MONO-η-ARENEBIS(TRIMETHYLPHOSPHINE)RHENIUM CHEMISTRY: ALKYL, HYDRIDO, HALOGENO AND OLEFIN DERIVATIVES

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Abstract—Co-condensation of rhenium atoms with a benzene-trimethylphosphine mixture gives the dimer $[\text{Re}(\eta-C_6H_6)(\text{PMe}_3)_2]_2$ which is a precursor to the new compounds $\text{Re}(\eta-C_6H_6)(\text{PMe}_3)_2\text{R}$ (R = H, Cl, I, Me, Et, CH=CH₂ or Ph), $[\text{Re}(\eta-C_6H_6)(\text{PMe}_3)_2\text{X}_2]\text{BF}_4$ (X₂ = H₂ or HI), $[\text{Re}(\eta-C_6H_6)(\text{PMe}_3)_2\text{H}_2][\text{BF}_4]_2$, and $[\text{Re}(\eta-C_6H_6)(\text{PMe}_3)_2\text{L}]\text{BF}_4$ (L = η -C₂H₄ or CO). Co-condensation of manganese atoms with benzene-trimethylphosphine gives Mn(η -C₆H₆)(PMe₃)₂H.

There are relatively few mono-*η*-arene rhenium complexes known, with the majority of these being members of the class of cations $[(\eta - arene)Re$ $(CO)_3$ ^{+.1} Recently, the η -arene complex (η -C₆H₆) $Re(PPh_3)_2H$, synthesized from $Re(PPh_3)_2H_7$, has been described.² Co-condensation of rhenium atoms with a mixture of benzene and alkanes, or with alkyl-substituted benzenes gives binuclear compounds in the class $(\eta$ -arene)Re $(\mu$ -H)₂ $(\mu$ alkylidene)Re(η -arene).^{3,4} The compounds Re(η - C_6H_6 $(\eta-C_6H_8)H$ and $(\eta-C_6H_6)Re(\mu-H)_2Re(\eta-H_6)Re(\mu-H_6)$ C_6H_8)₂ have also been synthesised via rhenium atom reactions.^{5,6} In a further development of η arene rhenium chemistry we explored the reaction between rhenium atoms and a mixture of benzene and trimethylphosphine and found that the dimer $[Re(\eta-C_6H_6)(PMe_3)_2]_2$ could be prepared on a 1-2-g scale. Here we describe the chemistry of the $\text{Re}(\eta - C_6H_6)(\text{PMe}_3)_2$ system. A brief report of part of this work has been communicated previously.7

RESULTS

Co-condensation of rhenium atoms with a benzene-trimethylphosphine mixture (5:1) gives a red oil. Chromatography on alumina separated three rhenium compounds. Elution with toluene separated a small yellow band from which the compound $\text{Re}(\eta-\text{C}_6\text{H}_6)(\text{PMe}_3)_2\text{Ph}$ (1) was isolated. Further elution with diethyl ether separated a second band from which orange crystals of the dimer $[\text{Re}(\eta-C_6H_6)(\text{PMe}_3)_2]_2$ (2) were obtained. Finally, elution with acetone-water followed by addition of sodium tetrafluoroborate to the eluate gave the dihydride $[\text{Re}(\eta-C_6H_6)(\text{PMe}_3)_2H_2]\text{BF}_4$ (3).

Elemental analysis, NMR spectroscopic data and other characterizing data for compounds 1-3, and for all the other new compounds described below, are given in Table 1 and, except where interpretation is not straightforward, the data are not further discussed.

The ${}^{13}C - {}^{1}H$ NMR spectrum of 1 shows a virtual triplet at δ 23.5 assigned to two trimethylphosphine ligands, and a triplet η -benzene resonance at δ 72.9 (J = 2.08 Hz). Resonances at δ 120.0, 126.1 and 144.2 are, respectively, assigned to the para-, meta- and ortho-carbons of the phenyl group: the ipso-carbon was not observed. The ¹H NMR spectrum of 3 showed the two Re-hydrogens to be equivalent and the data are consistent with either a trans- or a fluxional cisstructure. Compound 3 is presumed to be formed from the protonation on the chromatography column of the neutral hydride $\text{Re}(\eta - C_6 H_6)(\text{PMe}_3)_2 H$, which is described below. Evidence for this comes from the fact that the ¹H NMR spectrum of the sublimate from a crude sample of the cocondensation mixture showed a triplet hydride at δ 8.70, assignable to Re(η -C₆H₆)(PMe₃)₂H.

Treatment of 2 with iodine gave no tractable product, neither did 2 react with sodium amalgam (2%). However, stirring a tetrahydrofuran (thf) solution of 2 in the presence of a K film caused the

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Yellow Orange Orange Orange ange-pink Yellow/
Compound e(r-C ₆ H ₆)(PMe ₃) ₂ Ph (e(r-C ₆ H ₆)(PMe ₃) ₂ H ₂]BF 4 ^d (e(r-C ₆ H ₆)(PMe ₃) ₂ H ₂]BF 4 ^d (r-C ₆ H ₆)(PMe ₃) ₂ H ₂ (BF 4) ₂ (r-C ₆ H ₆)(PMe ₃) ₂ H ₂ (BF 4) ₂ (r-C ₆ H ₆)(PMe ₃) ₂ Me

Table 1. Analytical and spectroscopic data

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6) Re(ŋ-C ₆ H ₆)(PMe ₃) ₂ (CH _ CH ₂)	Yellow ^f			¹ H: 8.63 [1H, ddt, J(H _a -H _{tran}) 18.7, J(H _a -H _{cs}) 12.2, J(P-H) 9.9, H _a], 6.87 [1H, ddt, J(H _a -H _{cs}) 12.2, J(H _{ci} -H _{tran}) 5.6, J(P-H) 2.7, H _{cia}], 5.82 [1H, ddt, J(H _a -H _{tran}) 18.5, J(H _{ci} -H _{tran}) 5.6, J(P-H) 1.7, H _{tran}], 4.10 [6H, t, J(P-H) 1.5, <i>n</i> -C ₆ H _d],
					1.21 (18H, vt, 2PMe ₃). ^c ³¹ P-{ ¹ H}: -58.1 (s, 2PMe ₃). ^c
9	Re(η -C ₆ H ₆)(PMe ₃) ₂ H ⁶	Yellow	34.3 (34.5)	5.9 (6.0)	¹ H: 4.28 (6H, s, <i>η</i> -C ₆ H ₆), 1.39 (18H, vt, 2PMe ₃), -8.70 [1H, t, <i>J</i> (P-H)
					36.8, ReH]. ^c ³¹ P–{ ¹ H}: – 45.5 (s. 2PMe ₄). ^c
(II)	Pre(n-C ₆ H ₆)(PMe ₃) ₂ HIJBF ₄	Red	23.7	4.2	1 H: 6.20 (6H, s, η -C ₆ H ₆),
			(22.8)	(4.0)	2.06 (18H, vt, 2PMe ₃), – 10.43 [1H, t, .//P–H) 49 4 ReH1 *
					${}^{31}P-{}^{1}H$: -51.9 (s, 2PMe ₃).
(12)	$[\text{Re}(\eta\text{-}C_6\text{H}_6)(\text{PMe}_3)_2(\text{CH}_2\text{CH}_2)]\text{BF}_4$	Yellow			¹ H: 5.48 [6H, t, <i>J</i> (P–H) 1.1, <i>n</i> -C ₆ H ₆],
					$2.30 [4H, t, J(P-H) 5, \eta-CH_2-CH_2],$
					1.65 (18H, vt, 2PMe ₃). [*] ³¹ D_f ¹ U1 · _ 57 1 / ₅ - 2DMe) /
					$^{13}C-^{11}H$: 85.04 (6C, s, <i>n</i> -C, H,), 22.98
	-			Ň	(2C, s, <i>n</i> -CH ₂ -CH ₂), 20.94 (6C, vt, 2PMe ₃).
(13)	[Re(η-C ₆ H ₆)(PMe ₃) ₂ CO]BF₄ ^A	Colourless			¹ H: 5.74 (6H, s, η-C ₆ H ₆), 1 83.08H, νt 2PMe.) ¢
(14)	Re(ŋ-C ₆ H ₆)(PMe ₃) ₂ Cl	Yellow	32.4	5.3	¹ H: 4.26 [6H, t, $J(P-H)$ 2.44, η -C, H,].
			(31.9)	(5.4)	1.24 (18H, vt, 2PMe ₃).
					${}^{31}P-{}^{1}H$: -45.8 (s, 2PMe ₃) ^c
(15)	$Mn(\eta-C_6H_6)(PMe_3)_2H^{t}$	Orange-red	49.2	8.5	¹ H : 4.36 (6H, s, <i>η</i> -C ₆ H ₆),
			(50.4)	(8.8)	1.04 (18H, vt, 2PMe ₃), -10.39 [1H, t,
					J(P-H) 82.8, MnH].
					³¹ P-{ ¹ H}: 24.3 (s, 2PMe ₃).
<i>a</i>]	Found (required) (%).			**************************************	

^b Given as: chemical shift (δ) [relative intensity, multiplicity, J (in Hz), assignment]. Spectra were referenced using tetramethylsilane (¹H and ¹³C) or trimethylphosphate in D₂O (³¹P). ^c In C₆D₆. ^d v(Re-H) = 1814 cm⁻¹. ^d v(Re-H) = 1997 cm⁻¹. $f_{v}(\text{Re-H}) = 1814 \text{ cm}^{-1}$. $h_{v}(\text{Ca=O}) = 1912 \text{ cm}^{-1}$. $f_{v}(\text{Mn-H}) = 1722 \text{ cm}^{-1}$. ⁴ In CD₃COCD₃. ⁷Characterized spectroscopically only. initial orange solution to darken gradually to deep red; this reaction could be facilitated by addition of a catalytic amount of naphthalene. The red thf solution was very air- and water-sensitive, and this intermediate species, which we presume to be the K salt of the 18-electron anion $[\text{Re}(\eta-\text{C}_6\text{H}_6)(\text{PMe}_3)_2]^-$ (4), was not characterized. Indirect evidence for the nature of 4 comes from its reaction with water; dropwise addition of the red thf solution into wet Et₂O causes an immediate decolorization to give a bright yellow solution. Chromatography of the solution gave 3 as the only isolated complex.

Treatment of the red solution (4) with MeI gave orange crystals of $\text{Re}(\eta-\text{C}_6\text{H}_6)(\text{PMe}_3)_2\text{I}$ (5). Addition of HBF₄ in Et₂O to 2 gives orange-pink crystalline [Re $(\eta-\text{C}_6\text{H}_6)(\text{PMe}_3)_2\text{H}]_2[\text{BF}_4]_2$ (6). The protonation may be reversed by treatment of 6 with NaOH_{a0} or potassium hydride (KH).

The iodo compound 5 is a useful synthetic intermediate for development of the chemistry of the $Re(\eta-C_6H_6)(PMe_3)_2$ radical. Thus, treatment of 5 with Grignard reagents (RMgX) (RX = MeI, EtI or CH₂=CHBr) or PhLi gives the compounds $Re(\eta-C_6H_6)(PMe_3)_2Me(7), Re(\eta-C_6H_6)(PMe_3)_2Et$ (8), $Re(\eta-C_6H_6)(PMe_3)_2(CH=CH_2)$ (9 and 1), respectively. Treatment of 5 with lithium tetrahydridoaluminate(III) gives the hydrido derivative $Re(\eta-C_6H_6)(PMe_3)_2H$ (10).

Treatment of the iodo compound 5 with HBF₄ in Et₂O gives the iodohydride [Re(η -C₆H₆)(PMe₃)₂ HI]BF₄ (11). The η -ethylene compound [Re(η -C₆H₆)(PMe₃)₂(η -C₂H₄)]BF₄ (12), is formed by treatment of 5 with TlBF₄ in the presence of 1 atm ethylene; by abstraction of a hydride ion from the β -hydrogen of 8 using trityl tetrafluoroborate and also by protonation of 9 with HBF₄in Et₂O. The ¹H and ¹³C NMR spectra of 12 show the hydrogen and carbon atoms to be equivalent and coupled to two ³¹P nuclei. This suggests that the ethylene hydrogens are made equivalent by rotation of the ethylene ligand about the Reethylene bond.

Treatment of 5 with TlBF₄ in the presence of CO gives colourless crystals of the monocarbonyl $[\text{Re}(\eta-\text{C}_6\text{H}_6)(\text{PMe}_3)_2\text{CO}]\text{BF}_4$ (13), for which the IR spectrum shows a strong band assignable to v(C=O) at 1912 cm⁻¹.

The hydride 10 is highly reactive towards CH_2Cl_2 , giving the chloro compound $Re(\eta - C_6H_6)(PMe_3)_2Cl$ (14), in excellent yields. Treatment of 10 with triethyloxonium tetrafluoroborate gives the dihydride $[Re(\eta - C_6H_6)(PMe_3)_2H_2]BF_4$ (3); it is possible that protonation resulted from adventitious water. Compound 3 is stable in aqueous base but may be deprotonated using potassium hydride.



Co-condensation of manganese atoms with benzene-trimethylphosphine (5:1) affords, on workup, volatile, orange-red, petroleum ether soluble crystals of $Mn(\eta-C_6H_6)(PMe_3)_2H$ (15). The ¹H NMR spectrum of 15 shows three resonances; a singlet at δ 4.36 may be assigned to a coordinated η -benzene ring, a virtual triplet at δ 1.04 is assignable to the two trimethylphosphine ligands, and a high-field triplet at δ 10.39 (J = 82.8 Hz) is attributable to a single metal hydride ligand (see Scheme 1).

The photoelectron spectra of 2, 5, 10 and 15 show the first ionization potentials to be 6.18, 6.40, 6.21 and 6.06 eV, respectively.⁸

DISCUSSION

The structures proposed for compounds 1-14 are shown in Scheme 2. The low ionization energies for the compounds 2, 5 and 10 show them to be classifiable as high-energy (electron-rich) compounds. This is supported by the basicity of these compounds as exemplified by their ease of protonation. Unlike the well-known dimer [Fe(η - C_5H_5 (CO)₂, the dimer 2 is not cleaved by sodium amalgam but requires more vigorous conditions, namely a K film. The formation of the iodo compound from the reaction between the anion $[\text{Re}(\eta-\text{C}_6\text{H}_6)(\text{PMe}_3)_2]^-$ and iodomethane may be presumed to proceed via a radical process and contrast with the reaction between methyl iodide and the anion $[Fe(\eta - C_5H_5)(CO)_2]^-$, in which the methyl derivative $Fe(\eta - C_5H_5)(CO)_2Me$ is formed. In other respects the chemistry of the radical $\operatorname{Re}(\eta$ - C_6H_6 (PMe₃)₂ follows expected patterns.

EXPERIMENTAL

All preparations and reactions described were carried out under an atmosphere of dinitrogen using standard Schlenk vessel and vacuum line techniques. Solvents were pre-dried over molecular sieves and then distilled from K (toluene, benzene, cyclohexane or thf), Na-K alloy [pentane, petroleum ether (40-60°C) or Et₂O] or phosphorus pentoxide (CH₂Cl₂), under dinitrogen.



Scheme 2. (i) Rhenium atoms with benzene-trimethylphosphine, 2% for 1, 20% for 2, (ii) HBF₄ in Et₂O (90%), (iii) NaOH_{aq} (>90%), (iv) K metal film in thf (>90%), (v) PhLi in Et₂O at rt (>70%), (vi) MeI in thf at rt for 30 min (62%), (vii) LiAlH₄ in thf at rt for 3 h (85%), (viii) MeMgBr in thf at 50°C for 2 h (70%), (ix) EtMgBr in Et₂O at rt for 1 h (49%), (x) TlBF₄ and ethylene (2 atm) in thf for 2 days (30%), (xi) vinylmagnesium bromide in thf at rt (49%), (xii) TlBF₄ and CO (2 atm) in thf at rt for 16 h (20%), (xiii) CH₂Cl₂ at rt for 2 h (93%), (xiv) [Ph₃C][BF₄] in CH₂Cl₂ at rt (21%).

Elemental analyses were performed by the Analysis Department in this laboratory, or, in the case of very air-sensitive materials, by the Analytische Laboratorien, 5270 Gummersbach 1 Elbach, F.R.G.

IR spectra were recorded on a Pye-Unicam SP2000 double-beam grating spectrophotometer, or on a Perkin-Elmer 457 double-beam grating spectrophotometer. NMR spectra were recorded on a JEOL PMX60 (¹H NMR 60 MHz, c.w.), a Bruker WH300 (¹H NMR, 300 MHz) or a Bruker AM250 (heteronuclear NMR, 250 MHz). ¹³C NMR and ³¹P NMR spectra were run at frequencies of 62.9 and 101.2 MHz, respectively. Low-resolution mass spectra were recorded on an AEI MS902 mass spectrometer. Photoelectron spectra were recorded on a PES Laboratories 0078 spectrometer using a heated inlet system. The spectrometer was calibrated using He, Xe and N₂ ionization potentials. Syntheses with metal atoms were carried out using the apparatus described elsewhere,⁹ metals were vaporized from a positive-hearth, electron-gun furnace, based on designs provided by G. V. Planer Co. Ltd.

Reaction of rhenium atoms with benzene-trimethylphosphine: η -benzenebis(trimethylphosphine)phenylrhenium (1), bis[η -benzene-bis(trimethylphosphine) rhenium (2) and η -benzenebis(trimethylphosphine) dihydridorhenium tetrafluoroborate (3)

A sample of rhenium powder (ca 12 g) was melted in an electron-gun furnace giving a rhenium ingot free of volatiles. This sample was then heated to ca 2600°C at which temperature rhenium vaporizes steadily. The vacuum in the reaction chamber, measured at a point below the furnace was $ca \ 10^{-4}$ torr. The input power to the electron-gun furnace was maintained at 6 kV and 450 mA throughout. Rhenium atoms (4.1 g, 22 mmol) were co-condensed with a 5:1 molar mixture of benzene and trimethylphosphine (100 cm³) for 4 h. After warming to room temperature (rt) the red-brown mixture was washed out of the machine with toluene (750 cm³), filtered through a bed of Celite and reduced to a brown oil under reduced pressure at 50°C. The oil was extracted with petroleum ether (40-60°C, 5×300 cm³), filtered through Celite and reduced in volume to 50 cm³, giving a deep red solution. The red solution was adsorbed onto a chromatography column (neutral alumina, 6% water by weight, 50×4 cm).

Elution with toluene gave an orange band, which upon concentration of the eluate gave a deep red oil. Extraction with petroleum ether (40–60°C, 50 cm³) gave an orange solution, which, on cooling to -80° C, yielded yellow crystals of 1. Yield 0.2 g (2%).

Further elution with Et_2O produced a yellow band, which upon reduction in volume of the eluate and cooling to $-20^{\circ}C$ gave orange crystals of 2. Yield 1.8 g (20%), based on rhenium evaporated from the furnace.

Further elution with aqueous acetone (1:1) gave a quickly moving brown band. Removal of the acetone under reduced pressure, followed by the addition of excess aqueous ammonium tetrafluoroborate produced an orange precipitate, which was collected and dried. Recrystallization from acetone (20 cm^3) gave yellow microcrystals of 3. Yield 0.2 g (2%).

10 (50 mg, 0.12 mmol) was dissolved in Et₂O (30 cm³), and three drops of ethereal HBF₄ were added. An immediate orange precipitate formed, which was washed with Et₂O (3×20 cm³), and dried *in vacuo*. Recrystallization from acetonewater afforded orange crystals of (η -benzene) bis(trimethylphosphine)dihydridorhenium tetra-fluoroborate. Yield 58 mg (95%).

Reaction beween 2 and K metal: synthesis of 4

2(1.0 g, 1.2 mmol) in thf (70 cm³) was transferred on to a freshly prepared K film. One crystal of naphthalene was added to the orange solution. The solution was stirred and turned to deep red after 10 min. The colour deepened markedly over 8 h. The resulting solution was filtered and used immediately in subsequent reactions.

η -Benzenebis(trimethylphosphine)iodorhenium (5)

2 (1.0 g, 1.2 mmol) was used to prepare a red solution, as described above. Freshly distilled MeI (0.5 cm³, 8.0 mmol) was added dropwise to the deep red solution with stirring. A white precipitate immediately developed and the solution changed from deep red to orange. The mixture was stirred for 30 min and then reduced to an oily solid under reduced pressure. Extraction with toluene (3×20 cm³), followed by filtration and concentration produced a red oil. Extraction with petroleum ether ($40-60^{\circ}$ C, 3×20 cm³) yielded, on concentration and cooling to -20° C, orange crystals of Re(η -C₆H₆)(PMe₃)₂I. Yield 0.8 g (62%).

Bis[$(\eta - benzenebis(trimethylphosphine)hydridorhe$ nium] bis-tetrafluoroborate (6)

The $(\eta$ -benzene)bis(trimethylphosphine)rhenium dimer (70 mg, 0.08 mmol) was dissolved in Et₂O (30 cm³), and excess of HBF₄ in Et₂O was added dropwise. An immediate orange-pink precipitate

formed, leaving a colourless solution. After washing with ether $(3 \times 20 \text{ cm}^3)$, the solid was collected and dried *in vacuo*. Recrystallization from acetone-water gave orange crystals of **6**. Yield 76 mg (90%).

Reaction of 6 with NaOH_{aq}

6 (50 mg, 0.05 mmol) in thf (10 cm³) was treated wih NaOH_{aq.} solution (5 cm³). The mixture was stirred at rt for 3 h and the organic layer developed a yellow colour. Addition of pentane (30 cm³), followed by separation of the organic layer, and partial removal of solvent under reduced pressure gave yellow crystals of **2** (¹H NMR). Yield > 80%.

5 (50 mg, 0.09 mmol) in petroleum ether (40– 60°C, 30 cm³) was treated with an excess of PhLi (3 cm³, 1 M solution in Et₂O) at -78°C. After warming to rt the solvent was removed under reduced pressure. The residue was extracted with petroleum ether (40–60°C, 50 cm³), the extract was filtered and the orange filtrate was cooled to -80°C giving yellow crystals which were collected, washed and dried *in vacuo*. Yield > 70%.

η -Benzenebis(trimethylphosphine)methylrhenium (7)

A solution of 14 (vide infra) (20 mg, 0.044 mmol) in thf (20 cm³) was stirred while a saturated solution of MeMgBr in thf (1 cm³) was added dropwise. No colour change was observed in the yellow-orange solution. Warming to 50°C for 2 h, followed by removal of solvent, gave a white powder and a yellow solid. Extraction with petroleum ether (40-60°C, 2×20 cm³) and removal of the solvent under reduced pressure gave a yellow solid. This was recrystallized from light petroleum ether yielding yellow microcrystals of $Re(\eta-C_6H_6)(PMe_3)_2Me$. Yield 13 mg (70%).

η -Benzenebis(trimethylphosphine)ethylrhenium (8)

5 (50 mg, 0.09 mmol) in petroleum ether (40-60°C, 30 cm³) was treated with an excess of EtMgBr (4 cm³, 1 M solution in Et₂O) at -78°C. On warming to rt an off-white precipitate developed in a yellow solution. The solution was filtered, and the remaining solid was washed with petroleum ether (40-60°C, 2×20 cm³). The combined extracts were reduced to a yellow oil under reduced pressure. Sublimation at 90°C (2×10^{-2} mmHg) gave yellow microcrystals of 8. Yield 20 mg (49%).

η -Benzenebis(trimethylphosphine)vinylrhenium (9)

5 (50 mg, 0.09 mmol) was dissolved in petroleum ether (40-60°C, 30 cm³) and cooled to -78° C.

Dropwise addition of vinylmagnesium bromide (3 cm³, 1.3 M solution in thf), followed by warming to rt, gave an orange solution and a white precipitate. Petroleum ether (40–60°C, 40 cm³) was added, and the solution was filtered. Degassed water (30 cm³) was added to the orange petroleum ether solution, and the two phases were shaken vigorously. The organic layer was decanted off, and upon removal of the solvent an orange oil remained. Repeated extraction with petroleum ether (40–60°C) yielded orange crystals of **9**. Yield 20 mg (49%).

η - Benzenebis(trimethylphosphine)hydridorhenium (10)

5 (70 mg, 0.13 mmol) was dissolved in thf (40 cm³) and transferred on to excess LiAlH₄ (150 mg, 4.0 mmol). After stirring for 3 h at rt, the mixture was reduced to an oily yellow solid *in vacuo*. Extraction with toluene (2×20 cm³), followed by removal of solvent gave an oily solid. Extraction with pentane (2×20 cm³), and concentration (to 10 cm³) and cooling to -20° C gave yellow crystals of 10. Yield 46 mg (85%).

Reaction of 3 with potassium hydride

3 (40 mg, 0.08 mmol) was suspended in thf (30 cm³), and a suspension of potassium hydride (excess, 1.2 g) in petroleum ether (60–80°C) was added with stirring. Over 4 h the orange solid dissolved, forming a yellow solution. Removal of solvent, followed by extraction with petroleum ether (40–60°C, 2×20 cm³) gave a bright yellow solution. Concentration to low volume gave a high yield of yellow crystals. Comparison of the ¹H NMR data with that of an authentic sample of **10** showed them to be identical.

η - Benzenebis(trimethylphosphine)hydridoiodorhenium tetrafluoroborate (11)

5 (40 mg, 0.07 mmol) was dissolved in Et₂O (30 cm³), giving an orange solution. Dropwise addition of ethereal HBF₄ produced an immediate orange precipitate, and the colour of the solution was completely discharged. The solution was decanted, and the residual solid was washed with Et₂O (3×20 cm³). Recrystallization from acetone-water afforded orange-red microcrystals of 11. Yield 40 mg (86%).

Reaction of 5 with silver tetrafluoroborate

Dropwise addition of silver tetrafluoroborate (10 mg, 0.05 mmol) in thf (10 cm³) to an orange solution

of 5 (20 mg, 0.04 mmol) in thf (20 cm³) at -78° C, followed by slow warming to rt produced a black precipitate and a bright red solution. Filtration of the solution followed by careful removal of the solvent under reduced pressure gave red crystals, which were shown to be 11 by ¹H NMR spectroscopy. Yield *ca* 30%.

η - Benzenebis(trimethylphosphine)(η - ethylene) rhenium tetrafluoroborate (12)

Method A. 5 (70 mg, 0.13 mmol) was dissolved in thf (30 cm³) and TlBF₄ (200 mg, 0.69 mmol) was added with stirring. The solution was saturated with ethylene, and the Schlenk vessel was pressurized to 2 atm with ethylene. The orange solution containing a suspension of TlBF₄ was stirred at rt for 2 days. After that time a white solid remained suspended in a yellow-green solution. The solution was filtered, and the solvent was removed from the filtrate under reduced pressure, giving a yellow solid, which was washed with petroleum ether (40–60°C, 2×20 cm³). Recrystallization from aetone-water afforded yellow microcrystals of **12**. Yield 20 mg (30%).

Method B. A solution of trityl hexafluorophosphate in CH₂Cl₂ was added dropwise to a stirred solution of 8 (20 mg, 0.045 mmol) in CH_2Cl_2 (20 cm³). An immediate fine purple precipitate formed, and the solution became completely decolorized. The solvent was removed under reduced pressure, and the resulting pink solid was washed with petroleum ether (40–60°C, 2×20 cm³). The solid was redissolved in thf $(2 \times 20 \text{ cm}^3)$, filtered, and concentrated to ca 10 cm³. Addition of petroleum ether (40-60°C, 30 cm³) caused the pink solution to decolorize, and deposit a pale pink powder, which was collected and dried in vacuo. A ¹H NMR spectrum of the pink solid showed it to be identical to that of an authentic sample of the [Re(n- C_6H_6 (PMe₃)₂(η -CH₂=CH₂)]⁺ cation. Yield 5 mg (21%).

Method C. Two drops of ethereal HBF₄ were added to an orange solution of 9 (15 mg, 0.03 mmol) in petroleum ether (40–60°C, 10 cm³). An immediate pale orange precipitate formed. The orange solid was washed with Et₂O (3×20 cm³), collected, and dried *in vacuo*. Yield 5 mg (28%). The ¹H NMR spectrum showed the product to be the [Re(η -C₆H₆)(PMe₃)₂(CH₂=CH₂)]⁺ cation, by comparison with that of a known sample.

η - Benzenebis(trimethylphosphine)carbonylrhenium tetrafluoroborate (13)

5 (50 mg, 0.09 mmol) was dissolved in thf (30 cm^3) and a suspension of TlBF₄ (150 mg, 0.52

mmol) in thf (20 cm³) was added. The atmosphere and solution were charged with CO to 2-atm pressure. The orange solution and white suspension was stirred at rt for 16 h, and then the atmosphere was repressurized to 2 atm, and stirred for a further 16 h. After this time the solution had become almost colourless, and was filtered off the white insoluble material. The solution was reduced to a white solid *in vacuo*. This solid was re-extracted with thf (2×20 cm³), filtered, and concentrated; on cooling to -20° C a white powder precipitated. This was collected and dried. Yield 10 mg (20%).

n-Benzenebis(trimethylphosphine)chlororhenium (14)

8 (30 mg, 0.07 mmol) was dissolved in dry, distilled CH₂Cl₂ (20 cm³) giving a yellow solution, which on extraction with petroleum ether (40-60°C, 2×20 cm³) and filtration yielded a bright yellow solution. Concentration and cooling to -20°C afforded yellow microcrystals (30 mg, 93%) of (η -C₆H₆)Re(PMe₃)₂Cl.

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