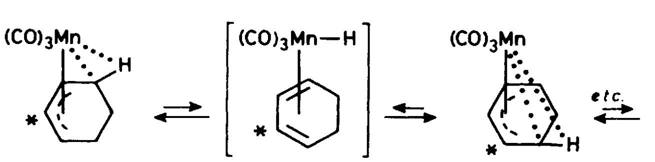
(A)



(B)



(C) **(D)**



(E) **(F)**

were co-condensed with a mixture of benzene and cyclo-octa-1,3-diene (1 : 1 v/v, 80 cm^3) onto the reactor wall for 4 h. The power input for the positive-hearth furnace was 1.8 kW. The reaction wall was cooled by liquid dinitrogen; the apparatus is described elsewhere.[11,12] The reaction mixture was allowed to warm to room temperature and was washed from the reaction vessel with tetrahydrofuran (500 cm^3). The extract was filtered through a Celite bed and the solvent and excess ligands removed under reduced pressure. Sublimation of the residue [110 °C, 10^{-4} Torr (Torr ≈ 133 Pa)] onto a liquid-dinitrogen cooled probe gave a yellow oily solid. The oily solid was extracted with pentane (2 × 25 cm^3), filtered and the filtrate concentrated to *ca.* 10 cm^3 under reduced pressure. Cooling to −20 °C for 1–2 h and then to −80 °C overnight gave orange crystals of (**1**) which were separated and dried *in vacuo*, yield 0.3 g (15%) {Found: C, 44.8; H, 4.6%; *m/e* (^{187}Re) 372 [P^+]. Calc. for $C_{14}H_{17}Re$: C, 45.2; H, 4.6%}.

(η-*Benzene*)(η^5-*cyclo-octadienyl*)*hydridorhenium*(III) Tetrafluoroborate, (**2**).—The compound [Re(η-C_6H_6)(η^5-C_8H_{11})] (0.2 g, 0.5 mmol) in diethyl ether (30 cm^3) was cooled to −78 °C and treated in a dropwise manner with tetrafluoroboric acid in Et_2O (10%) (1 cm^3). The solution was allowed to warm to room temperature and the resulting pale orange precipitate was separated, washed with diethyl ether (2 × 30 cm^3), and then extracted with tetrahydrofuran (50 cm^3) giving an orange solution. This was concentrated and diethyl ether was added slowly (50—60 cm^3). Pale orange microcrystals were deposited which were separated, washed with diethyl ether (2 × 20 cm^3)

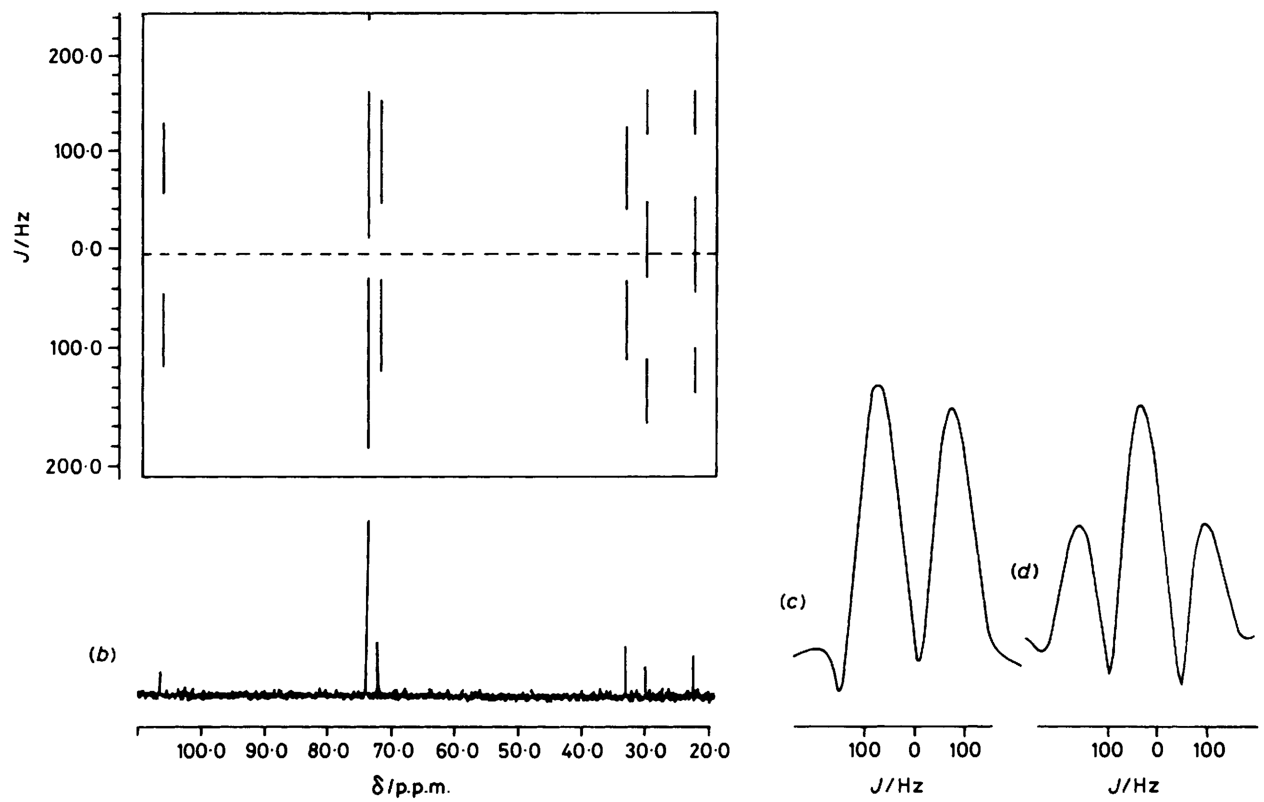


Figure 2. (*a*) Two-dimensional $^{13}C-^{1}H$ heteronuclear *J*-spectrum of (**1**) (contour plot) run on Bruker AM-250. A (recycle delay–90°–t_1–180°–t_1–free induction decay) pulse sequence was used. Except for the second t_1 period, broad-band proton decoupling was used throughout; eight t_1 values each of 16k data points were accumulated. The spectral width was 130 Hz in the f_1 dimension and 5 850 Hz in the f_2 dimension. Sine-bell squared multiplication and zero-filling to 64 data points was applied to the f_1 dimension and Gaussian weighting to the f_2 dimension prior to Fourier transformation in both dimensions. Resolution in f_1 was 2 Hz per point. (*b*) Horizontal projection of the 2-D $^{13}C-^{1}H$ *J*-spectrum of (**1**). (*c*) Vertical cross-section through resonance at 74.5 p.p.m. (η-C_6H_6). (*d*) Vertical cross-section through resonance at 22.5 p.p.m. (–CH_2)

Table. N.m.r. data[a]

Compound	^{1}H N.m.r.	^{13}C N.m.r.
(**1**) $[Re(\eta\text{-}C_6H_6)(\eta^5\text{-}C_8H_{11})]$[b]	6.3 [1 H, t, $J(H_a-H_b)$ 6.0, H_a], 4.9 [2 H, dd, $J(H_a-H_b)$ 6.0, $J(H_b-H_c)$ 8.0, H_b], 4.4 (6 H, s, η-C_6H_6), 4.1 [2 H, m (5 lines), H_c], 2.3 [2 H, dq, $J(H_d-H_e)$ 14.0, $J(H_e-H_c) = J(H_e-H_g)$ 3.0, H_e], 1.5 [2 H, tt, $J(H_e-H_d) = J(H_d-H_g)$ 14.0, $J(H_d-H_f) = J(H_d-H_c)$ 3, H_d], 1.4 [1 H, m (17 lines), H_f], 0.7 [1 H, tq, $J(H_f-H_g) = J(H_g-H_e)$ 14.0, $J(H_g-H_d)$ 3.0, H_g]	106.8 [d, J(CH), 180, C_a], 74.5 [d, J(CH) 172, η-C_6H_6], 72.6 [d, J(CH) 175, C_b], 33.2 [d, J(CH) 165, C_c], 32.0 [t, J(CH) 126, $C_{d,e}$], 22.5 [t, J(CH) 134, $C_{f,g}$]
(**2**) $[Re(\eta\text{-}C_6H_6)(\eta^5\text{-}C_8H_{11})H]BF_4$[c]	7.2 [1 H, t, $J(H_a-H_b)$ 6.0, H_a], 6.4 (6 H, s, η-C_6H_6), 5.9 [2 H, t, $J(H_a-H_b) = J(H_a-H_c)$ 6.0, H_b], 4.8 [2 H, m, (10 lines), H_c], 2.7 [2 H, m (10 lines), H_d], 1.85 [2 H, m (9 lines), H_e], 1.6 [1 H, m (15 lines), H_f], 0.65 [1 H, tq, $J(H_g-H_f) = J(H_g-H_e)$ 14.0, $J(H_g-H_d)$ 3 H_g], -7.8 (1 H, s, Re–H)	100.8 (d, C_a), 88.1 (d, η-C_6H_6), 74.0 (d, C_b), 38.8 (d, C_c), 27.6 (t, $C_{d,e}$), 20.3 (t, $C_{f,g}$)
(**3**) $[Re(\eta\text{-}C_6H_6)(\eta^4\text{-}C_8H_{12})Ph]$[b]	7.8 [2 H, m (5 lines), Ph], 7.18 [3 H, m (obscured), Ph], 4.6 [2 H, m (11 lines), H_a],[d] 3.9 (6 H, s, η-C_6H_6), 3.1 [2 H, m (11 lines), H_b], 2.3 [2 H, m (11 lines), H_e or H_f], 2.1 [2 H, m (8 lines), H_f or H_e], 1.9 [2 H, m (8 lines), H_c or H_d], 1.3 [2 H, m (11 lines), H_d or H_c]	143.4 [d, J(CH) 164, Ph], 126.6 [d, J(CH) 170, Ph], 121.2 [d, J(CH) 170, Ph], 82.9 [d, J(CH) 172, η-C_6H_6], 75.7 [d, J(CH) 148, C_a], 66.7 [d, J(CH) 150, C_b], 34.0 [t, J(CH) 134, $C_{e,f}$], 32.1 [t, J(CH) 135, $C_{c,d}$]

[a] Given as chemical shift (δ), relative intensity, multiplicity, coupling constants in Hz, assignment. All spectra were referenced with respect to solvent. [b] In [$^2H_6$]benzene. [c] In [$^2H_8$]tetrahydrofuran. [d] The absolute assignment of $H_{a,a'}$ and $H_{b,b'}$ has not been determined.

and dried *in vacuo*, yield 0.2 g (90%). Instability in solution prevented isolation of an analytically pure sample.

(η-*Benzene*)(η^4-*cyclo-octa-*1,5-*diene*)*phenylrhenium*(I), (**3**).—Rhenium atoms (1.0 g, 5.2 mmol), generated from a molten ingot (*ca.* 5.0 g) were co-condensed with a mixture of benzene and cyclo-octa-1,5-diene (1 : 1 v/v, 80 cm^3) onto the reactor wall for 4 h. The mixture was allowed to warm to room temperature and was washed from the reaction vessel with tetrahydrofuran (500 cm^3). The extract was filtered through a Celite bed and the solvent and excess ligands removed under reduced pressure. Sublimation of the residue (110 °C, 10^{-4} Torr) onto a liquid-dinitrogen cooled probe gave a dark yellow oily solid. The oily solid was extracted with light petroleum (b.p. 40—60 °C, 2 × 20 cm^3) and chromatographed on an alumina column (6 wt.% H_2O). Elution with toluene gave a yellow band which was collected. The toluene was removed under reduced pressure and the resulting yellow oily solid extracted with pentane (2 × 10 cm^3), filtered and concentrated to *ca.* 10 cm^3. Cooling to -20 °C for 1-2 h and then -80 °C overnight gave yellow crystals. These were separated and dried *in vacuo*, yield 0.15 g (7%) {Found: C, 53.6; H, 5.2%; *m*/*e* (^{187}Re) 372 [P^+ − Ph]. Calc. for $C_{20}H_{23}Re$: C, 53.4; H, 5.1%}.

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