

Manganese and rhenium triphosphorus macrocycle complexes and reactions with alkenes

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The synthesis of Re(III), Re(I) and Mn(I) compounds of the macrocyclic phosphine ligand 1,5,9-trialkyl-1,5,9-triphosphacyclododecane, 12[ane]P₃R₃ (R = Et, ⁱBu) is described. The reaction of 12[ane]P₃R₃ with ReCl₃(PPh₃)₂ (CH₃CN) or ReCl₃(PPhMe₂)₃ gives rise to the octahedral d⁴ complexes (12[ane]P₃R₃)ReCl₃ (**1^R**). Reduction of **1^{iBu}** with Na/Hg under a CO atmosphere gives the rhenium(I) compound (12[ane]P₃R₃)Re(CO)₂Cl, **2^R** which undergoes further reactivity to give hydride (**3^R**), vinylidene (**4^R**) and allenylidene (**5^R**) compounds. With Mn(CO)₅Br, 12[ane]P₃Et₃ gives the octahedral d⁶ complex, (12[ane]P₃Et₃)Mn(CO)₂Br, **6^{Et}**. The crystal structures of (12[ane]P₃ⁱBu₃)ReCl₃ and (12[ane]P₃Et₃)Mn(CO)₂Br are presented.

Introduction

We are interested in the application of multidentate and macrocyclic phosphines due to their ability to form robust metal–ligand units and also potentially control coordination geometry and shape in their metal complexes. The macrocyclic coordination effect does indeed impart substantial robustness in these macrocycle complexes in comparison to analogous acyclic ligand systems and this robustness appears to be a factor leading to catalytic activity for which metal phosphine complexes are typically not well noted. This is exemplified in our recent study¹ of the coordination behaviour of the 12-membered triphosphorus macrocycle, 12[ane]P₃R₃, and its complexes of the early first row transition metal halides of Ti, V, Cr which all show alkene polymerisation activity.^{1b} The coordination properties of these ligands with heavier transition elements has not been investigated in detail, the only reported third row transition metal complex being (12[ane]P₃H₃)W(CO)₃.² The influences these ligands may have upon the reactivity of their complexes may be of significant value, especially in view of their ability to act as facially capping six-electron donors which require remaining ligands to occupy mutually *cis* positions. In view of the catalytic activity of rhenium compounds in alkene metathesis,³ the properties of rhenium complexes of phosphorus macrocycles are of interest. In comparison, the chemistry of manganese-phosphine complexes differs significantly from that of its heaviest congener in a number of respects and we have previously shown that triphosphacyclododecanes are capable of stabilising metal complexes with a range of metals of differing radii.⁴ Consequently, we have chosen to study the coordination properties of these ligands with both manganese and rhenium and in this paper, we report the synthesis of a range of Re(III), Re(I) and Mn(I) compounds. We also report on a study of the reactivity of the Re(I) and Mn(I) compounds towards alkenes and applications in ring opening metathesis polymerisation catalysis. As ruthenium phosphine complexes are also now well established in ROMP catalysis, we compare the reactivity of the new Re and Mn compounds with that of a related ruthenium macrocycle derivative.

Results and discussion

Rhenium(III) complexes

Addition of 12[ane]P₃Et₃ or the bulkier 12[ane]P₃ⁱBu₃ to ReCl₃(PPh₃)₂(MeCN) 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]P₃Bu₃ⁱ gives rise to a dichloromethane soluble green solid (**1^{iBu}**). The same compound can be obtained from *mer*-ReCl₃(PMe₂Ph)₃, albeit in lower yields and in both cases the reaction can be followed by monitoring the decay of free macrocycle and growth of PPh₃ or PMe₂Ph respectively in the ³¹P NMR spectrum. **1^{iBu}** is obtained as an air 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^{iBu}** has been characterised by spectroscopic and analytical methods. The formula (12[ane]P₃ⁱBu₃)ReCl₃ 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 ($\mu_{\text{eff}} = 1.42 \mu_{\text{B}}$) indicating a large spin–orbit coupling and is consistent with d⁴ Re(III).⁵ Sharp, shifted proton NMR spectra are observed which are spread over a +18 to –5 ppm range; the terminal ⁱBu methyl groups, being furthest from the metal are shifted the least ($\delta = 2.8$, methyl protons; $\delta = 8.8$, methine protons), and these can be assigned from the ¹H–¹H 2D spectra which also clearly indicates the diastereotopic nature of the ligand backbone ring protons. Only the ⁱBu methyl groups were observed in the ¹³C NMR spectrum ($\delta = 42$) and no ³¹P NMR signals were observed as might be expected.⁶ Two bands attributable to $\nu(\text{Re–Cl})$ 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^{iBu}** clearly shows two, one-electron reduction waves and one oxidation wave ($E_{1/2(\text{ox})} = +0.46$, $E_{1/2(\text{red})} = -1.15$, -1.60). The standard oxidation potential is quite different to reported data for similar com-

plexes {e.g. for $[\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2]\text{ReCl}_3$, $E_{1/2(\text{ox})} = +0.63$; for $[\text{triphos}]\text{ReCl}_3$, $E_{1/2(\text{ox})} = +0.63$; $\text{PP}_2 = \text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$, $\text{triphos} = \text{MeC}(\text{CH}_2\text{PPh}_2)_3$ }.⁷ This shows that the macrocycle complex is easier to oxidise than the other acyclic phosphine ligand complexes, i.e. the macrocycle stabilises higher oxidation states and implies that the macrocycle is a better electron donor than either the tripodal or acyclic triphosphine ligands (PP_2).

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.⁸ Phosphorus ligand complexes that show a *facial* arrangement include $\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{ReCl}_3$,^{7a} which has been structurally characterised, and the phosphite complex, $\text{ReCl}_3(\text{P}(\text{OEt})_3)_3$, which is assigned a *fac* configuration on the basis of IR and ¹H spectroscopy.⁹ $\text{ReCl}_3(\text{PR}_3)_3$ 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 $\mathbf{1}^{\text{tBu}}$ 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 propanediyl 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 ^tBu group is similarly disordered over two positions. This model is more clearly represented in Fig. 1(b). The overall coordination geometry of $\mathbf{1}^{\text{tBu}}$ 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 ^tBu substituents 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 $(\text{triphos})\text{ReCl}_3$ ^{7a} [Re–P_{av} = 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 $\mathbf{1}^{\text{tBu}}$ are also significantly greater than in the triphos case (84.8, 85.4 and 86.1°) which indicates the lack of flexibility of the triphos ligand in comparison to the macrocycle.

Rhenium(I) complexes

The CV of $\mathbf{1}^{\text{tBu}}$ shows that the 2e[−] reduction to a d⁶, Re(I) state should be readily accessible. Chemical reduction of $\mathbf{1}^{\text{tBu}}$ using two equivalents of sodium amalgam under a CO atmosphere proceeded smoothly to give $12[\text{ane}]\text{P}_3\text{Bu}_3\text{Re}(\text{CO})_2\text{Cl}$, $\mathbf{2}^{\text{tBu}}$, in good yield. The same reaction using $\mathbf{1}^{\text{Et}}$ gives the analogue, $\mathbf{2}^{\text{Et}}$, in comparable yields. The spectroscopic 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 ³¹P NMR spectrum of $\mathbf{2}^{\text{tBu}}$ shows the expected AM₂ pattern (δ −8.72, (t) and −26.43 (d); $J_{\text{AM}} = 19.5$ Hz) which is temperature invariant, and the infrared spectrum shows two bands of equal intensity [$\nu(\text{CO}) = 1930$ and 1865 cm^{−1}] indicating a *cis* configuration of carbonyl ligands. Comparison of $\nu(\text{CO})$ with the reported $(\text{triphos})\text{Re}(\text{CO})_2\text{Cl}$ [$\nu(\text{CO}) = 1948$ and 1887 cm^{−1}]¹¹ shows that the macrocycle is a better electron donor than triphos, and this corroborates the CV evidence from $\mathbf{1}^{\text{tBu}}$. The ¹H NMR spectrum is uninformative since all the macrocycle protons resonate in the same area, except for the methyl groups of the ^tBu chain (δ 0.95). The ¹³C 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

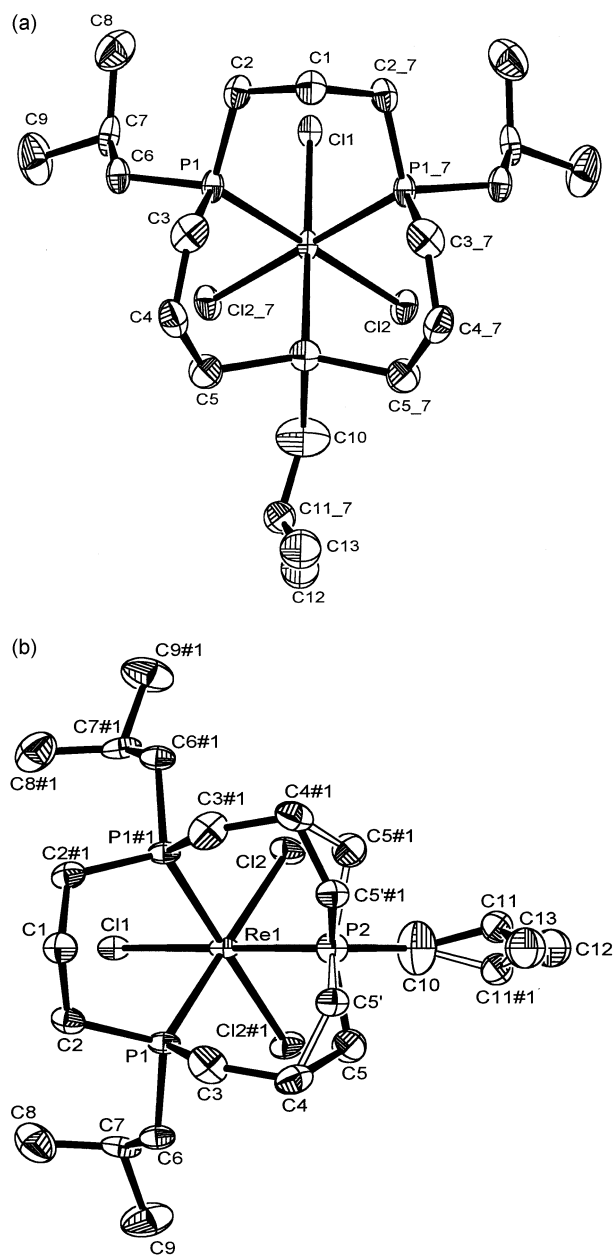
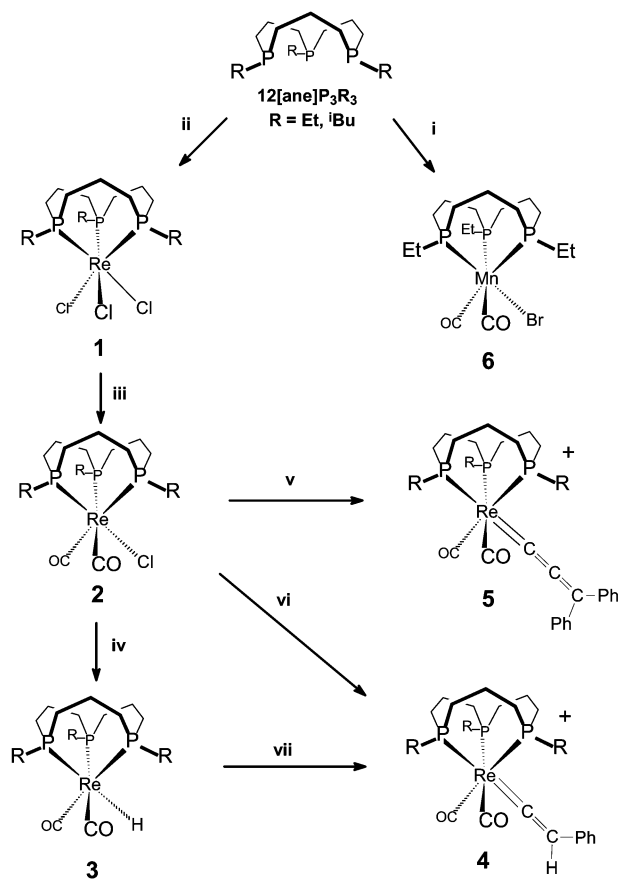


Fig. 1 (a) X-Ray structure of $(12[\text{ane}]\text{P}_3^{\text{tBu}})_3\text{ReCl}_3$, $\mathbf{1}^{\text{tBu}}$, showing the atom labelling scheme. (b) The C4–C5–P2 bridge and the C11 atoms are disordered. Thermal ellipsoids are drawn at 50% probability level. The symmetry $(x, \frac{1}{2} - y, z)$ generates the atoms marked with #1. Selected bond lengths (Å) and angles (°): Re–P1 2.389(2), Re–P2 2.381(3), Re–Cl1 2.411(2), Re–Cl2 2.423(2); P1–Re–P2 91.26(6), P1–Re–P1#1 90.33(8), P1–Re–Cl1 87.84(6), P1–Re–Cl2 178.47(6), P1–Re–Cl2#1 89.12(6), P2–Re–Cl1 178.73(9), P2–Re–Cl2 87.33(6), Cl1–Re–Cl2 93.56(6), Cl2–Re–Cl#1 91.40(8).

magnetically inequivalent, and the one axial phosphine, to give an AXX'Y spin system. This compares well with data for $[(\text{triphos})\text{Re}(\text{CO})_2\text{Cl}]^{11}$ and $(\text{triphos})\text{Ru}(\text{CO})_2\text{Cl}]^{+12}$.

Direct substitution of the carbonyl groups in $\text{Re}(\text{CO})_5\text{Br}$ 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 d⁶ 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 $\text{Re}(\text{CO})_5\text{X}$ (X = halide) compounds by acyclic PP_2 ligands has been studied and reported to be stubborn and to give rise to mixtures of products.¹³ The reaction of phosphines with $\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}$ is known to result in substitution,¹¹ but with the macrocycle $(12[\text{ane}]\text{P}_3^{\text{tBu}})_3$ no reaction was observed over prolonged reaction times in refluxing xylene.



Scheme 1 Reagents and conditions: (i) $\text{Mn}(\text{CO})_5\text{Br}$, CH_2Cl_2 ; (ii) $\text{ReCl}_3(\text{CH}_3\text{CN})(\text{PPh}_3)_2$, CH_2Cl_2 ; (iii) $\text{Na}/\text{Hg}/\text{CO}$, THF; (iv) LiAlH_4 , THF; (v) $\text{CF}_3\text{SO}_3\text{Ag}$, $\text{HC}\equiv\text{CCH}_2\text{C}(\text{OH})\text{Ph}_2$, CH_2Cl_2 ; (vi) $\text{CF}_3\text{SO}_3\text{Ag}$, $\text{HC}\equiv\text{CPh}$, CH_2Cl_2 ; (vii) Me_3OBF_4 , $\text{HC}\equiv\text{CPh}$, CH_2Cl_2 .

Reaction of $2^{i\text{Bu}}$ with LiAlH_4 proceeds under an inert atmosphere to give $12[\text{ane}]P_3^i\text{Bu}_3 \text{Re}(\text{CO})_2\text{H}$, $3^{i\text{Bu}}$, selectively and in good yield. The analogous reaction with the related (triphos)- ReCl_3 , under the same conditions, gives rise to a trihydride,¹⁴ an atmosphere of CO is required for the formation of the dicarbonyl mono-hydride. The IR spectrum of $3^{i\text{Bu}}$ 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 $2^{i\text{Bu}}$ as a result of substitution of chloride by the more electron donating hydride. No bands attributable to $\nu(\text{M}-\text{H})$ were observed, they are presumably masked by the carbonyl absorptions. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at room temperature appears as a broad singlet ($\delta -23.7$) which separates into two peaks at -20°C in a ratio of 1:2; further cooling to -90°C gives rise to two broad singlets ($\delta -19.9, -23.4$). This spectrum is consistent with magnetically inequivalent phosphines in a ratio of 1:2, any P-P coupling being obscured by the line width of the peaks; the broadened ^{31}P NMR spectrum also obscures any fine structure attributable to $^2J_{\text{P-H}}$. The ^1H NMR spectrum at room temperature shows, in addition to resonances due to macrocycle protons, a triplet attributable to the hydride resonance ($\delta -6.76$, $J_{\text{P-H}} = 27.5$ Hz) which is temperature invariant (to -90°C) indicating the absence of phosphine dissociation on the NMR timescale. The analogous (triphos) $\text{Re}(\text{CO})_2\text{H}$ also shows a temperature invariant triplet in the ^1H NMR spectrum, this is explained by a reduced interaction with the *trans* phosphine as a result of structural distortions.¹⁴ The ^{13}C NMR spectrum of $3^{i\text{Bu}}$ is also consistent with the structure proposed, a 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.

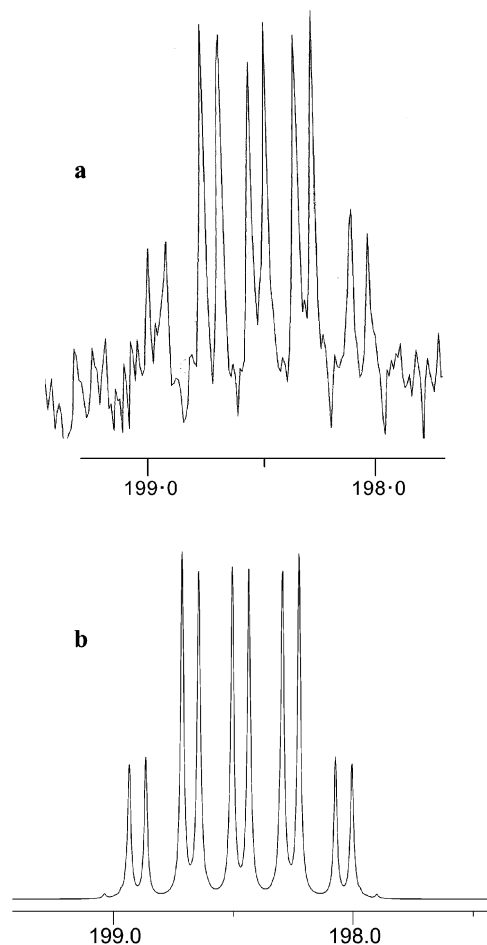


Fig. 2 100 MHz ^{13}C NMR spectrum of $2^{i\text{Bu}}$ in the carbonyl region, scale units are δ . **a**: observed spectrum. **b**: calculated spectrum based on an $\text{AXX}'\text{Y}$ spin system ($\text{A} = ^{13}\text{C}$; $\text{X}, \text{X}', \text{Y} = ^{31}\text{P}$), $J_{\text{AX}}(\text{cis}) = 50.0$ Hz, $J_{\text{AX}'}(\text{trans}) = -8.0$ Hz, $J_{\text{AY}} = 7.0$ Hz, $J_{\text{XX}'} = 32.0$ Hz, $J_{\text{XY}} = J_{\text{X}'\text{Y}} = 0.5$ Hz.

In addition, the formulation is supported by observation of the molecular ion in the mass spectrum which displays the appropriate isotopic distribution.

Rhenium vinylidenes and cumulenes

In view of the activity of compounds containing $\text{Re}=\text{C}$ 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 $2^{i\text{Bu}}$ using silver triflate or trimethylsilyl triflate followed by reaction with a terminal acetylene results in the formation of a vinylidene complex ($4^{i\text{Bu}}$) via a 1,2-hydrogen shift. Alternatively, the reaction of the macrocycle hydride complex $3^{i\text{Bu}}$ with Me_3OBF_4 , 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 $4^{i\text{Bu}}$ shows an increase in $\nu(\text{CO})$ in comparison to compound $3^{i\text{Bu}}$ as might be expected for a cationic complex and the presence of the relatively π -acidic vinylidene ligands;¹⁵ bands attributable to the vinylidene $\text{C}=\text{C}$ function (1649 cm^{-1}) and the OTf^- counterion (1276 cm^{-1}) are also observed. In the ^1H NMR spectrum, the vinylidene proton is split into a quartet ($\delta 4.75$, $^4J_{\text{P-H}} = 7.06$ 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.¹¹ The ^{31}P NMR spectrum of $4^{i\text{Bu}}$ shows an A_2B pattern of a doublet and a triplet ($\delta -38.1, -31.7$ respectively; $^2J_{\text{P-P}} = 28.3$ Hz) indicating magnetically inequivalent phosphorus nuclei in a ratio of

2:1 and that the complex appears stereochemically rigid at ambient temperature under these conditions.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum confirms the presence of a vinylidene ligand (as opposed to a π -alkyne or σ -alkynyl ligand), *i.e.* a resonance attributable to the α -C bonded to Re is observed as a broadened singlet at δ 352.1 reflecting 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 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 ($\text{M}=\text{C}=\text{C}-\text{C}$) compounds have been synthesised in a similar manner to the vinylidene complex, 4^{tBu} , using propargyl alcohols.¹⁶ Addition of silver triflate to a dichloromethane solution of 2^{tBu} followed by $\text{HC}\equiv\text{CC}(\text{OH})\text{Ph}_2$ leads to directly to the unsaturated cumulene complex 5^{tBu} , presumably by the allenylidene intermediate $\{(12[\text{ane}]\text{P}_3^{\text{tBu}})(\text{CO})_2\text{Re}=\text{C}=\text{CHC}(\text{OH})\text{Ph}_2\}$ which eliminates water spontaneously and was not observed. 5^{tBu} was isolated as a yellow solid after work up. The IR spectrum shows absorptions due to $\nu(\text{CO})$ at a lower frequency than observed in 4^{tBu} indicating the cumulene ligand to be a better donor than the vinylidene; bands attributable to the $\text{C}=\text{C}$ function (1894 cm^{-1}) and the OTf^- anion (1278 cm^{-1}) are also observed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum consists of an A_2B pattern of a doublet and a triplet (δ -31.4 , -48.9 respectively; $^2J_{\text{P-P}} = 30.5\text{ Hz}$) indicating stereochemical rigidity. Again the molecular ion is observed in the mass spectrum with the appropriate Re isotope pattern.

Manganese

The manganese bromodicarbonyl analogue of **2** is readily prepared by the white-light photolysis of solutions of $\text{Mn}(\text{CO})_5\text{Br}$ in the presence of the macrocycle, $12[\text{ane}]\text{P}_3\text{Et}_3$ which gives rise to a yellow crystalline solid for which analytical data indicates the formula $(12[\text{ane}]\text{P}_3\text{Et}_3)\text{Mn}(\text{CO})_2\text{Br}$, 6^{Et} . The IR spectrum of 6^{Et} showed two bands corresponding to a *cis*-dicarbonyl unit (1907 , 1847 cm^{-1}). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum consists of a doublet and a triplet (δ 10.5 , 58.6 respectively; $^2J_{\text{P-P}} = 48\text{ Hz}$) corresponding to an A_2B spin system; this spectrum is temperature invariant (30 to $-80\text{ }^\circ\text{C}$) indicating the complex to be stereochemically rigid under these conditions. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, broadened resonances are observed for the macrocycle carbons and a weak and broadened multiplet may be assigned to the carbonyl carbon resonance (δ 194).

The X-ray crystal structure of the manganese compound, 6^{Et} , 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 ($\text{Mn}-\text{P}_{\text{av}} = 2.300(2)\text{ \AA}$, $\text{Mn}-\text{C}_{\text{av}} = 1.807(8)\text{ \AA}$, $\text{Mn}-\text{Br} = 2.569(1)\text{ \AA}$) and deviations from idealised angles ($\text{P}-\text{Mn}-\text{P}_{\text{av}} = 93.81(7)^\circ$, $\text{P}-\text{Mn}-\text{C}_{\text{av}} = 89.4(3)^\circ$, $\text{P}-\text{Mn}-\text{Br}_{\text{av}} = 84.59(6)^\circ$). These values compare closely with those for other manganese bromo-carbonyl phosphine complexes in the literature. For example, in *mer*, *cis*, *cis*- $[\text{MnBr}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2(\text{dppm})]$ the corresponding average bond lengths are very similar ($\text{Mn}-\text{P} = 2.294(2)\text{ \AA}$, $\text{Mn}-\text{C} = 1.78(6)\text{ \AA}$, $\text{Mn}-\text{Br} = 2.527(1)\text{ \AA}$).¹⁷

In 6^{Et} , the $\text{Mn}-\text{P}$ distances *trans* to CO are significantly longer than that *trans* to Br ($2.329(2)$ and $2.243(2)\text{ \AA}$ respectively) indicating a stronger *trans* influence of the π -acidic CO ligands in comparison to Br as is expected.

Reactions with alkenes

Rhenium and manganese

In view of the known activity of rhenium carbonyl halides in alkene metathesis, the reactivity of the phosphorus macrocycle

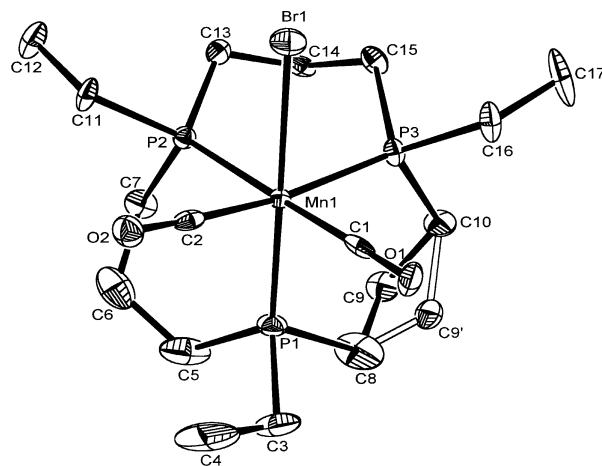


Fig. 3 X-Ray structure of $(12[\text{ane}]\text{P}_3\text{Et}_3)\text{Mn}(\text{CO})_2\text{Br}$, 6^{Et} , showing the atom labelling scheme. One position of the disordered $\text{CH}_2\text{CH}_2\text{CH}_2$ bridge is indicated by open bonds. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths (\AA) and angles ($^\circ$): $\text{Mn}-\text{Br}$ 2.569(1), $\text{Mn}-\text{C}1$ 1.821(8), $\text{Mn}-\text{C}2$ 1.793(7), $\text{Mn}-\text{P}2$ 2.327(2), $\text{Mn}-\text{P}1$ 2.243(2), $\text{Mn}-\text{P}3$ 2.331(2); $\text{C}1-\text{Mn}-\text{C}2$ 91.2(3), $\text{C}1-\text{Mn}-\text{P}2$ 178.2(2), $\text{C}2-\text{Mn}-\text{P}2$ 87.8(2), $\text{C}1-\text{Mn}-\text{P}1$ 87.9(2), $\text{C}2-\text{Mn}-\text{P}1$ 93.8(2), $\text{P}2-\text{Mn}-\text{P}1$ 93.78(6), $\text{C}1-\text{Mn}-\text{P}3$ 88.1(2), $\text{C}2-\text{Mn}-\text{P}3$ 171.1(2), $\text{P}2-\text{Mn}-\text{P}3$ 92.57(7), $\text{P}1-\text{Mn}-\text{P}3$ 95.08(6), $\text{C}1-\text{Mn}-\text{Br}1$ 93.5(2), $\text{C}2-\text{Mn}-\text{Br}1$ 86.8(2), $\text{P}2-\text{Mn}-\text{Br}1$ 84.85(4), $\text{P}1-\text{Mn}-\text{Br}1$ 178.47(6), $\text{P}3-\text{Mn}-\text{Br}1$ 84.32(4).

complexes 2^{R} and 3^{R} 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 $\text{Re}(\text{CO})_5\text{Cl}$ ¹⁸) 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 $0\text{ }^\circ\text{C}$, however for the collection of comparative data and polymer properties, reactions were performed at $25\text{ }^\circ\text{C}$ (Table 1). For both compounds **2** ($\text{R}=\text{Et}$, $^{\text{tBu}}$), a polymeric product is formed by ring opening metathesis polymerisation (ROMP) as indicated by a strong $\text{C}=\text{C}$ stretching frequency in the IR spectrum [$\nu(\text{C}=\text{C}) = 1645\text{ cm}^{-1}$]. The behaviour of the P-alkyl substituents is dramatically influenced by the nature of the P-alkyl substituents. Thus, with 2^{tBu} , a low molecular weight polymer is obtained (also with a relatively narrow polydispersity). For the ethyl derivative, 2^{Et} , 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. Integration of the vinyl protons in the ^1H 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^{tBu} again gives rise to red solutions which show two bands attributable to $\nu(\text{CO})$ (1981 , 1917 cm^{-1}) in the IR spectrum and which are consistent with the presence of *cis* carbonyls. In addition, the reaction of 2^{tBu} 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 rhenium halide followed by α -hydride abstraction, as has been proposed for the metathesis catalyst system derived from WCl_6 and EtAlCl_2 .¹⁹ The vinylidene and cumulene complexes, 4^{tBu} and 5^{tBu} , 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^{Et} , is also active in ROMP under similar conditions. For 6^{Et} , the activity of the catalyst is similar to that of the rhenium analogue (2^{Et}) although the molecular weight of the polymer is very substantially lower. ^{13}C NMR and

Table 1 Polymerisation data for Re, Mn and Ru complexes.

Complex/mmol	Monomer (g)	Initiator	Solvent (temp./°C)	Yield (g, %)	Activity (kg P mol ⁻¹)	<i>M_w</i>	PDI
(12[ane]P ₃ ⁱ Bu ₃)Re(CO) ₂ Cl (2^{iBu}) (0.03)	Norbornene (1.00)	EtAlCl ₂ (4:1)	CH ₂ Cl ₂ (25)	0.875, 87%	11.8	510	1.6
(12[ane]P ₃ Et ₃)Re(CO) ₂ Cl (2^{Et}) (0.015)	Norbornene (0.50)	EtAlCl ₂ (4)	CH ₂ Cl ₂ (25)	0.495, 98%	14.6	217,500	5.1
(12[ane]P ₃ Et ₃)Mn(CO) ₂ Br (6^{Et}) (0.02)	Norbornene (0.50)	EtAlCl ₂ (4:1)	CH ₂ Cl ₂ (25)	0.30, 60%	12.6	3710	2.9
(12[ane]P ₃ Et ₃)-RuCl ₂ dmsO (0.035)	Norbornene (0.55)	EtAlCl ₂ (4:1)	CH ₂ Cl ₂ (25)	0.137, 25%	13.2	10,400	6.4
(12[ane]P ₃ Et ₃)-RuCl ₂ dmsO (0.09)	Norbornadiene (1.0)	EtAlCl ₂ (4:1)	CH ₂ Cl ₂ (25)	0.871, 87%	9.67	188,000	67
(12[ane]P ₃ Et ₃)RuCl ₂ dmsO (0.072)	Norbornene (0.50)	TMSCHN ₂ /AgOTf (2)	C ₆ H ₅ Cl (120)	0.12, 24%	1.67	56 300	2.3

¹H NMR data imply the polymer to be atactic with respect to the double bond geometry. To our knowledge, this is the first example of a manganese compound active in ROMP catalysis. Also of interest are comparisons of the product polymer complexes and activity of the catalysts between ligands of different bulk and metals of different sizes; thus, the combination of the least sterically demanding macrocycle and the largest metal gives rise to the most active catalyst and the highest molecular weight polymer. Clearly steric factors radically influence the catalytic behaviour, higher molecular weight products being favoured by a more open and easily accessible metal centre.

Ruthenium

The well known Grubbs' catalyst, Cl₂Ru(=CHPh)(PR₃)₂, has been extensively studied and modified, for example replacing the phosphines with N-heterocyclic carbenes,²⁰ or changing the benzylidene for a vinylidene²¹ or allenylidene²² moiety. The original Ru(II) complex has a trigonal bipyramidal structure and the more basic PCy₃ phosphine is more active than PPh₃. It is of interest to compare the behaviour of the known catalytically active complexes with that of the d⁶ octahedral Ru(II) macrocycle compound, (12[ane]P₃Et₃)RuCl₂(dmsO), **7^{Et}**.^{4a} Addition of EtAlCl₂ to solutions of **7^{Et}** in CH₂Cl₂ causes a colour change from yellow to orange, subsequent addition of norbornene results in a further colour change to red and the solutions very quickly became viscous as poly(vinylcyclopentene) is formed. This activity is similar to that of the rhenium and manganese complexes; the yield decreases with increasing temperature and **7^{Et}** is inactive in the absence of the initiator. Using trimethylsilyldiazomethane and silver triflate as the initiator, no reaction was observed with norbornene in CH₂Cl₂ but in refluxing chlorobenzene a polymer was formed. Presumably the methyl-substituted carbene is thermally more sensitive than the trimethylsilyl substituted carbene formed from trimethylsilyldiazomethane. The polymers produced by the two routes were also different in their physical properties. The catalyst formed by initiation with EtAlCl₂ gives a polymer which is soluble in chloroform and has a relatively low molecular weight and high polydispersity, the catalyst formed by initiation with trimethylsilyldiazomethane and silver triflate has a lower activity and the polymer formed is insoluble in chloroform (GPC analysis was performed by dissolution in boiling 1,2-dichlorobenzene) but it has a significantly higher molecular weight and narrower polydispersity. The ¹³C NMR spectrum of this latter polymer product shows a bias towards *trans-trans* stereochemistry.

There have been other studies using tridentate donors in the coordination sphere of Grubbs' catalyst. Using the Tp ligand gives the complex Tp(PCy₃)(Cl)Ru=CHPh which is inactive for alkene metathesis.²³ The authors explain this lack of activity by the inability of any ligand to dissociate and form a vacant site; however the complex Tp(Cl)(PPh₃)Ru=C=CHPh is active under similar conditions and gives high yields of polymer (99%, *M_n* = 5.9 × 10⁴, PDI = 5.0) although relatively slowly (72 h at 40 °C).²⁴ The macrocycle 9[ane]S₃ has also been used in ROMP reactions. The compound 9[ane]S₃Ru(=CHPh)(PCy₃)Cl⁺ does ring-open norbornene giving rise to good yields of polymer after 2 h at

room temperature (92%, *M_n* = 2.7 × 10⁵, 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 **1^{Et}** 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 site²⁶ which helps explain the high activities observed with bulky phosphines. A recent report using the chelating dtbpm ligand (dtbpm = ^tBu₂PCH₂P^tBu₂) also shows high activities in the ring opening of cycloalkenes,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 carbene 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 **7^{Et}** as there is a temperature invariant (to -60 °C) singlet in the ³¹P{¹H} NMR spectrum; this behaviour being previously commented on^{4a} 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 phosphine ligands. The complex has 18 electrons so an associative mechanism is unlikely and free dmsO was observed by ¹H and 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 carbene in the ¹H NMR spectrum was not observed (as in other examples),²⁹ neither was the formation of a metallacycle on addition of one equivalent of monomer.

Experimental

All reactions were carried out in an atmosphere of dry nitrogen or argon passed through a CrO (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]P₃Et₃,³⁰ **7^{Et}**,^{4a} ReCl₃(MeCN)(PPh₃)₃,³¹ Re(CO)₅Br,³² Re(CO)₃(PPh₃)₂Cl,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 recrystallised. 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 Lamda Eclipse 300 at 121.65 MHz (³¹P), 300.52 MHz (¹H) and 75.57 MHz (¹³C), or a Bruker AMX-360

at 145.78 MHz (^{31}P). All chemical shifts are quoted in units of δ (ppm). ^1H and ^{13}C NMR chemical shifts are relative to solvent resonances, ^{31}P chemical shifts are relative to 85% external H_3PO_4 ($\delta = 0$). For ^{13}C assignments see Fig. 2. Magnetic susceptibilities were determined by Evans' method³⁴ or by the Gouy method on a Johnson Matthey magnetic susceptibility balance; an experimental diamagnetic correction was measured for $12[\text{ane}]_3\text{P}_3\text{R}_3$ 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.³⁵ Molecular weight determinations were carried out in chloroform or 1,2-dichlorobenzene solution by RAPRA Technologies Ltd. using a PLgel $2 \times$ mixed bed-D, 30 cm, 5 μm column at 40 $^\circ\text{C}$ 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 CH_2Cl_2 with Bu_4NPF_6 (0.1 M) supporting electrolyte vs. a Ag/Ag^+ reference electrode and Fc/Fc^+ internal reference (0.46 vs. SCE); data were processed on a PC operating an Autolab program. The labelling scheme for NMR assignments for compounds **2^R**, **3^{Bu}**, **4^{Bu}**, and **5^{Bu}** is defined in Fig. 4.

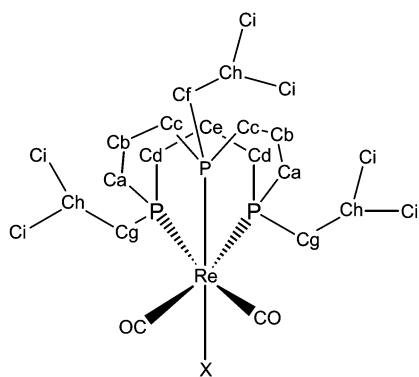


Fig. 4 Labelling scheme for NMR assignments for Re(I) compounds.

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^{Bu}**, Re) and a FAST area detector (compound **6**, Mn) by using monochromated Mo-K α radiation ($\lambda = 0.71073$ \AA) and following previously described procedures.³⁶ The data sets were corrected for absorption effects using SORTAV³⁷ and DIFABS³⁸ for compounds **1^{Bu}** and **6**, respectively.

The structures were solved by direct methods (SHELXS-97)³⁹ and refined by full-matrix least squares (SHELX-97)⁴⁰ on F^2 using all unique data. The Re(1), Cl(1), C(10), C(12) and C(13) atoms of the $-\text{CH}_2\text{CHMe}_2$ group on P(2) in compound **1^{Bu}** 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)(CH_2)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 \AA , respectively. In compound **6**, the P(1)(CH_2)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 $-\text{CH}_2\text{CHMe}_2$ group in **1^{Bu}** 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[ane]P₃ⁱBu₃ReCl₃, **1^{Bu}**

To $\text{ReCl}_3(\text{MeCN})(\text{PPh}_3)_2$ (0.066 g, 0.77 mmol) dissolved in CH_2Cl_2 (10 cm^3) was added $12[\text{ane}]_3\text{P}_3\text{Bu}_3$ (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 ($5 \times 30 \text{ cm}^3$). The green powder was redissolved in CH_2Cl_2 (3 cm^3) and light petroleum (5 cm^3) added. After cooling to -30 $^\circ\text{C}$ 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 CD_2Cl_2 solution (Found: C, 36.4; H, 6.35. $\text{C}_{21}\text{H}_{45}\text{Cl}_3\text{P}_3\text{Re}$ requires: C, 36.93; H, 6.64%). ^1H NMR (CD_2Cl_2): δ 18.1 (br, 3H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$); 9.3 (m, 3H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$); 8.8 (br, 3H, $\text{PCH}_2\text{CH}(\text{CH}_3)_2$); 4.75 (br, 6H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$); 2.8 (d, $^2J_{\text{HH}} = 7$ Hz, 18H, $\text{PCH}_2\text{CH}(\text{CH}_3)_2$); -1.1 (m, 6H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$); -4.2 (m, 6H, $\text{PCH}_2\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (CD_2Cl_2): δ 42.0 ($\text{PCH}_2\text{CH}(\text{CH}_3)_2$). IR (CsI disk, cm^{-1}): 2959 (s), 1482 (s), 1434 (s), 1363 (m), 1261 (m), 1187 (w), 1162 (m), 1092 (s), 1068 (m), 1026 (m), 801 (m), 746 (sh), 696 (sh), 519 (sh), 497 (m), 461 (s), 347 (w), 308 (m). $\mu_{\text{eff}} = 1.42 \mu_{\text{B}}$. MS (APCI): 681.1 (M^+ , correct isotope distribution for $^{185/187}\text{Re}$ and $^{35/37}\text{Cl}$), 647.65 ($\text{M} - \text{Cl}$), 612.2 ($\text{M}^+ - 2\text{Cl}$).

12[ane]P₃ⁱBu₃Re(CO)₂Cl, **2^{Bu}**

To sodium amalgam (0.007 g Na, 0.31 mmol) suspended in THF (25 cm^3) was added **1^{Bu}** (0.096 g, 0.15 mmol) as a solid. The N_2 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 cm^3 and diluted with light petroleum (3 cm^3). On cooling to -30 $^\circ\text{C}$ a yellow powder was obtained which was washed with light petroleum ($2 \times 5 \text{ cm}^3$) and dried *in vacuo*. Yield, 0.099 g (96%) (Found: C, 40.9; H, 6.55. $\text{C}_{23}\text{H}_{45}\text{O}_2\text{ClP}_3\text{Re}$ requires: C, 41.34; H, 6.79%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -8.72 (t), -26.43 (d, $J_{\text{P-P}} = 19.5$ Hz). ^1H NMR (CD_2Cl_2): δ 0.95 (m, 18 H, $\text{CH}(\text{CH}_3)_2$); 1.5–2.3 (m, 27 H, $\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}$, $\text{PCH}_2\text{CH}_2\text{P}$, $\text{PCH}_2\text{CH}(\text{CH}_3)_2$, $\text{PCH}_2\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (CD_2Cl_2): δ 19.84 (s, C_d); 20.73 (s, C_b); 22.27 (t, $^1J_{\text{PC}} = 13.5$ Hz, C_d); 23.74 (s, C_i); 24.47 (d, $^2J_{\text{PC}} = 4$ Hz, C_b); 25.94 (t, $^1J_{\text{PC}} = 11.5$ Hz, C_a, C_d); 29.83 (d, $^1J_{\text{PC}} = 29$ Hz, C_g); 36.39 (t, $^1J_{\text{PC}} = 14$ Hz, C_c); 45.10 (d, $^1J_{\text{PC}} = 35$ Hz, C_f); 198.2 (m, AX $\text{X}'\text{Y}$ spin system $J_{\text{AX}} = 50.0$ Hz, $J_{\text{AX}'} = -8.0$ Hz, $J_{\text{AY}} = 7.0$ Hz, $J_{\text{XX}'} = 32.0$, $J_{\text{XY}} = J_{\text{X}'\text{Y}} = 0.5$ Hz). IR (THF soln., cm^{-1}): $\nu(\text{CO})$ 1930 (s), 1865 (s). MS (APCI): 632.1 (M^+ , correct isotope distribution for $^{185/187}\text{Re}$), 568.1 ($\text{M} - 2\text{CO}$).

12[ane]P₃Et₃Re(CO)₂Cl, **2^{Et}**

Addition of $12[\text{ane}]_3\text{P}_3\text{Et}_3$ to $\text{ReCl}_3(\text{MeCN})(\text{PPh}_3)_2$ followed by refluxing for 3 h in a manner identical to the synthesis of **1^{Bu}** 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 **1^{Bu}**, although it was not further characterised. The green solid isolated by filtration, washed with CH_2Cl_2 ($3 \times 5 \text{ cm}^3$) and dried *in vacuo*. ($\mu_{\text{eff}} = 1.54 \mu_{\text{B}}$). The subsequent preparation and work-up of **2^{Et}** was continued in a manner identical to that of **2^{Bu}**. The yellow product was isolated in 65% overall yield [based on $\text{ReCl}_3(\text{MeCN})(\text{PPh}_3)_2$] (Found: C, 35.3; H, 5.84. $\text{C}_{17}\text{H}_{33}\text{O}_2\text{ClP}_3\text{Re}$ requires: C, 34.96; H, 5.70%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -8.09 (t), -25.39 (d, $J_{\text{PP}} =$

Table 2 Crystallographic data for 12[ane]P₃ⁱBu₃ReCl₃, **1ⁱBu** and 12[ane]P₃Et₃Mn(CO)₂Br, **6^{Et}**

Complex	1ⁱBu	6^{Et}
Empirical formula	C ₂₁ H ₄₅ Cl ₃ P ₃ Re	C ₁₇ H ₃₃ BrMnO ₂ P ₃
Formula weight	683.03	497.19
Temperature/K	150(2)	150(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i>	<i>P2₁2₁2₁</i>
Unit cell dimensions/Å	<i>a</i> = 14.409(3) <i>b</i> = 15.947(3) <i>c</i> = 11.737(2)	<i>a</i> = 7.962(2) <i>b</i> = 15.473(3) <i>c</i> = 17.228(3)
Volume/Å ³	2696.9(9)	2122.4(8)
<i>Z</i>	4	4
<i>D_c</i> /Mg m ⁻³	1.682	1.556
Absorption coefficient/mm ⁻¹	4.988	2.739
<i>F</i> (000)	1368	1024
Crystal size/mm	0.25 × 0.20 × 0.20	0.18 × 0.15 × 0.12
θ Range (data collection)/°	2.24–25.35	1.77–24.90
Index ranges	−17 ≤ <i>h</i> < 0, −19 ≤ <i>k</i> ≤ 0, −14 ≤ <i>l</i> ≤ 14	−9 ≤ <i>h</i> ≤ 8, −14 ≤ <i>k</i> ≤ 17, −17 ≤ <i>l</i> ≤ 20
Reflections collected	9845	9181
Independent reflections	2556 [<i>R</i> (int) = 0.2675]	3279 [<i>R</i> (int) = 0.0928]
Max. and min. transmission	0.4353 and 0.3686	0.7346 and 0.6385
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2556/8/151	3279/18/230
Goodness-of-fit on <i>F</i> ²	1.004	1.006
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0641, <i>wR</i> 2 = 0.1492	<i>R</i> 1 = 0.0360, <i>wR</i> 2 = 0.0831
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0677, <i>wR</i> 2 = 0.1508	<i>R</i> 1 = 0.0430, <i>wR</i> 2 = 0.0841
Largest diff. peak and hole/e Å ⁻³	4.555 and −4.258	0.409 and −0.465

20.7 Hz). ¹H NMR (CD₂Cl₂): δ 1.5–2.3 (m, 33H, PCH₂CH₂-CH₂P, PCH₂CH₂CH₂P, PCH₂CH₃, PCH₂CH₃). ¹³C NMR (CD₂Cl₂): δ 19.91 (s, C_e); 21.04 (s, C_b); 23.01 (s, C_i); 25.21 (d, ²*J*_{PC} = 4 Hz, C_h); 29.91 (d, ¹*J*_{PC} = 29 Hz, C_g); 46.80 (d, ¹*J*_{PC} = 35 Hz, C_g); 36.42 (t, ¹*J*_{PC} = 14 Hz, C); 27.12 (t, ¹*J*_{PC} = 11.5 Hz, C); 22.86 (t, ¹*J*_{PC} = 13.5 Hz, C); 198.5 (m, CO). IR (THF soln., cm⁻¹): ν(CO) 1926 (s), 1860 (s).

12[ane]P₃ⁱBu₃Re(CO)₂H, **3ⁱBu**, **2ⁱBu**

(0.17 g, 0.02 mmol) was dissolved in THF (20 cm³) and cooled to 0 °C and LiAlH₄ (0.12 g, 3.16 mmol) 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 ~5 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. C₂₃H₄₆O₂P₃Re requires: C, 43.59; H, 7.32%). ³¹P{¹H} NMR (CD₂Cl₂): δ −23.69 (br s). ¹H NMR (CD₂Cl₂): δ −6.76 (t, ²*J*_{PH} = 27.5 Hz, 1H, ReH); 0.70 (m, 18 H, CH₂CH(CH₃)₂), 1.2–2.3 (m, 27 H, PCH₂CH₂CH₂P, PCH₂CH₂CH₂P, PCH₂CH(CH₃)₂, PCH₂CH(CH₃)₂). ¹³C NMR (CD₂Cl₂): δ 19.82 (s, C_e); 20.72 (s, C_b); 23.72 (t, ¹*J*_{PC} = 13 Hz, C_d); 24.18 (s, C_i); 24.70 (d, ¹*J*_{PC} = 4 Hz, C_h); 28.63 (t, ¹*J*_{PC} = 10 Hz, C_a, C_d); 30.05 (d, ¹*J*_{PC} = 31 Hz, C_g); 36.21 (t, ¹*J*_{PC} = 12 Hz, C_e); 45.28 (d, ¹*J*_{PC} = 35 Hz, C_f); 198.4 (m, CO). IR (THF soln., cm⁻¹): ν(CO) 1910 (s), 1845 (s). MS (APCI): 587.6 (M⁺, correct isotope distribution for ^{185/187}Re), 533.6 (M − 2CO).

[12[ane]P₃ⁱBu₃Re(=C=CHPh)(CO)₂]⁺(BF₄)[−], **4ⁱBu**

Method 1. To a solution of **3ⁱBu** (0.15 g, 0.25 mmol) in CH₂Cl₂ (20 cm³) at −78 °C was added Me₃OBF₄ (0.038 g, 0.25 mmol) and this was allowed to warm to 0 °C with stirring to give an orange solution. This was stirred for 10 min, re-cooled to −78 °C and phenylacetylene (0.07 g, 0.76 mmol) added. On warming to room temperature, the solution became deep red and was stirred for 2 h, followed by concentration under reduced pressure to ~3 cm³ and addition of light petroleum (10 cm³) to precipitate a red powder. This was isolated by filtration and dried *in vacuo*. Yield, 0.15 g (76%) (Found: C, 45.7; H, 6.42. C₃₁H₅₁BO₂F₄P₃Re requires: C, 45.32; H, 6.26%).

Method 2. To a solution of **2ⁱBu** (0.20 g, 0.32 mmol) in CH₂Cl₂ (20 cm³) was added silver triflate (0.081 g, 0.32 mmol) followed by phenylacetylene (0.10 g, 0.95 mmol). This was stirred for 2 h and the resultant red solution worked up as above. Yield, 0.22 g (81%). ³¹P NMR (CD₂Cl₂): δ −38.1 (d, ²*J*_{PP} = 28.3 Hz), −31.7 (t, ²*J*_{PP} = 28.3 Hz). ¹H NMR (CD₂Cl₂): δ 7.6 (d, ³*J*_{HH} = 6.04 Hz), 7.25 (m), 6.95 (d, ³*J*_{HH} = 7.34 Hz, 5 H, Re=C=CHPh); 4.75 (q, ⁴*J*_{P-H} = 7.06 Hz, 1H, Re=C=CHPh); 0.95 (m, 18 H, CH(CH₃)₂), 1.05–2.2 (m, 27 H, PCH₂CH₂CH₂P, PCH₂CH₂CH₂P, PCH₂-CH(CH₃)₂, PCH₂CH(CH₃)₂). ¹³C NMR (CD₂Cl₂): δ 19.82 (s, C_e); 20.72 (s, C_b); 23.72 (t, ¹*J*_{PC} = 13 Hz, C_d); 24.18 (s, C_i); 24.70 (d, ¹*J*_{PC} = 4 Hz, C_h); 28.63 (t, ¹*J*_{PC} = 10 Hz, C_a, C_d); 30.05 (d, ¹*J*_{PC} = 31 Hz, C_g); 36.21 (t, ¹*J*_{PC} = 12 Hz, C_e); 45.28 (d, ¹*J*_{PC} = 35 Hz, C_f); 125.2, 127.6, 128.1, 128.2 (Ar); 131.2 (s, Re=C=CHPh); 352.1 (br s, Re=C=CHPh). IR (KBr disc cm⁻¹): ν(CO) 2000, 1937; ν(CC) 1649, ν(SO) 1276. MS (APCI): 699.8 (M⁺, correct isotope distribution for ^{185/187}Re), 635.8 (M − 2CO).

[12[ane]P₃ⁱBu₃Re(=C=C=CPh₂)(CO)₂]⁺(CF₃SO₃)[−], **5ⁱBu**

To a cold (0 °C) solution of **2ⁱBu** (0.09 g, 0.14 mmol) in CH₂Cl₂ (10 cm³) was added AgOTf (0.036 g, 0.14 mmol). After warming to room temperature the mixture was stirred for 10 min then re-cooled to 0 °C. Propargyl alcohol (0.035 g, 0.17 mmol) was then added as a solid and this 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 ~2 cm³ 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. C₃₉H₆₀O₅F₃SP₃Re requires: C, 47.94; H, 6.19%). ³¹P{¹H} NMR (CD₂Cl₂): δ −48.91 (t), −31.45 (d) *J*_{PP} = 30.46 Hz. ¹H NMR (CD₂Cl₂): δ 7.6–7.0 (m, 10 H, C=CPh₂), 0.70 (m, 18 H, CH(CH₃)₂), 1.1–2.3 (m, 27 H, PCH₂CH₂CH₂P, PCH₂CH₂CH₂P, PCH₂CH(CH₃)₂, PCH₂CH(CH₃)₂). ¹³C NMR (CD₂Cl₂): δ 19.82 (s, C_e); 21.31 (s, C_b); 24.81 (t, ¹*J*_{PC} = 13 Hz, C_d); 24.42 (s, C_i); 25.02 (d, ¹*J*_{PC} = 4 Hz, C_h); 28.84 (t, ¹*J*_{PC} = 10 Hz, C_a, C_d); 31.07 (d, ¹*J*_{PC} = 31 Hz, C_g); 36.48 (t, ¹*J*_{PC} = 12 Hz, C_e); 45.42 (d, ¹*J*_{PC} = 35 Hz, C_f); 125.8, 126.9, 128.8, 129.1 (Ar); 248.7 (s, Re=C=C=C); 133.05 (s, Re=C=C=C). IR (KBr disc, cm⁻¹): ν(SO) 1278. MS (APCI): 787.9 (M⁺, correct isotope distribution for ^{185/187}Re), 723.9 (M − 2CO).

12[ane]P₃Et₃Mn(CO)₂Br, 6^{Et}

To a solution of 12[ane]P₃Et₃ (0.13 g, 0.42 mmol) in Et₂O (25 cm³) was added Mn(CO)₅Br (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 -30 °C overnight 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. C₁₇H₃₃O₂BrP₃Mn requires: C, 41.07; H, 6.69%). ³¹P{¹H} NMR (CDCl₃): δ 10.5 (t), 58.6 (d, J_{PP} = 50 Hz). ¹H NMR (CDCl₃): δ 1.03 (br s, 9H, PCH₂CH₃); 1.28 (br s, 2H, PCH₂CH₂CH₂); 1.47 (br s, 6H, PCH₂CH₃); 1.63 (br s, 4H, PCH₂CH₂CH₂); 1.79 (br s, 2H, PCH₂CH₂CH₂); 1.92 (br s, 6H, PCH₂CH₂CH₂); 2.08 (br s, 2H, PCH₂CH₂CH₂); 2.3 (br s, 2H, PCH₂CH₂CH₂). IR (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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