Manganese and rhenium triphosphorus macrocycle complexes and reactions with alkenes

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The synthesis of Re(III), Re(I) and Mn(II) compounds of the macrocyclic phosphine ligand 1,5,9-trialkyl-1,5,9-triphosphacyclododecane, 12[ane]P 3R 6 (R = Et, i-Bu) is described. The reaction of 12[ane]P 3R 6 with ReCl 3(PPh 3) 3 or ReCl 3(PPhMe 3) 3 gives rise to the octahedral d 6 complexes 12[ane]P 3R 6ReCl 4 (1 a). Reduction of 1 a with Na/Hg under a CO atmosphere gives the rhenium(i) compound (12[ane]P 3R 6) 2Re(CO) 3Cl. 2 a which undergoes further reactivity to give hydride (3 a), vinylidene (4 a) and allenylidene (5 a) compounds. With Mn(CO) 3Br, 12[ane]P 3Et 3 gives the octahedral d 6 complex, (12[ane]P 3Et 3)Mn(CO) 3Cl 2. 6 a The crystal structures of (12[ane]P 3Bu 3)ReCl 4 and (12[ane]P 3Et 3)Mn(CO) 3Cl 2 are presented.

Results and discussion

Rhenium(III) complexes

Addition of 12[ane]P 3Et 3 or the bulkier 12[ane]P 3Pr 3 to ReCl 3(PPh 3) 3 or ReCl 3(PMePh 3) 3 gives rise to green powders which are insoluble in all common solvents, except hot DMSO in which they decompose. These compounds were not further investigated since reaction with 12[ane]P 3Bu 3 gives rise to a dichloromethane soluble green solid (1 b). The same compound can be obtained from mner-ReCl 3(PMe 2Ph) 3, albeit in lower yields and in both cases the reaction can be followed by monitoring the decay of free macrocycle and growth of PPh 3 or PMePh respectively in the 31P NMR spectrum. 1 b has been shown to be a stable green powder, after workup, which is air-sensitive in solution and readily oxidises yielding unidentified brown paramagnetic solutions that do not contain a Re=O unit (by IR). 1 b has been characterised by spectroscopic and analytical methods. The formula (12[ane]P 3Bu 3)ReCl 4 is confirmed by mass spectrometry in which the molecular ion is observed which displays the expected characteristic isotope pattern for Re and Cl. The complex is paramagnetic with a magnetic susceptibility (μ eff = 1.42 μ B) indicating a large spin–orbit coupling and is consistent with d 6 Re(I). 5 a Sharp, shifted proton NMR spectra are observed which are spread over a +18 to −5 ppm range: the terminal i-Bu methyl groups, being furthest from the metal are shifted the least (δ = 2.8, methyl protons; δ = 8.8, methine protons), and these can be assigned from the 1 H− 1 H 2D spectra which also clearly indicates the diastereotopic nature of the ligand backbone ring protons. Only the i-Bu methyl groups were observed in the 13C NMR spectrum (δ = 42) and no 31P NMR signals were observed as might be expected. b Two bands attributable to 1 (Re−Cl) consistent with approximate C 3v symmetry were observed in the IR spectrum (347, 308 cm −1).

Cyclic voltammetry (CV) has also been used to characterise rhenium compounds and the CV of 1 b clearly shows two, one-electron reduction waves and one oxidation wave (E 1/2ox = +0.46, E 1/2red = −1.15, −1.60). The standard oxidation potential is quite different to reported data for similar com-

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Mononuclear rhenium(III) complexes containing three tertiary phosphines and three halides are well known but the majority have meridional geometries, even those with polydentate phosphines that are flexible enough to adopt a facial configuration. Phosphorus ligand complexes that show a facial arrangement include MeC(CH$_3$)$_2$P$_3$ReCl$_2$, which has been structurally characterised, and the phosphite complex, ReCl$_3$(P(OEt)$_3$)$_2$, which is assigned a fac configuration on the basis of IR and $^1$H spectroscopy. ReCl$_3$(PR$_3$)$_2$ complexes (R = alkyl or aryl) may also be formed as a mixture of mer and fac isomers.$^{10}$

In the present compounds, the constraints imposed by the macrocycle means that the complex must have a fac geometry and this is confirmed by a crystal structure determination.

The crystal structure of 1$^{\text{th}}$ is shown in Fig. 1(a) along with selected bond lengths and angles. The Re, Cl(1), P(2) and central carbon of the backbone propanediol bridge opposite to P(2) all sit on a crystallographic mirror plane. The remaining backbone functions are disordered with the carbons bonded to P(2) being satisfactorily refined in two split-occupancy positions; the β-carbon of the Bu group is similarly disordered over two positions. This model is more clearly represented in Fig. 1(b). The overall coordination geometry of 1$^{\text{th}}$ is very close to regular octahedral, the average Re–P bond length is similar (2.386(3) Å) to the average Re–Cl length (2.419(2) Å) and the average interligand angles are also close to 90° [P–Re–P = 90.95(8)°, Cl–Re–Cl = 92.84(8)°]. The structure gives a clear indication of the bulk of the ‘Bu substitutents and how they protrude below the girth of the complex, this feature has implications for the reactivity of complexes of this ligand (vide supra). The Re–P distances are significantly shorter than those found in (triphos)ReCl$_3$ (Re–P$_{ax}$ = 2.447(5) Å), presumably due to the inflexible nature of the tripodal phosphine; the more sterically demanding phenyl groups may also help to force the ligand away from the metal centre. The P–Re–P angles in 1$^{\text{th}}$ are also significantly greater than in the triphos case (84.8, 85.4 and 86.1°) which indicates the lack of flexibility of the tripodal ligand in comparison to the macrocycle.

Rhenium(I) complexes

The CV of 1$^{\text{th}}$ shows that the 2e$^-$ reduction to a d$^0$, Re(I) state should be readily accessible. Chemical reduction of 1$^{\text{th}}$ using two equivalents of sodium amalgam under a CO atmosphere proceeded smoothly to give 12[ane]P$_2$Bu$_3$ReCl$_3$, 2$^{\text{nd}}$, in good yield. The same reaction using H$_2$ gives the analogue, 2$^{\text{nd}}$, in comparable yields. The NMR data is consistent with the proposed structure (Scheme 1), and comparison with the NMR data for the manganese complex (described below) also suggests the same structure.

The $^{31}$P NMR spectrum of 2$^{\text{nd}}$ shows the expected AM$_2$ pattern ($\delta$ = 8.72, 1; and 26.43, 4; $J_{AM}$ = 19.5 Hz) which is temperature invariant, and the infrared spectrum shows two bands of equal intensity [ν(CO) = 1930 and 1865 cm$^{-1}$] indicating a cis configuration of carbonyl ligands. Comparison of ν(CO) with the reported (triphos)Re(CO)$_2$Cl$_2$ [ν(CO) = 1948 and 1887 cm$^{-1}$]$^{11}$ shows that the macrocycle is a better electron donor than triphos, and this corroborates the CV evidence from 1$^{\text{th}}$. The $^1$H NMR spectrum is uninformative since all the macrocycle protons resonate in the same area, except for the methyl groups of the Bu chain ($\delta$ 0.95). The $^{13}$C NMR spectrum is much more informative, especially the carbonyl resonance which is shown in Fig. 2. This shows coupling with two equatorial phosphines that are chemically equivalent but magnetically inequivalent, and the one axial phosphine, to give an AXX'Y spin system. This compares well with data for (triphos)Re(CO)$_2$Cl$_2$ and (triphos)Ru(CO)$_2$Cl$_2$.$^{12}$

Direct substitution of the carbonyl groups in Re(CO)$_3$Br by the macrocycle, either thermally or photolytically, occurs in poor yield and is accompanied by decomposition products which could not be separated. The kinetic inertness of d$^0$ Re(I) and poor solubility may contribute to the low yield observed in this reaction as is consistent with previous observations where direct substitution of carbonyls in Re(CO)$_3$X (X = halide) compounds by acyclic PP$_3$ ligands has been studied and reported to be stubborn and to give rise to mixtures of products.$^{13}$

The reaction of phosphines with Re(CO)$_3$(PP$_3$)$_2$Cl$_2$ is known to result in substitution,$^{11}$ but with the macrocycle (12[ane]P$_2$Bu$_3$) no reaction was observed over prolonged reaction times in refluxing xylene.

Fig. 1 (a) X-Ray structure of (12[ane]P$_2$Bu$_3$)ReCl$_3$, 1$^{\text{st}}$, showing the atom labelling scheme. (b) The C4–C5–P2 bridge and the C11 atoms are disordered. Thermal ellipsoids are drawn at 50% probability level. The symmetry (x, 1–y, z) generates the atoms marked with #. Selected bond lengths (Å) and angles (°): Re–P$_{Axx}$ 2.396(2), Re–P$_{A}$ 2.497(2), Re–Cl$_{A}$ 2.415(2), Re–Cl$_{B}$ 2.424(2), P$_{A}$–Cl$_{B}$ 178.72(9), P$_{A}$–Cl$_{A}$ 178.87(9), P$_{B}$–Cl$_{A}$ 179.32(9), P$_{B}$–Cl$_{B}$ 179.45(9).
Reaction of \(2^\text{th} \) with LiAlH\(_4\) proceeds under an inert atmosphere to give 12[ane]P\(_3^\text{Bu}\)Re(CO)\(_2\). The analogous reaction with the related (triphos)-ReCl\(_3\), under the same conditions, gives rise to a trihydride; an atmosphere of CO is required for the formation of the dicarbonyl mono-hydride. The IR spectrum of \(3^\text{th} \) shows two bands due to carbonyl ligands at 1910 and 1845 cm\(^{-1}\) consistent with a cis orientation of the carbonyl groups and at a lower energy compared to \(2^\text{th} \) as a result of substitution of chloride by the more electron donating hydride. No bands attributable to \(\nu(M-H)\) were observed, they are presumably masked by the carbonyl absorptions. The \(\text{\(^{31}P\)}^{\text{[H]}\)} NMR spectrum at room temperature shows, in addition to resonances due to the carbonyl carbons, a triplet attributable to the hydride resonance due to the carbonyl carbons appears as a poorly resolved multiplet (\(\delta 198.4\)), the inequivalence of the backbone functions and the P-alkyl substituents is clearly indicated and resonances due to all carbons could be assigned; again this behaviour indicates that the complex is stereochemically rigid.

\[\text{Scheme 1} \quad \text{Reagents and conditions: (i) Mn(CO)Br, CHCl}_3; \text{(ii) ReCl}_3(CH_2CN)_2(PPh)_2, CHCl}_3; \text{(iii) Na/Hg/CO, THF; (iv) LiAlH}_4, \text{THF; (v) CF}_3SO_2Ag, HC=CCCH_3O(H)PPh}_3, \text{CHCl}_3; \text{(vi) CF}_3SO_2Ag, \text{HC=CPh, CHCl}_3; \text{(vii) Me}_3OBF}_2, \text{HC=CPh, CHCl}_3.\]

**Rhenium vinylidenes and cumulenes**

In view of the activity of compounds containing Re=C bonds in alkene metathesis catalysis, the formation of vinylidene and cumulene complexes supporting rhenium–carbon multiple bonds stabilised by the macrocyclic triphosphine has been studied.

Abstraction of halide from \(2^\text{th} \) using silver triflate or trimethylsilyl triflate followed by reaction with a terminal acetylene results in the formation of a vinylidene complex (\(4^\text{th} \)) via a 1,2-hydrogen shift. Alternatively, the reaction of the macrocycle hydride complex \(3^\text{th} \) with Me\(_3\)OBF\(_2\) followed by addition of the terminal acetylene gives rise to the same material which is isolated as a red powder after work up. The IR spectrum of \(4^\text{th} \) shows an increase in \(\nu(CO)\) in comparison to compound \(3^\text{th} \); in the \({^1}H\) NMR spectrum, the vinylidene proton is split into a quartet (\(\delta 4.75, J_{P-H} = 7.06 \text{ Hz}) due to coupling to three apparently equivalent phosphines on the NMR timescale. Low energy barriers for ligand rotation have previously been observed for vinylidene compounds. The \(\text{\(^{31}P\)}\) NMR spectrum of \(4^\text{th} \) shows an AB pattern of a doublet and a triplet (\(\delta 38.1, -31.7\) respectively; \(J_{P-P} = 28.3 \text{ Hz}) indicating magnetically inequivalent phosphorus nuclei in a ratio of 1:2:1.

Fig. 2 100 MHz \(\text{\(^{13}C\)}\) NMR spectrum of \(2^\text{th} \) in the carbonyl region, scale units are \(\delta\): a observed spectrum, b calculated spectrum based on an AXX'Y spin system (\(A = \text{\(^{13}C\)}\) X, X', Y = \(\text{\(^{31}P\)}\)); \(J_{AX}(cis) = 50.0 \text{ Hz,}\ J_{AX}(trans) = -8.0 \text{ Hz,}\ J_{AY} = 32.0 \text{ Hz,}\ J_{AX} = J_{AX} = 0.5 \text{ Hz.}\)

In addition, the formulation is supported by observation of the molecular ion in the mass spectrum which displays the appropriate isotopic distribution.
2:1 and that the complex appears stereomERICally rigid at ambient temperature under these conditions.

The $^{13}$C($^1$H) NMR spectrum confirms the presence of a vinylidene ligand (as opposed to a $\pi$-alkyne or $\pi$-alkynyl ligand), i.e. a resonance attributable to the $\pi$-C bonded to Re is observed as a broadened singlet at $\delta$ 352.1 indicating unresolved coupling to the inequivalent phosphorus nuclei. The inequivalence of the macrocycle ring is also indicated by the resonances attributable to the ring carbons and P-alkyl substituents. Resonances to attributable to the aromatic and secondary carbons may also be assigned; in addition, the molecular ion is observed in the mass spectrum with the appropriate isotopic distribution.

Allenylidene ($M$=C–C–C) compounds have been synthesised in a similar manner to the vinylidene complex, $^{4}$ms using propargyl alcohols.$^{16}$ Addition of silver triflate to a dichloromethane solution of $2^m$ followed by HCl=CC(OH)P$_4$ leads to directly to the unsaturated cumulene complex $3^m$, presumably by the allenylidene intermediate $[(12[ane]P,Bu)(CO)_{2}Re=C-\text{CHC(OH)Ph}],$ which eliminates water spontaneously and was not observed. $5^m$ was isolated as a yellow solid after work up. The IR spectrum shows absorptions due to ν(CO) at a lower frequency than observed in $4^m$ indicating the cumulene ligand to be a better donor than the vinylidene; bands attributable to the ring carbons and P-alkyl substituents. Thus, with $2^m$, a low molecular weight polymer is obtained (also with a relatively narrow polydispersity). For the ethyl derivative, $2^u$, the catalyst system is more active than for its bulkier analogue and a polymeric product with a much higher molecular weight (and also a higher polydispersity) is obtained. Integration of the vinyl protons in the $^1$H NMR spectrum of this polymer indicates a random distribution of cis and trans substituted double bonds. Addition of 2 equivalents of EtAlCl$_2$ to solutions of $2^m$ again gives rise to red solutions which show two bands attributable to ν(CO) (1981, 1917 cm$^{-1}$) in the IR spectrum and which are consistent with the presence of cis and trans carbonyls. In addition, the reaction of $2^m$ with MeLi does not result in any colour change and the starting complex may be recovered unchanged from the residue. These observations support a mechanism of activation based upon the formation of alkylidenes by substitution of the rhodium halide followed by α-hydride abstraction, as has been proposed for the metathesis catalyst system derived from WCl$_6$ and EtAlCl$_2$. The vinylidene and cumulene complexes, $4^m$ and $5^m$, are inactive in the presence of a suitable initiator, presumably due to the absence of labile ligands at the metal preventing coordination of substrate alkenes.

The manganese complexes, $6^m$, is also active in ROM under similar conditions. For $6^m$, the activity of the catalyst is similar to that of the rhodium analogue ($2^m$) although the molecular weight of the polymer is very substantially lower. $^{13}$C NMR and

Manganese

The manganese bromodicarbonyl analogue of 2 is readily prepared by the white-light photolysis of solutions of Mn(CO)$_3$Br in the presence of the macrocycle, $[12$[ane]P$_4$Et$_4$]Mn(CO)$_3$Br. $^6^m$. The IR spectrum of $6^m$ shows two bands corresponding to a cis-dicarbonyl unit (1907, 1847 cm$^{-1}$). The $^{31}$P($^1$H) NMR spectrum consists of a doublet and a triplet ($\delta$ 10.5, 58.6 respectively; $\nu_{J_{P-H}} = 48$ Hz) corresponding to an A,B spin system; this spectrum is temperature invariant (30 to 80 °C) indicating the complex to the stereochemically rigid under these conditions. In the $^{13}$C($^1$H) NMR spectrum, broadened resonances are observed for the macrocycle carbons and a weak and broadened multiplet may be assigned to the carbonyl carbon resonance ($\delta$ 194).

The X-ray crystal structure of the manganese compound, $6^m$, has been determined and is represented in Fig. 3 along with selected bond lengths and angles. The overall structure is close to octahedral with distortions arising from differences in bond lengths (Mn–P$_m$= 2.300(2)Å, Mn–C$_u$= 1.807(8)Å, Mn–Br= 2.569(1)Å and deviations from idealised angles (P–Mn–P$_m$= 93.81(7)$^\circ$, P–Mn–C$_u$= 89.4(3)$^\circ$, P–Mn–Br$_u$= 84.59(6)$^\circ$). These values compare closely with those for other manganese bromocarbonyl phosphine complexes in the literature. For example, in mer, cis, cis-[MnBr(CO)$_3$(P(OH)$_2$)$_2$](dppm) the corresponding average bond lengths are very similar (Mn–P= 2.294(2)Å, Mn–C= 1.786(6)Å, Mn–Br= 2.527(1)Å).$^{17}$

In $4^m$, the Mn–P distances trans to CO are significantly longer than those for cis to Br (2.329(2) and 2.243(2)Å respectively) indicating a stronger trans influence of the $\pi$-acidic CO ligands in comparison to Br as is expected.

Reactions with alkenes

Rhenium and manganese

In view of the known activity of rhenium carboxyl halides in alkene metathesis, the reactivity of the phosphorus macrocycle complexes $2^m$ and $3^m$ with cyclic alkenes was studied. Addition of the initiator, ethyl aluminium dichloride to a solution of the chloro complexes (conditions similar to the initiation of the metathesis of 1-hexene by Re(CO)$_3$Cl($^1$H) results in a colour change from colourless through green, to red. Addition of norbornene to this solution results in the strongly exothermic reaction and the evolution of gas whilst the solution becomes increasingly viscous. These reactions proceed at a reasonable rate at 0 °C, however for the collection of comparative data and polymer properties, reactions were performed at 25 °C (Table 1). For both compounds 2 (R=Et, Bu), a polymeric product is formed by ring opening metathesis polymerisation (ROM) as indicated by a strong C=C stretching frequency in the IR spectrum ($\nu$(C–C)= 1645 cm$^{-1}$). The behaviour of the catalyst is dramatically influenced by the nature of the P-alkyl substituents. Thus, with $2^m$, a low molecular weight polymer is obtained (also with a relatively narrow polydispersity). For the ethyl derivative, $2^u$, the catalyst system is more active than for its bulkier analogue and a polymer product with a much higher molecular weight (and also a higher polydispersity) is obtained.

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The inability of any ligand to dissociate and form a vacant site;
gives the complex Tp(PCy₃)initiator. Using trimethylsilyldiazomethane and silver tri-
CH₂Cl₂, norbornene in
pentene) is formed. This activity is similar to that of the
norbornene giving rise to good yields of polymer after 2 h at
room temperature (92%, M₅ = 2.7 × 10⁷, PDI = 3.5) and the authors suggest that ligand dissociation
occurs before alkene coordination.²⁵ The performance of these complexes (quoted as yields by the authors) indicate that our Re and Ru compounds compare very favourably with literature values, indeed ¹⁰
appears to be significantly more effective as it polymerises norbornene in excellent yield (Table 1) but in shorter timescales (1 h) and under milder conditions (0 °C).

The path of this reaction is intriguing because the accepted mechanism for Grubbs’ catalyst involves phosphine dissociation and subsequent alkene coordination to the resultant vacant site,²⁶ which helps explain the high activities observed with bulky phosphines. A recent report using the chelating dbpm ligand (dbpm = Bu₄PCH₂PBU₄) also shows high activities in the ring opening of cycloalkanes;²⁷ the geometry of the ligand imposes cis coordination of the phosphines but the Ru complex is square pyramidal and the high activity has been attributed to halide dissociation. By the use of the facially capping macrocycle, the octahedral metal centre must hold the carbone and the alkene cis. Detailed kinetic studies were not performed; from the NMR measurements however, observations relevant to mechanistic considerations can be made. Firstly, there is no evidence of phosphine dissociation in ⁷⁹ as there is a temperature invariant (to −60 °C) singlet in the
¹³C[¹H] NMR spectrum; this behaviour being previously commented on⁶⁷ and is consistent with facile dmso ligand exchange processes.²⁸ Phosphine dissociation in macrocycle complexes of this nature would also be expected to be restricted in comparison to acyclic or monodentate phosphate ligands. The complex has 18 electrons so an associative mechanism is unlikely and free dmso was observed by ¹³C NMR spectroscopy, indicating that it is labile under the reaction conditions and capable of generating available coordination sites required in active species. Unfortunately, a resonance due to the propagating carbone in the ¹³C NMR spectrum was not observed (as in other examples),²⁹ neither was the formation of a metalacycle on addition of one equivalent of monomer.

**Experimental**
All reactions were carried out in an atmosphere of dry nitrogen or argon passed through a CrO₃ (supported on silica) column using standard Schlenk techniques or in a Vacuum Atmospheres glove box. All solvents were dried by refluxing over standard drying agents and distilled immediately prior to use. The light petroleum used had a boiling point range of 40–60 °C. The compounds 12[ane]P₃/(CHPh)(PR)Cl₂, ⁴⁰ ⁴⁰ ReCl₃(MeCN)-(PPPh₃),¹¹ Re(CO)₅Br,³² Re(CO)₅(PPPh₃)Cl,³³ were prepared by literature methods. All other chemicals were obtained from commercial sources and where appropriate, dried over molecular sieves and deoxygenated by repeated freeze-thaw degassing or recrystallisation. Photolyses were carried out using a Hanovia 125 W mercury discharge lamp (254 nm) or a 100 W incandescent tungsten filament lamp as indicated. NMR spectra were recorded on a Bruker DPX-400 instrument at 400 MHz (¹H) and 100 MHz (¹³C) or a JEOL FX-90Q at 36.23 MHz (³¹P) or a JEOL Lambda Eclipse 300 at 121.65 MHz (³¹P), 300.52 MHz (¹H) and 75.57 MHz (¹³C), or a Bruker AMX-360.

<table>
<thead>
<tr>
<th>Complex/mmol</th>
<th>Monomer (g)</th>
<th>Initiator</th>
<th>Solvent temp.(°C)</th>
<th>Yield (g. %)</th>
<th>Activity (kg P mol⁻¹)</th>
<th>M₅</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>(12[ane]P₃Bu₄)ReCl₂ (2²⁶) (0.03)</td>
<td>Norbornene (1.00)</td>
<td>EtAlCl₃ (4.1)</td>
<td>CH₂Cl₂ (25)</td>
<td>0.875, 87%</td>
<td>11.8</td>
<td>510</td>
<td>1.6</td>
</tr>
<tr>
<td>(12[ane]P₃Et₄)ReCl₂ (2²⁶) (0.015)</td>
<td>Norbornene (0.50)</td>
<td>EtAlCl₃ (4)</td>
<td>CH₂Cl₂ (25)</td>
<td>0.495, 98%</td>
<td>16.6</td>
<td>3710</td>
<td>2.9</td>
</tr>
<tr>
<td>(12[ane]P₃Et₄(MeCN))ReCl₂ (0.03)</td>
<td>Norbornene (0.50)</td>
<td>EtAlCl₃ (4)</td>
<td>CH₂Cl₂ (25)</td>
<td>0.30, 60%</td>
<td>12.6</td>
<td>1280</td>
<td>2.0</td>
</tr>
<tr>
<td>(12[ane]P₃Et₄)RuCl₃ (0.03)</td>
<td>Norbornene (0.55)</td>
<td>EtAlCl₃ (4.1)</td>
<td>CH₂Cl₂ (25)</td>
<td>0.137, 25%</td>
<td>13.2</td>
<td>10,400</td>
<td>6.4</td>
</tr>
<tr>
<td>(12[ane]P₃Et₄)RuCl₃ (0.09)</td>
<td>Norbornadine (1.0)</td>
<td>EtAlCl₃ (4.1)</td>
<td>CH₂Cl₂ (25)</td>
<td>0.871, 87%</td>
<td>9.67</td>
<td>188,000</td>
<td>67</td>
</tr>
<tr>
<td>(12[ane]P₃Et₄)RuCl₃ (0.072)</td>
<td>Norbornene (0.50)</td>
<td>TMSCHN₂AgOT (2)</td>
<td>CH₂Cl₂ (120)</td>
<td>0.12, 24%</td>
<td>1.67</td>
<td>56,300</td>
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at 145.78 MHz (1P). All chemical shifts are quoted in units of δ (ppm).1H and 13C NMR chemical shifts are relative to solvent resonances, 1H chemical shifts are relative to 85% external H3PO4 (δ = 0). For 13C assignments see Fig. 2. Magnetic susceptibilities were determined by Evans’ method11 or by the Gouy method on a Johnson Matthey magnetic susceptibility balance; an experimental diamagnetic correction was measured for 12aneP2, and applied. Mass spectra (EI and APCI) were recorded on a VG Platform II Fisons mass spectrometer. Infrared spectra were recorded on a Perkin Elmer 1600 or a Nicolet 510 FT-IR spectrometer as a CsI disk or in solution using KBr solution cells. NMR simulations were carried out using gNMR.12 Molecular weight determinations were carried out in chloroform or 1,2-dichlorobenzene solution by RAPRA Technologies Ltd. using a PLgel 2 × mixed-bed D, 30 cm, 5 μm column at 40 °C and a flow rate of 1.0 ml min⁻¹ (nominal) and using a refractive index (and differential pressure) detector. The GPC system used was calibrated with polystyrene and the results are expressed as the “polystyrene equivalent” molecular weights. Cyclic voltammetry was performed on a Windsor PGStat 12 potentiostat in CH2Cl2 with Bu4NPF6 (0.1 M) supporting electrolyte vs. an Ag/AgCl reference electrode and Fe/Fe2⁺ internal reference (0.46 vs. SCE); data were processed on a PC operating an Autolab program. The labelling scheme for NMR assignments for compounds 2a, 3a, 4a, and 5a is defined in Fig. 4.

**Fig. 4 Labelling scheme for NMR assignments for Re(II) compounds.**

**X-Ray crystallography**

Crystals suitable for X-ray structure determination were mounted in silicone oil. X-Ray intensity data were recorded on a Bruker-Nonius CCD area detector (compound 1, Re, and a FAST area detector (compound 6, Mn) by using mono- chromated Mo-Kα radiation (λ = 0.71073 Å) and following previously described procedures.36 The data sets were corrected for absorption effects using SORVAT47 and DIFABS38 for compounds 1b and 6, respectively.

The structures were solved by direct methods (SHELXS-97)19 and refined by full-matrix least squares (SHELXL-97)19 on F² using all unique data. The Re(1), Cl(1), C(10), C(12) and C(13) atoms of the –CH(Me)2 group on P(2) in compound 1b were located on a mirror plane of symmetry; the C(11) atom of this group was located off the mirror plane. The unique P(1)(CH2)3P(2) bridge in this compound was also disordered with atom C(5) occupying two half-occupied positions. The P–C and C–C distances in the disordered groups were constrained to remain at 1.83 and 1.53 Å, respectively. In compound 6, the P(1)(CH2)3P(3) bridge was disordered and the C(9) and C(9') atoms were refined with 70 and 30% site occupancies respectively. All non-hydrogen atoms were anisotropic in both structures, but an ISOR = 0.005 constraint was applied for the atoms C(1), C(9) and C(9') in 6. The hydrogen atoms on the C(4) and C(5) atoms of the disordered chain and the C(10)–C(13) atoms of the –CH(Me)2 group in 1b and those on the C(8)–C(10) atoms of the disordered chain in 6 were ignored. Other hydrogen atoms were included in calculated positions (riding model). Compound 6 was refined as a 48/52 racemic twin. Details of crystal data and refinement parameters are given in Table 2.

**CCDC reference numbers 153078 and 187745.** See http://www.rsc.org/suppdata/dt/b2/b205754a/ for crystallographic data in CIF or other electronic format.

12[aneP2,4BuReCl3](1a)

To ReCl3(MeCN)(PPh3)2 (0.066 g, 0.77 mmol) dissolved in CH2Cl2 (10 cm³) was added 12[aneP2,4Bu3] (0.03 g 0.77 mmol) and this was heated to reflux for 3 h to give a dark green solution. The solvent was removed in vacuo and the resulting sticky green solid washed with light petroleum (5 × 30 cm³). The green powder was redissolved in CH2Cl2 (3 cm³) and light petroleum (5 cm³) added. After cooling to –30 °C the resultant green microcrystals were isolated by filtration and dried in vacuo. Yield, 0.33 g (68%). Crystals suitable for X-Ray diffraction were grown by slow evaporation of a CD2Cl2 solution (Found: C, 36.4; H, 6.35; C9H12Cl2P4Re requires: C, 36.93; H, 6.64%).18 1H NMR (CD2Cl2): δ 18.1 (br, 3H, PCH2CH2CH2P); 9.3 (m, 3H, PCH2CH2CH2P); 8.8 (br, 3H, PCH2CH2CH2P); 4.75 (br, 4H, PCH2CH2CH2P). 2.8 (d, JRe-H = 7 Hz, 18H, PCH2CH2CH2P); 1.1–1.4 (m, 6H, PCH2CH2CH2P); 4.2 (m, 6H, PCH2CH2CH2P).19 1C NMR (CD2Cl2): δ 42.0 (PCH2CH2CH2P). IR (CsI disk, cm⁻¹): 2959, 2982, 2934, 1363 (m), 1261 (m), 1187 (w), 1162 (m), 1092 (s), 1026 (m), 746 (sh), 696 (s), 519 (s), 497 (m), 461 (s), 347 (w), 308 (m). η = 1.42 με MS (APCI): 681.1 (M⁻, correct isotope distribution for 191Re and 303Cl), 647.65 (M – Cl), 612.2 (M – 2Cl).

12[aneP2,4Bu3Re2(CO)Cl2](2a)

To sodium amalgam (0.007 g Na, 0.31 mmol) suspended in THF (25 cm³) was added 1a (0.096 g, 0.77 mmol) as a solid. The Na₂ atmosphere was removed in vacuo and the flask back-filled with CO (1 atm). This was stirred for 5 h to give a colourless solution that was filtered through a short plug of Celite, concentrated to 2 cm³ and diluted with light petroleum (3 cm³). On cooling to −30 °C a yellow powder was obtained which was washed with light petroleum (2 × 5 cm³) and dried in vacuo. Yield, 0.099 g (96%) (Found: C, 40.9; H, 6.55. C51H34O3ClP4Re requires: C, 41.34; H, 6.79%).30 [1H] NMR (CD2Cl2): δ −8.72 (t, JRe-P = 19.5 Hz).1H NMR (CD2Cl2): δ 0.95 (m, 18 H, CH(CH2)2); 1.5–2.3 (m, 27 H, PCH2CH2CH2P, PCH2CH2CH2P, PCH2CH2CH2P); 2.73 (s, C5); 22.77 (t, JPC = 13.5 Hz, C5); 25.74 (s, C5); 24.47 (d, JPC = 4 Hz, C5); 25.94 (t, JPC = 11.5 Hz, C5); 29.83 (d, JPC = 29 Hz, C5); 36.39 (t, JPC = 14 Hz, C5); 45.10 (d, JPC = 35 Hz, C5); 198.2 (m, AXX’Y’ spin system JAX = 50.0 Hz, JAX = −8.0 Hz, JAY = 7.0 Hz, JAX = 32.0, JAY = JXY = 0.5 Hz). IR (THF soln., cm⁻¹): ν(CO) (1930) 3865 (s). MS (APCI): 632.1 (M⁻, correct isotope distribution for 185Re and 303Cl), 568.1 (M–2CO).

12[aneP2,4Et3Re2(CO)Cl2](3a)

Addition of 12[aneP2,4Et3] to ReCl3(MeCN)(PPh3)2 followed by refluxing for 3 h in a manner identical to the synthesis of 1a gave rise to an intractable green precipitate that did not dissolve in solvents with which it did not react. This material is presumably the ethyl analogue of 1a, although it was not further characterised. The green solid isolated by filtration, washed with CH2Cl2 (3 × 5 cm³) and dried in vacuo (µ = 1.54 με). The subsequent preparation and work-up of 3a was continued in a manner identical to that of 2a. The yellow product was isolated in 65% overall yield [based on ReCl3(MeCN)2PPh2] (Found: C, 35.3; H, 5.84. C41H36O3ClP4Re requires: C, 34.96 H, 5.70%).30 [1H] NMR (CD2Cl2): δ −8.09 (t), −25.39 (d, JPC =
The solution was added as a solid in several small portions. This was allowed to warm to room temperature and then refluxed overnight. The cooled reaction mixture was filtered and the solvent concentrated to ρ cm³. Toluene (10 cm³) was added and on cooling to −30 °C, small white microcrystals formed which were isolated by filtration and dried in vacuo. Yield, 0.16 g (91%): Found: C, 43.1; H, 6.95; C₂H₃O₂P,Re requires: C, 43.59; H, 7.32%. ¹H NMR (CDCl₃): δ 23.69 (br s). ¹³C NMR (CDCl₃): δ −6.76 (t, J = 20 Hz), 1H, ReH), 0.70 (m, 18, H₂C₆H₄CH₂H₂), 1.2–2.3 (m, 27 H, PCH₂CH₂CH₂P, PCH₂CH₂CH₂P, PCH₂CH₂CH₂), ¹³C NMR (CDCl₃): δ 19.82 (s, C₃, 20.72 (s, C₄, 23.72 (t, J = 13 Hz, C₅, 24.18 (s, C₆, 24.70 (d, J = 4 Hz, C₇, 28.63 (t, J = 10 Hz, C₈, 30.05 (d, J = 31 Hz, C₉, 36.21 (t, J = 12 Hz, C₁₀, 45.28 (d, J = 35 Hz, C₁₁, 198.4 (m, CO), IR (THF soln., cm⁻¹): ν(CO) 1910 (s), 1849 (s) (MP): 857 (M), correct isotope distribution for Re(C₅H₈PO₂)₅, 533.6 (M − 2CO).

To a cold (0 °C) solution of 2 mmol (0.9 g, 0.14 mmol) in CH₂Cl₂ (10 cm³) was added AgOTf (0.36 g, 0.14 mmol). After warming to room temperature the mixture was stirred for 10 min then recooled to 0 °C. Propargyl alcohol (0.035 g, 0.17 mmol) was then added as a solid and was warmed to room temperature and stirred for 1 h to give a yellow solution and a white solid. The solution was filtered, concentrated to ca. 2 mm³ and light petroleum (10 cm³) added to precipitate a dark yellow solid. This was isolated by filtration and dried in vacuo. Yield, 0.06 g (51%): Found: C, 48.6; H, 6.41. C₅H₈O₂F,SP,Re requires: C, 47.94; H, 6.19%. ¹H NMR (CDCl₃): δ 7.6–7.0 (m, 10 H, C₆–C₁₀, 0.70 (m, 18, H₂C₆H₄CH₂H₂), 1.2–2.3 (m, 27 H, PCH₂CH₂CH₂P, PCH₂CH₂CH₂P, PCH₂CH₂CH₂), ¹³C NMR (CDCl₃): δ 19.82 (s, C₃, 21.31 (s, C₄, 24.81 (t, J = 13 Hz, C₅, 24.42 (s, C₆, 25.03 (d, J = 4 Hz, C₇, 28.84 (t, J = 10 Hz, C₈, 31.07 (d, J = 31 Hz, C₉, 36.48 (t, J = 12 Hz, C₁₀, 45.42 (d, J = 35 Hz, C₁₁, 125.8, 126.9, 128.9, 129.1 (Ar), 248.7 (s, Re(C₅H₈PO₂)₅(C₅H₈PO₂)₅), IR (KBr disc, cm⁻¹): ν(CO) 1278. MS (APCI): 787.9 (M⁺, correct isotope distribution for Re(C₅H₈PO₂)₅, 723.9 (M − 2CO).
12[ane]P₃Et₃Mn(CO)₂Br, 6b

To a solution of 12[ane]P₃Et (0.13 g, 0.42 mmol) in Et₂O (25 cm³) was added Mn(CO)₂Br (0.12 g, 0.4 mmol) as a solid. This was irradiated (100 W tungsten filament lamp) for 1.5 h to give a yellow suspension. The solvent was removed in vacuo and the product extracted into CH₂Cl₂ (3 × 20 cm³). The solvent was reduced in volume and light petroleum added. Cooling to 0°C then yielded a yellow microcrystalline solid. Crystals suitable for X-ray diffraction were obtained by vapour diffusion of light petroleum into a CH₂Cl₂ solution. Yield, 0.044 g (20%) (Found: C, 40.7; H, 6.45. C₁₆H₂₆O₂Br₃P₃Mn requires: C, 41.07; H, 6.69%). ³¹P{¹H} NMR (CDCl₃): δ 10.5 (t), 58.6 (d, JPP = 50 Hz). ¹H NMR (CDCl₃): δ 1.03 (br s, 9H PCH₃CH₂CH₃), 1.28 (br s, 2H, PCH₂CH₂CH₃), 1.47 (br s, 6H, PCH₂CH₂CH₃), 1.63 (br s, 4H, PCH₂CH₃), 1.79 (br s, 2H, PCH₂CH₃), 1.92 (br s, 6H, PCH₂CH₂CH₃), 2.08 (br s, 2H, PCH₂CH₂CH₃), 2.3 (br s, 2H, PCH₂CH₃). ¹R (KBr disc cm⁻¹): ν(CO) 1907 (s), 1847 (s). MS (APCI): 405.3 (M⁺, the expected isotope ratio for 79Br was observed).

**ROMP reactions**

In a typical experiment in a Schlenk flask, 12[ane]P₃R₃Re(CO)₂Cl (0.02 g, 0.03 mmol) was dissolved in CH₂Cl₂ (10 cm³) and EtAlCl₂ (0.1 cm³ of a 1.8 M solution in toluene, 0.12 mmol) added via syringe. An immediate colour change to deep red occurred. This solution was stirred for 15 min then cooled to 0°C and a solution of norbornene (0.5 g, 5.31 mmol) in CH₂Cl₂ (5 cm³) was added via canula. This was stirred for 1 h and then poured onto vigorously stirred MeOH (100 cm³) to precipitate a yellow or white solid, which was washed with MeOH (3 × 50 cm³) and dried in vacuo (6 h at 0.1 mm).

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**References**