

Syntheses and redox properties of the first phosphirene–dinitrogen and phosphirene–diazenide complexes

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The first mixed phosphirene–dinitrogen and phosphirene–diazenide complexes $mer\text{-}[\text{ReCl}(\text{N}_2)(\overline{\text{PPhCPh}=\text{CPh}})\text{L}_3]$ ($\text{L} = \text{PMe}_2\text{Ph}$ **1a** or PMePh_2 **1b**) and $[\text{ReBr}(\text{NNPh})_2(\overline{\text{PPhCPh}=\text{CPh}})_2(\text{PPh}_3)_2]$ **2** have been prepared by treatment of the corresponding thf solutions of $trans\text{-}[\text{ReCl}(\text{N}_2)\text{L}_4]$ or $[\text{ReBr}_3(\text{NNPh})(\text{PPh}_3)_2]$ with $\overline{\text{PPhCPh}=\text{CPh}}$. Their redox properties have been investigated by cyclic voltammetry in an aprotic medium, at a platinum electrode, and the electrochemical E_L and P_L parameters estimated for the phosphirene ligand indicating that its overall electron donor/acceptor properties are similar to those of PMePh_2 .

Introduction

The chemistry of phosphirene and phosphirane ring systems has been reviewed^{1,2} and also more recently discussed with other phosphorus containing heterocycles.³ The phosphirene ring is characterised by a significant positive charge at phosphorus and two bent intracyclic P–C bonds corresponding to the bonding combination of π (phosphinidene) and π^* alkyne orbitals. A transition metal–ligand fragment can either coordinate to the phosphorus lone-pair electrons or insert into one of the P–C bonds via a transient $\eta^2\text{-}(\text{P}-\text{C})$ complex. Several complexes have been synthesised directly in the co-ordination sphere of metals or made from the preformed heterocycle.^{4–7} Interestingly palladium catalysed alkyne insertions of phosphirenes ligated to $[\text{W}(\text{CO})_5]$ ^{8,9} are known and CO can also be incorporated into the ring of phosphirene complexes¹⁰ at high temperature. These reactions no doubt involve transient four-membered metallacycles and in support of this several 14-electron fragments of the type ML_2 ($\text{M} = \text{Ni}$ or Pt) readily react with the P–C bonds of phosphirenes and phosphiranes,^{11–14} and subsequently with CO under mild conditions.

In spite of this rich co-ordination chemistry, the electron σ -donor and π -acceptor characters of the phosphirenes have not yet been investigated in detail. In addition, mixed complexes of phosphirenes with dinitrogen (N_2) or potentially derived ligands, such as diazenides (NNR), have not been reported to date although organophosphine complexes with such nitrogen ligands are widely known^{15,16} and present a versatile chemistry which is of current and growing interest.

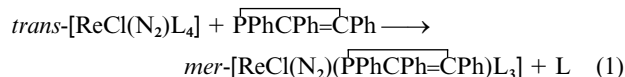
In attempting to address these points, we have investigated the reactivity of triphenylphosphirene $\overline{\text{PPhCPh}=\text{CPh}}$, with the dinitrogen and the phenyldiazenide complexes $trans\text{-}[\text{ReCl}(\text{N}_2)\text{L}_4]$ ($\text{L} = \text{PMe}_2\text{Ph}$ or PMePh_2) and $[\text{ReBr}_3(\text{NNPh})(\text{PPh}_3)_2]$, respectively, since these types of complexes are particularly promising synthetic starting materials in co-ordination chemistry of nitrogen ligands.^{15–19} We have obtained from these reactions the first dinitrogen and diazenide complexes with a phosphirene co-ligand, $mer\text{-}[\text{ReCl}(\text{N}_2)(\overline{\text{PPhCPh}=\text{CPh}})\text{L}_3]$ ($\text{L} = \text{PMe}_2\text{Ph}$ **1a** or PMePh_2 **1b**) and $[\text{ReBr}(\text{NNPh})_2(\overline{\text{PPhCPh}=\text{CPh}})_2(\text{PPh}_3)_2]$ **2**, respectively and have investigated their redox behaviour which allowed us to quantify the net electron donor/acceptor ability of the triphenylphosphirene

ligand by estimating, for the first time, its electrochemical E_L and P_L ligand parameters.

Results and discussion

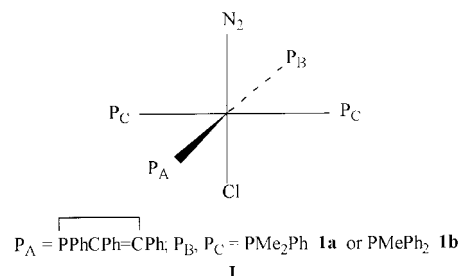
Chemical studies

Treatment of a thf solution of $trans\text{-}[\text{ReCl}(\text{N}_2)\text{L}_4]$ ($\text{L} = \text{PMe}_2\text{Ph}$ or PMePh_2) with $\overline{\text{PPhCPh}=\text{CPh}}$, in a stoichiometric amount, for ca. 2–3 d, leads to the formation of the corresponding mixed dinitrogen–phosphirene complexes $mer\text{-}[\text{ReCl}(\text{N}_2)(\overline{\text{PPhCPh}=\text{CPh}})\text{L}_3]$ ($\text{L} = \text{PMe}_2\text{Ph}$ **1a** or PMePh_2 **1b**) via replacement of one of the phosphine ligands by the phosphirene, eqn. (1). Although N_2 is often the most labile ligand



in transition metal dinitrogen complexes, in this reaction it is retained as was observed previously by us^{17a} in the formation of $mer\text{-}[\text{ReCl}(\text{N}_2)(\text{CNMe})(\text{PMe}_2\text{Ph})_3]$ on treatment of $trans\text{-}[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ with CNMe .

Complexes **1a** and **1b** were isolated (ca. 40–50% yields) as a pale orange or a dark yellow solid, respectively, having strong IR bands readily assigned to $\nu(\text{N}=\text{N})$ at 1944–1930 cm^{-1} , lying within the range of frequencies (1950–1920 cm^{-1}) displayed by other N_2 complexes of related electron-rich rhenium centres, typified by $mer\text{-}[\text{ReCl}(\text{N}_2)(\text{CNMe})(\text{PMe}_2\text{Ph})_3]$ ^{17a} or $mer\text{-}[\text{Re}(\text{S}_2\text{PPh}_2)(\text{N}_2)(\text{PMe}_2\text{Ph})_3]$,²⁰ in which N_2 is *trans* to a strong electron-donor anionic co-ligand and behaves as an effective π -electron acceptor. This is also a feature of our complexes **1a** and **1b** (see below) which accounts for the



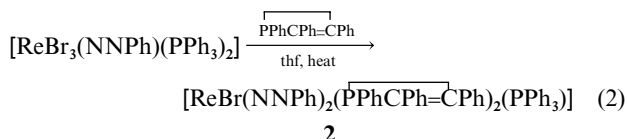
stabilization of their Re–N₂ bond which is preserved during the reaction.

The meridional arrangement of the phosphines (P_B and P_C) in complex **1**, with the phosphirene ligand (P_A) *trans* to one of them (P_B) (see **I**), implies that the N₂ and the Cl ligands are mutually *trans* and is clearly indicated by the [ABC₂] patterns exhibited by their ³¹P-¹H NMR spectra.

The phosphirene-³¹P resonance (P_A at δ –119.71 **1a** or –131.10 **1b** relative to H₃PO₄) occurs at a lower field than that observed for the “free” ligand (δ –186.37) and lies within the expected range^{5,6} for terminal phosphorus-co-ordination without cleavage of the ring (a shift to a much lower field should occur⁶ for ring opening). The fine structure for complex **1a** consists of a doublet [²J(P_AP_B) = 253.8 Hz] of broad triplets [²J(P_AP_C) = 24 Hz], in agreement with the patterns observed for the *trans*-phosphine [P_B at δ –28.54 as a doublet, ²J(P_BP_A) = 253.1, of triplets, ²J(P_BP_C) = 17.5 Hz] and the *cis*-phosphines [P_C at δ –28.39 as a triplet, ²J(P_CP_B) ≈ ²J(P_CP_A) ≈ 22 Hz]. A more simplified ³¹P-¹H NMR pattern is observed for **1b** (in CDCl₃) in view of the lack of resolution of the *cis* couplings: P_A and P_B appear simply as doublets [²J(P_AP_B) ≈ 240 Hz] (the latter at δ –30.83), whereas 2P_C resonate as a broad singlet at δ –26.70.

The ¹H NMR spectrum of complex **1a** is also consistent with the meridional arrangement of the phosphines, since the resonance of the methyl protons of the unique phosphine P_B(CH₃)₂Ph is a doublet [²J(HP_B) = 7.6 Hz] at δ 1.26, whereas the resonance of the two *trans* P_C(CH₃)₂Ph phosphines occurs as two triplets (at δ 1.66 and 1.62), each of them as a result of virtual coupling to the two P_C nuclei [³J²J(HP_C) + ⁴J(HP_C)] ≈ 2.9 Hz]. Such a type of resonance pattern associated with the meridional arrangement of PMe₂Ph ligands has been recognized^{17a,21} for other complexes.

The phenyldiazene complex [ReBr₃(NNPh)(PPh₃)₂] also reacts with the phosphirene, in refluxing thf for 2 d, leading to the formation of the orange complex [ReBr(NNPh)₂(PPhCPh=CPh)₂(PPh₃)₂] **2**, eqn. (2), which precipitated (*ca.* 20%



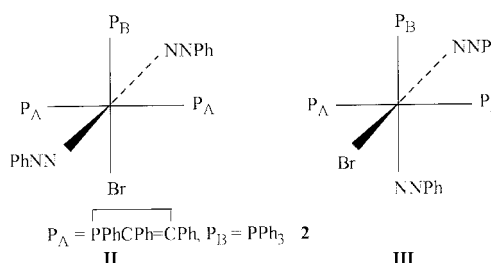
yield) as the first product on concentration of the solution and addition of pentane. From the mother-liquor it was possible to isolate (in *ca.* the same yield) another product, already identified¹⁹ as [ReBr₂(NNPh)₂(PPh₃)₂], which does not contain any phosphirene ligand.

The formation of these products is unexpected, involving the formal replacement of a bromide by a diazenide ligand and, in the case of **2**, also metal reduction (possibly by PPh₃ producing Ph₃PBr₂) and further displacement of bromide and phosphine by phosphirene. The mechanisms for these conversions are unknown, but they conceivably occur *via* the formation of bromide and diazenide bridges between two metal centres. The starting diazenide complex [ReBr₃(NNPh)(PPh₃)₂] is known¹⁹ to undergo reduction reactions with isocyanides to form products of the type [ReBr₂(NNPh)(CNR)(PPh₃)₂] (R = Me or C₆H₄Cl-4), [ReBr₂(NNPh)(CNMe)₂(PPh₃)] or [ReBr(NNPh)(CNMe)₂(PPh₃)₂], but, in contrast to the present case, there is no increase in the number of diazenide ligands.

The IR spectrum (KBr pellet) of [ReBr(NNPh)₂(PPhCPh=CPh)₂(PPh₃)₂] **2** displays two bands at 1660 and 1560 cm⁻¹, assigned to ν(NN) of the phenyldiazene ligand, which are within the range observed¹⁹ for related diazenide complexes such as the parent one (1700 and 1575 cm⁻¹) and [ReCl(NNPh)₂(PPh₃)₂] (1540 and 1510 cm⁻¹) and the presence of the diazenide ligands is confirmed by elemental analysis. It seems likely that one NNPh presents a doubly bent geometry

(one-electron donor) whereas the other one should be singly bent (three-electron donor) in order to provide the complex with the inert gas electron configuration. Such an arrangement of phenyldiazene conformations was shown¹⁹ by an X-ray study on [ReBr₂(NNPh)₂(PPh₃)₂], the other isolated product (see above) of the attempted reaction of the parent diazenide with the phosphirene.

Complex **2** appears to exist in solution in two isomeric forms, both having equivalent phosphirene ligands, such as **II** and **III** (although isomerism resulting from different relative conformations of the two types of diazenide ligands²² cannot be ruled out), as indicated by its ³¹P-¹H NMR spectrum (CDCl₃) which consists of two similar sets of resonances, with a slight predominance of one of them. In each set the resonance of the phosphirene-phosphorus nuclei (2P_A) occurs as a doublet [²J(P_AP_B) = 13.8 Hz] at a chemical shift (δ –144.43 or –147.85 relative to H₃PO₄) that, as for complexes **1a** and **1b**, is typical for phosphorus-co-ordination without ring rupture, whereas the phosphine-phosphorus (P_B) resonance is the expected triplet (with the same coupling constant and half the intensity of the above doublet) at δ 5.68 or 3.63.



Electrochemical studies

The anodic behaviours of complexes **1a**, **1b** and **2** were investigated by cyclic voltammetry, at a platinum-wire electrode, in 0.2 M [NBu₄][BF₄]–CH₂Cl₂. Each of the dinitrogen complexes presents a first reversible single-electron anodic wave at ¹E_{1/2}^{ox} = 0.19 (**1a**) or 0.27 (**1b**) V vs. SCE, assigned to the Re^I → Re^{II} oxidation, which is followed by a second irreversible one, at a higher potential (^{II}E_p^{ox} = 1.25 **1a** or 1.35 V **1b**) involving the Re^{II} → Re^{III} oxidation with N₂ loss.

For *mer*-[ReCl(N₂)(PPhCPh=CPh)(PMePh₂)₃] **1b** the value of ¹E_{1/2}^{ox} is identical to that observed for the parent complex *trans*-[ReCl(N₂)(PMePh₂)₄] (0.27 V, measured under identical experimental conditions), whereas for the PMe₂Ph analogues, **1a** is oxidized at a higher potential than the parent N₂ complex (0.13 V), thus indicating that the phosphirene ligand behaves as a net electron σ donor minus π-acceptor ligand identical to PMePh₂ but weaker than PMe₂Ph. Hence, the values of the electrochemical E_L²³ and P_L²⁴ parameters (which constitute a measure of such a ligand character) for the phosphirene should be identical to those of PMePh₂, *i.e.* 0.37 V vs. NHE²³ and –0.43 V, respectively [the latter estimated from the observed²³ linear correlation between those two parameters, *i.e.* P_L = 1.17, E_L –0.86].

The measured values of the oxidation potential for complexes **1a** and **1b** (0.43 and 0.52 V vs. NHE, respectively) are in very good agreement with those (0.44 and 0.51 V vs. NHE, respectively) predicted by using the Lever eqn. (3)²³ in which

$$E = S_M (\Sigma E_L) + I_M \quad (\text{V vs. NHE}) \quad (3)$$

ΣE_L is the sum of the E_L values for all the ligands, S_M and I_M are dependent on the redox metal couple, spin state and stereochemistry (S_M = 0.76 and I_M = –0.95 V vs. NHE for Re^I/Re^{II} sites),^{23b} thus confirming our estimate of the E_L parameter for the phosphirene ligand and the additive character of this parameter for complexes **1a** and **1b**.

Also in accord with this expression, the oxidation potentials of complexes **1a** and **1b** and related ones follow the order of E_L for the phosphorus variable ligand in the following way: $trans\text{-}[\text{ReCl}(\text{N}_2)\{\text{P}(\text{OMe})_3\}_4]$ ($E_{1/2}^{\text{ox}} = 0.42$ V,^{18a} $E_L = 0.42$ V vs. NHE^{23a}) > $trans\text{-}[\text{ReCl}(\text{N}_2)(\text{PMePh}_2)_4]$, **1b** ($E_{1/2}^{\text{ox}} = 0.27$ V, $E_L = 0.37$ V vs. NHE^{23a}) or $trans\text{-}[\text{ReCl}(\text{N}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ ($E_{1/2}^{\text{ox}} = 0.28$ V,^{18a} $E_L = 0.36$ V vs. NHE^{23a}) > **1a** [$E_{1/2}^{\text{ox}} = 0.19$ V, $E_L(\text{PMe}_2\text{Ph}) = 0.34$ V vs. NHE,^{23a} $E_L(\overline{\text{PPhCPh}}=\text{CPh}) = 0.37$ V vs. NHE] > $trans\text{-}[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ ($E_{1/2}^{\text{ox}} = 0.13$ V, $E_L = 0.34$ V vs. NHE^{23a}).

An increase in the oxidation potential of the two dinitrogen complexes **1a** and **1b** corresponds to a decrease of the net electron donor ability of the phosphorus ligands and is also followed by an increase of $\nu(\text{N}\equiv\text{N})$ which reflects the lowering of the π -electron release from the metal to the N_2 ligand. Moreover, the $^1E_{1/2}^{\text{ox}}$ and $\nu(\text{N}\equiv\text{N})$ data for complexes **1a** and **1b** fit reasonably the linear correlation between these parameters recognised^{18a} for a series of other rhenium(i) complexes with the common Cl–Re– N_2 axis.

The diazenide complex $[\text{ReBr}(\text{NNPh})_2(\overline{\text{PPhCPh}}=\text{CPh})_2(\text{PPh}_3)]$ **2** also exhibits, by cyclic voltammetry, a single-electron reversible anodic wave which, however, occurs at $E_{1/2}^{\text{ox}} = 0.95$ V vs. SCE, a value much higher than those of the above Re^{I} -dinitrogen complexes, in agreement with the higher metal oxidation state for the former complex. In accord, the oxidation potential of **2** is not so anodic as that exhibited by its parent complex $[\text{ReBr}_3(\text{NNPh})(\text{PPh}_3)_2]$, having a higher metal oxidation state, which displays an irreversible oxidation wave at $E_p^{\text{ox}} = 1.49$ V vs. SCE.

The above electrochemical results, which are indicative that the phosphirene as a ligand behaves as a net electron donor/acceptor similar to PMePh_2 and is also compatible with N_2 co-ordination, suggest that a novel phosphirene-based nitrogen-fixation chemistry conceivably can be developed, paralleling that known¹⁵ for dinitrogen–phosphine complexes.

Experimental

Solvents were dried and degassed by using standard techniques. All reactions were performed under an inert atmosphere (N_2). Triphenylphosphirene,²⁵ $trans\text{-}[\text{ReCl}(\text{N}_2)\text{L}_4]$ ($\text{L} = \text{PMe}_2\text{Ph}$ or PMePh_2)^{18b} and $[\text{ReBr}_3(\text{NNPh})(\text{PPh}_3)_2]$ ¹⁹ were prepared according to published methods.

Infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer and NMR spectra on a Varian Unity 300 MHz or a Bruker AMX 500 MHz (or 80 MHz) spectrometer; δ values are in ppm relative to SiMe_4 (^1H) or to H_3PO_4 (^{31}P). Abbreviations: s = singlet, d = doublet, t = triplet, br = broad, dt = doublet of triplets, dbtr = doublet of broad triplets.

The electrochemical experiments were carried out either on an EG&G PAR 173 potentiostat/galvanostat and an EG&G PARC 175 Universal programmer or on an HI-TEK DT 2101 potentiostat/galvanostat and an HI-TEK PP RI waveform generator. Cyclic voltammetry studies were undertaken in a two-compartment three-electrode cell, at a platinum wire working electrode, probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode; a platinum or tungsten auxiliary electrode was employed. The first anodic wave in the cyclic voltammograms of the complexes **1a** and **1b** has ΔE_p of ca. 100 mV, $i_p(\text{anodic})/i_p(\text{cathodic})$ close to one, and the current function $i_p C^{-1} \nu^{-1/2}$ (C = concentration, ν = scan rate) without appreciable variation in the 50–1000 mV s^{-1} scan rate range, thus following the usual criteria for a single-electron reversible process. The oxidation potentials of the complexes were measured by cyclic voltammetry in 0.2 mol dm^{-3} $[\text{NBu}_4][\text{BF}_4]\text{-CH}_2\text{Cl}_2$, and are quoted, unless stated otherwise, relative to the SCE (saturated calomel electrode) by using the $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^{0/+}$ couple (0.55 V vs. SCE) as an internal reference. The values of the oxidation potentials relative to

NHE (normal hydrogen electrode) were estimated by adding 0.245 V to the corresponding ones quoted relative to SCE.

Syntheses

mer- $[\text{ReCl}(\text{N}_2)(\overline{\text{PPhCPh}}=\text{CPh})(\text{PMe}_2\text{Ph})_3]$ **1a.** The compound $\overline{\text{PPhCPh}}=\text{CPh}$ (0.105 g, 0.366 mmol) was added to a thf (13 cm^3) solution of $trans\text{-}[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ (0.294 g, 0.366 mmol) and the system stirred for 3 d giving a pale orange precipitate of complex **1** which was filtered off, washed with thf–hexane and dried *in vacuo*. Further crops of product could be obtained from the mother-liquor upon concentration and addition of hexane (total ca. 0.17 g, 50% yield) (Found: C, 55.2; H, 5.1; N, 2.9. Calc. for $\text{C}_{44}\text{H}_{48}\text{ClN}_2\text{P}_4\text{Re}$: C, 55.6; H, 5.1; N, 3.0%). IR (Nujol mull): 1944s, 1930s [$\nu(\text{N}\equiv\text{N})$, split due to a solid state effect]. ^1H NMR (CD_2Cl_2): δ 8.1–6.8 (m, 30 H, C_6H_5), 1.66 [t, $\frac{1}{2}$ $^2J(\text{HP}_C) + ^4J(\text{HP}_C) = 2.8$, 6 H, $\text{P}_C(\text{CH}_3)_2\text{Ph}$], 1.62 [t, $\frac{1}{2}$ $^2J(\text{HP}_C) + ^4J(\text{HP}_C) = 2.9$, 6 H, $\text{P}_C(\text{CH}_3)_2\text{Ph}$] and 1.26 [d, $^2J(\text{HP}_B) = 7.6$ Hz, 6H, $\text{P}_B(\text{CH}_3)_2\text{Ph}$]. $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ –28.39 [t, $^2J(\text{P}_C\text{P}_B) \approx ^2J(\text{P}_C\text{P}_A) \approx 22$, $2\text{P}_C\text{Me}_2\text{Ph}$], –28.54 [dt, $^2J(\text{P}_B\text{P}_A) = 253.1$, $^2J(\text{P}_B\text{P}_C) = 17.5$, $\text{P}_B\text{Me}_2\text{Ph}$] and –119.71 [dbtr, $^2J(\text{P}_A\text{P}_B) = 253.8$, $^2J(\text{P}_A\text{P}_C) = 24$ Hz, $\overline{\text{P}}_A\text{PhCPh}=\text{CPh}]$.

mer- $[\text{ReCl}(\text{N}_2)(\overline{\text{PPhCPh}}=\text{CPh})(\text{PMePh}_2)_3]$ **1b.** The compound $\overline{\text{PPhCPh}}=\text{CPh}$ (0.057 g, 0.20 mmol) was added to a thf (40 cm^3) solution of $trans\text{-}[\text{ReCl}(\text{N}_2)(\text{PMePh}_2)_4]$ (0.20 g, 0.20 mmol) and the solution stirred for 2 d. Concentration *in vacuo* followed by addition of pentane led to the precipitation of complex **1b** as a dark yellow solid which was filtered off, washed with thf–pentane and dried *in vacuo*. Further product could be obtained from the mother-liquor upon concentration and addition of pentane (total ca. 0.080 g, 40% yield). (Found: C, 61.8; H, 4.4; N, 2.4. Calc. for $\text{C}_{59}\text{H}_{54}\text{ClN}_2\text{P}_4\text{Re}$: C, 62.3; H, 4.8; N, 2.5%). IR (KBr pellet): 1940s [$\nu(\text{N}\equiv\text{N})$]. ^1H NMR (CDCl_3): δ 7.51–6.78 (m, 45 H, C_6H_5), 1.88 [s, br, 3 H, $\text{P}_B(\text{CH}_3)_2\text{Ph}$] and 1.65 [s, br, 6 H, $2\text{P}_C(\text{CH}_3)_2\text{Ph}$]. $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR (CDCl_3): δ –26.70 (s, br, $2\text{P}_C\text{MePh}_2$), –30.83 [d, $^2J(\text{P}_B\text{P}_A) \approx 240$, P_BMePh_2] and –131.10 [d, $^2J(\text{P}_A\text{P}_B) \approx 240$ Hz, $\overline{\text{P}}_A\text{PhCPh}=\text{CPh}]$.

$[\text{ReBr}(\text{NNPh})_2(\overline{\text{PPhCPh}}=\text{CPh})_2(\text{PPh}_3)]$ **2.** The compound $\overline{\text{PPhCPh}}=\text{CPh}$ (60 mg, 0.21 mmol) was added to a suspension of $[\text{ReBr}_3(\text{NNPh})(\text{PPh}_3)_2]$ (0.20 g, 0.19 mmol) in thf (60 cm^3) and the system heated to reflux during 2 d forming a dark orange solution which was then concentrated *in vacuo* until ca. 10 cm^3 . Pentane was added and complex **2** precipitated as an orange solid which was filtered off, washed with a mixture of thf and pentane, dried *in vacuo* and recrystallised from $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ (ca. 0.050 g, 20% yield) (Found: C, 63.1; H, 4.1; N, 3.9. Calc. for $\text{C}_{70}\text{H}_{55}\text{BrN}_4\text{P}_3\text{Re}\cdot 0.25\text{CH}_2\text{Cl}_2$: C, 63.3; H, 4.2; N, 4.2%). IR (KBr pellet): 1660m, 1560m [$\nu(\text{NN})$]. ^1H NMR (CDCl_3): δ 7.71–6.64 (m, C_6H_5). $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR (CDCl_3) (2 isomers, the ^{31}P resonances of the dominant one being given in italics): δ 5.68 and 3.63 [t, $^2J(\text{P}_B\text{P}_A) = 14$, P_BPh_3], –144.43 and –147.85 [d, $^2J(\text{P}_B\text{P}_A) = 14$ Hz, $\overline{\text{P}}_A\text{PhCPh}=\text{CPh}]$. Concentration *in vacuo* of the mother-liquor, followed by addition of pentane, led to precipitation of the known¹⁹ complex $[\text{ReBr}_2(\text{NNPh})_2(\text{PPh}_3)_2]$ as a red crystalline solid which was filtered off, washed with Et_2O and dried *in vacuo* (ca. 15% yield).

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