DALTON
FULL PAPER

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

Armando J. L. Pombeiro,*[a] **Maria Teresa A. R. S. Costa,**[a] **Yu Wang**[a] **and John F. Nixon**[b]

[a] *Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal. E-mail: pombeiro@alfa.ist.utl.pt*
[b] *School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, UK BN1 9QJ. E-mail: J.Nixon@sussex.ac.uk*

Received 2nd August 1999, Accepted 7th September 1999

The first mixed phosphirene–dinitrogen and phosphirene–diazenide complexes *mer*-[ReCl(N_2)(PPhCPh=CPh)L_3] (L = PMe_2Ph **1a** or $PMePh_2$ **1b**) and [ReBr$(NNPh)_2$$(PPhCPh{=}CPh)_2$$(PPh_3)$] **2** have been prepared by treatment of the corresponding thf solutions of *trans*-[ReCl(N_2)L_4] or [ReBr_3(NNPh)$(PPh_3)_2$] with PPhCPh=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 co-ordinate to the phosphorus lone-pair electrons or insert into one of the P–C bonds *via* a transient η^2-(P–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 $[W(CO)_5]$[8,9] are known and CO can also be incorporated into the ring of phosphirene complexes[10] 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 (M = 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 PPhCPh=CPh, with the dinitrogen and the phenyldiazenide complexes *trans*-[ReCl(N_2)L_4] (L = PMe_2Ph or $PMePh_2$) and [ReBr_3(NNPh)$(PPh_3)_2$], 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*-[ReCl(N_2)(PPhCPh=CPh)L_3] (L = PMe_2Ph **1a** or $PMePh_2$ **1b**) and [ReBr$(NNPh)_2$$(PPhCPh{=}CPh)_2$$(PPh_3)$] **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

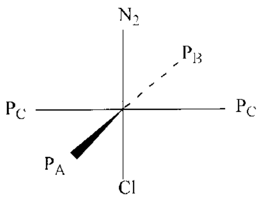
Chemical studies

Treatment of a thf solution of *trans*-[ReCl(N_2)L_4] (L = PMe_2Ph or $PMePh_2$) with PPhCPh=CPh, in a stoichiometric amount, for *ca.* 2–3 d, leads to the formation of the corresponding mixed dinitrogen–phosphirene complexes *mer*-[ReCl(N_2)(PPhCPh=CPh)L_3] (L = PMe_2Ph **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

$$\textit{trans}\text{-}[\mathrm{ReCl(N_2)L_4}] + \mathrm{PPhCPh{=}CPh} \longrightarrow \textit{mer}\text{-}[\mathrm{ReCl(N_2)(PPhCPh{=}CPh)L_3}] + \mathrm{L} \quad (1)$$

in transition metal dinitrogen complexes, in this reaction it is retained as was observed previously by us[17a] in the formation of *mer*-[ReCl(N_2)(CNMe)$(PMe_2Ph)_3$] on treatment of *trans*-[ReCl(N_2)$(PMe_2Ph)_4$] 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 ν(N≡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*-[ReCl(N_2)(CNMe)$(PMe_2Ph)_3$][17a] or *mer*-[Re(S_2PPh_2)(N_2)$(PMe_2Ph)_3$],[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



P_A = PPhCPh=CPh; P_B, P_C = PMe_2Ph **1a** or $PMePh_2$ **1b**

I

stabilization of their Re–N_2 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 N_2 and the Cl ligands are mutually *trans* and is clearly indicated by the [ABC_2] patterns exhibited by their ${}^{31}P\text{-}\{{}^1H\}$ NMR spectra.

The phosphirene-${}^{31}P$ resonance (P_A at δ −119.71 **1a** or −131.10 **1b** relative to H_3PO_4) 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 occur[6] 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 [$2P_C$ at δ −28.39 as a triplet, ${}^2J(P_CP_B) \approx {}^2J(P_CP_A) \approx 22$ Hz]. A more simplified ${}^{31}P\text{-}\{{}^1H\}$ NMR pattern is observed for **1b** (in $CDCl_3$) in view of the lack of resolution of the *cis* couplings: P_A and P_B appear simply as doublets [${}^2J(P_AP_B) \approx 240$ 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 $P_B(CH_3)_2Ph$ is a doublet [${}^2J(HP_B) = 7.6$ Hz] at δ 1.26, whereas the resonance of the two *trans* $P_C(CH_3)_2Ph$ 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 [$|\tfrac{1}{2}|{}^2J(HP_C) + {}^4J(HP_C)| \approx 2.9$ Hz]. Such a type of resonance pattern associated with the meridional arrangement of PMe_2Ph ligands has been recognized[17a,21] for other complexes.

The phenyldiazenide complex [$ReBr_3(NNPh)(PPh_3)_2$] also reacts with the phosphirene, in refluxing thf for 2 d, leading to the formation of the orange complex [$ReBr(NNPh)_2(\overline{PPhCPh{=}C}Ph)_2(PPh_3)$] **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 identified[19] as [$ReBr_2(NNPh)_2(PPh_3)_2$], which does not contain any phosphirene ligand.

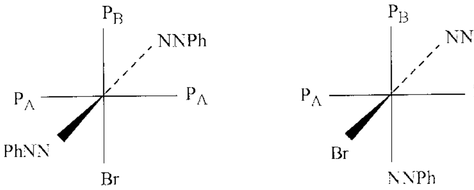
$$[ReBr_3(NNPh)(PPh_3)_2] \xrightarrow[\text{thf, heat}]{\overline{PPhCPh{=}C}Ph} [ReBr(NNPh)_2(\overline{PPhCPh{=}C}Ph)_2(PPh_3)] \quad (2)$$

2

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 PPh_3 producing Ph_3PBr_2) 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 [$ReBr_3(NNPh)(PPh_3)_2$] is known[19] to undergo reduction reactions with isocyanides to form products of the type [$ReBr_2(NNPh)(CNR)(PPh_3)_2$] (R = Me or C_6H_4Cl-4), [$ReBr_2(NNPh)(CNMe)_2(PPh_3)$] or [$ReBr(NNPh)(CNMe)_2(PPh_3)_2$], but, in contrast to the present case, there is no increase in the number of diazenide ligands.

The IR spectrum (KBr pellet) of [$ReBr(NNPh)_2(\overline{PPhCPh{=}C}Ph)_2(PPh_3)$] **2** displays two bands at 1660 and 1560 cm^{-1}, assigned to ν(NN) of the phenyldiazenide ligand, which are within the range observed[19] for related diazenide complexes such as the parent one (1700 and 1575 cm^{-1}) and [$ReCl(NNPh)_2(PPh_3)_2$] (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 phenyldiazenide conformations was shown[19] by an X-ray study on [$ReBr_2(NNPh)_2(PPh_3)_2$], 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 ligands[22] cannot be ruled out), as indicated by its ${}^{31}P\text{-}\{{}^1H\}$ NMR spectrum ($CDCl_3$) 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 H_3PO_4) 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.



$P_A = \overline{PPhCPh{=}C}Ph$, $P_B = PPh_3$ **2**

II **III**

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 [NBu_4][BF_4]–CH_2Cl_2. Each of the dinitrogen complexes presents a first reversible single-electron anodic wave at ${}^{I}E_{1/2}^{ox} = 0.19$ (**1a**) or 0.27 (**1b**) V *vs.* SCE, assigned to the $Re^I \longrightarrow Re^{II}$ 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 $Re^{II} \longrightarrow Re^{III}$ oxidation with N_2 loss.

For *mer*-[$ReCl(N_2)(\overline{PPhCPh{=}C}Ph)(PMePh_2)_3$] **1b** the value of ${}^{I}E_{1/2}^{ox}$ is identical to that observed for the parent complex *trans*-[$ReCl(N_2)(PMePh_2)_4$] (0.27 V, measured under identical experimental conditions), whereas for the PMe_2Ph analogues, **1a** is oxidized at a higher potential than the parent N_2 complex (0.13 V), thus indicating that the phosphirene ligand behaves as a net electron σ donor minus π-acceptor ligand identical to $PMePh_2$ but weaker than PMe_2Ph. Hence, the values of the electrochemical E_L[23] and P_L[24] parameters (which constitute a measure of such a ligand character) for the phosphirene should be identical to those of $PMePh_2$, *i.e.* 0.37 V *vs.* NHE[23] and −0.43 V, respectively [the latter estimated from the observed[23] 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

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

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*-[ReCl(N$_2$){P(OMe)$_3$}$_4$] ($E^{ox}_{1/2}$ = 0.42 V,[18a] E_L = 0.42 V *vs.* NHE[23a]) > *trans*-[ReCl(N$_2$)(PMePh$_2$)$_4$], **1b** ($E^{ox}_{1/2}$ = 0.27 V, E_L = 0.37 V *vs.* NHE[23a]) or *trans*-[ReCl(N$_2$)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] ($E^{ox}_{1/2}$ = 0.28 V,[18a] E_L = 0.36 V *vs.* NHE[23a]) > **1a** [$E^{ox}_{1/2}$ = 0.19 V, E_L (PMe$_2$Ph) = 0.34 V *vs.* NHE,[23a] E_L (PPhCPh=CPh) = 0.37 V *vs.* NHE] > *trans*-[ReCl(N$_2$)(PMe$_2$Ph)$_4$] ($E^{ox}_{1/2}$ = 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 ν(N≡N) which reflects the lowering of the π-electron release from the metal to the N$_2$ ligand. Moreover, the $^1E^{ox}_{1/2}$ and ν(N≡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 [ReBr(NNPh)$_2$(PPhCPh=CPh)$_2$(PPh$_3$)] **2** also exhibits, by cyclic voltammetry, a single-electron reversible anodic wave which, however, occurs at $E^{ox}_{1/2}$ = 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 [ReBr$_3$(NNPh)(PPh$_3$)$_2$], having a higher metal oxidation state, which displays an irreversible oxidation wave at E_p^{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 known[15] 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*-[ReCl(N$_2$)L$_4$] (L = PMe$_2$Ph or PMePh$_2$)[18b] and [ReBr$_3$(NNPh)(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$_4$ (^{1}H) or to H$_3$PO$_4$ (^{31}P). Abbreviations: s = singlet, d = doublet, t = triplet, br = broad, dt = doublet of triplets, dbrt = 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(anodic)/i_p(cathodic) close to one, and the current function $i_pC^{-1}v^{-1/2}$ (C = concentration, v = 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} [NBu$_4$][BF$_4$]–CH$_2$Cl$_2$, and are quoted, unless stated otherwise, relative to the SCE (saturated calomel electrode) by using the [Fe(η^5-C$_5$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*-[ReCl(N$_2$)(PPhCPh=CPh)(PMe$_2$Ph)$_3$] 1a.** The compound PPhCPh=CPh (0.105 g, 0.366 mmol) was added to a thf (13 cm^3) solution of *trans*-[ReCl(N$_2$)(PMe$_2$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 C$_{44}$H$_{48}$ClN$_2$P$_4$Re: C, 55.6; H, 5.1; N, 3.0%). IR (Nujol mull): 1944s, 1930s [ν(N≡N), split due to a solid state effect]. ^{1}H NMR (CD$_2$Cl$_2$): δ 8.1–6.8 (m, 30 H, C$_6$H$_5$), 1.66 [t, $\frac{1}{2}$ |^2J(HP$_C$) + ^4J(HP$_C$)| = 2.8, 6 H, P$_C$(CH_3)$_2$Ph], 1.62 [t, $\frac{1}{2}$ |^2J(HP$_C$) + ^4J(HP$_C$)| = 2.9, 6 H, P$_C$(CH_3)$_2$Ph] and 1.26 [d, ^2J(HP$_B$) = 7.6 Hz, 6H, P$_B$(CH_3)$_2$Ph]. ^{31}P-{^{1}H} NMR (CD$_2$Cl$_2$): δ −28.39 [t, ^2J(P$_C$P$_B$) ≈ ^2J(P$_C$P$_A$) ≈ 22, 2P$_C$Me$_2$Ph], −28.54 [dt, ^2J(P$_B$P$_A$) = 253.1, ^2J(P$_B$P$_C$) = 17.5, P$_B$Me$_2$Ph] and −119.71 [dbrt, ^2J(P$_A$P$_B$) = 253.8, ^2J(P$_A$P$_C$) = 24 Hz, P$_A$PhCPhC=CPh].

***mer*-[ReCl(N$_2$)(PPhCPh=CPh)(PMePh$_2$)$_3$] 1b.** The compound PPhCPh=CPh (0.057 g, 0.20 mmol) was added to a thf (40 cm^3) solution of *trans*-[ReCl(N$_2$)(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 C$_{59}$H$_{54}$ClN$_2$P$_4$Re: C, 62.3; H, 4.8; N, 2.5%). IR (KBr pellet): 1940s [ν(N≡N)]. ^{1}H NMR (CDCl$_3$): δ 7.51–6.78 (m, 45 H, C$_6$H$_5$), 1.88 [s, br, 3 H, P$_B$(CH_3)Ph$_2$] and 1.65 [s, br, 6 H, 2P$_C$(CH_3)Ph$_2$]. ^{31}P-{^{1}H}NMR (CDCl$_3$): δ −26.70 (s, br, 2P$_C$MePh$_2$), −30.83 [d, ^2J(P$_B$P$_A$) ≈ 240, P$_B$MePh$_2$] and −131.10 [d, ^2J(P$_A$P$_B$) ≈ 240 Hz, P$_A$PhCPh=CPh].

[ReBr(NNPh)$_2$(PPhCPh=CPh)$_2$(PPh$_3$)] 2. The compound PPhCPh=CPh (60 mg, 0.21 mmol) was added to a suspension of [ReBr$_3$(NNPh)(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 CH$_2$Cl$_2$–Et$_2$O (*ca.* 0.050 g, 20% yield) (Found: C, 63.1; H, 4.1; N, 3.9. Calc. for C$_{70}$H$_{55}$BrN$_4$P$_3$Re·0.25CH$_2$Cl$_2$: C, 63.3; H, 4.2; N, 4.2%). IR (KBr pellet): 1660m, 1560m [ν(NN)]. ^{1}H NMR (CDCl$_3$): δ 7.71–6.64 (m, C$_6$H$_5$). ^{31}P-{^{1}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(P$_B$P$_A$) = 14, P$_B$Ph$_3$], −*144.43* and −147.85 [d, ^2J(P$_B$P$_A$) = 14 Hz, P$_A$PhCPh=CPh]. Concentration *in vacuo* of the mother-liquor, followed by addition of pentane, led to precipitation of the known[19] complex [ReBr$_2$(NNPh)$_2$(PPh$_3$)$_2$] as a red crystalline solid which was filtered off, washed with Et$_2$O and dried *in vacuo* (*ca.* 15% yield).

Acknowledgements

This work has been partially supported by the PRAXIS XXI programme, the Junta Nacional de Investigação Científica e Tecnológica (JNICT) and the Foundation for Science and Technology (FCT) (Portugal), and the Treaty of Windsor programme (The Portuguese Council of Rectors/The British Council).

References

1 F. Mathey, *Chem. Rev.*, 1990, **90**, 997.

2 F. Mathey and M. Regitz, *Comprehensive Heterocyclic Chemistry*, Pergamon, Oxford, 1996.

3 K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, New York, 1998.

4 F. Mercier, B. Deschamps and F. Mathey, *J. Am. Chem. Soc.*, 1989, **111**, 9098.

5 A. Marinetti, F. Mathey, J. Fischer and A. Mitschler, *J. Am. Chem. Soc.*, 1982, **104**, 4484.

6 A. Marinetti and F. Mathey, *J. Am. Chem. Soc.*, 1985, **107**, 4700.

7 S. S. Al-Juaid, D. Carmichael, P. B. Hitchcock, S. Lochschmidt, A. Marinetti, F. Mathey and J. F. Nixon, *J. Chem. Soc.*, *Chem. Commun.*, 1988, 1156.

8 A. Marinetti and F. Mathey, *Tetrahedron Lett.*, 1987, **28**, 5021.

9 A. Espinosa Ferao, B. Deschamps and F. Mathey, *Bull. Soc. Chim. Fr.*, 1993, **130**, 695.

10 A. Marinetti, J. Fischer and F. Mathey, *J. Am. Chem. Soc.*, 1985, **107**, 5001.

11 D. Carmichael, P. B. Hitchcock, J. F. Nixon, F. Mathey and A. Pidcock, *J. Chem. Soc.*, *Chem. Commun.*, 1986, 762.

12 D. Carmichael, P. B. Hitchcock, A. Marinetti, F. Mathey and J. F. Nixon, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 905.

13 F. A. Ajulu, D. Carmichael, P. B. Hitchcock, F. Mathey, M. F. Meidine, J. F. Nixon, L. Ricard and M. L. Riley, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 750.

14 D. Carmichael, P. B. Hitchcock, F. Mathey, J. F. Nixon and L. Ricard, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 1811.

15 M. Hidai and Y. Mizobe, *Chem. Rev.*, 1995, **95**, 1115; J. Chatt, J. R. Dilworth and R. L. Richards, *Chem. Rev.*, 1978, **78**, 589; D. J. Evans, R. A. Henderson and B. E. Smith, in *Bioinorganic Catalysis*, ed. J. Reedijk, Marcel Dekker, New York, 1993, p. 89; G. J. Leigh, *Acc. Chem. Res.*, 1992, **25**, 177; R. L. Richards, in *Biology and Biochemistry of Nitrogen Fixation*, eds. M. J. Dilworth and A. R. Glenn, Elsevier, Amsterdam, 1991, p. 58; A. J. L. Pombeiro, in *New Trends in the Chemistry of Nitrogen Fixation*, eds. J. Chatt, L. M. Câmara Pina and R. L. Richards, Academic Press, New York, 1980, ch. 6, p. 153; R. A. Henderson, G. J. Leigh and C. J. Pickett, *Adv. Inorg. Chem.*, 1983, **27**, 197.

16 D. Sutton, *Chem. Rev.*, 1993, **93**, 995; B. F. G. Johnson, B. L. Haymore and J. R. Dilworth, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, ch. 13.3, p. 99.

17 (*a*) A. J. L. Pombeiro, P. B. Hitchcock and R. L. Richards, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 319; (*b*) A. J. L. Pombeiro, P. B. Hitchcock and R. L. Richards, *Inorg. Chim. Acta*, 1983, **76**, L225; (*c*) M. F. N. N. Carvalho, A. J. L. Pombeiro, U. Schubert, O. Orama, G. J. Pickett and R. L. Richards, *J. Chem. Soc.*, *Dalton Trans.*, 1985, 2079; (*d*) M. F. N. N. Carvalho and A. J. L. Pombeiro, *J. Organomet. Chem.*, 1990, **384**, 121.

18 (*a*) G. J. Leigh, R. H. Morris, C. J. Pickett and D. R. Stanley, *J. Chem. Soc.*, *Dalton Trans.*, 1981, 800; (*b*) J. Chatt, J. R. Dilworth and G. J. Leigh, *ibid.*, 1973, 612.

19 M. T. A. R. S. da Costa, J. R. Dilworth, M. T. Duarte, J. J. R. Fraústo da Silva, A. M. Galvão and A. J. L. Pombeiro, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2405.

20 J. Chatt, R. H. Crabtree, J. R. Dilworth and R. L. Richards, *J. Chem. Soc.*, *Dalton Trans.*, 1974, 2358.

21 A. J. L. Pombeiro, J. Chatt and R. L. Richards, *J. Organomet. Chem.*, 1980, **190**, 297.

22 T. Nicholson, N. de Vries, A. Davison and A. G. Jones, *Inorg. Chem.*, 1989, **28**, 3813.

23 A. B. P. Lever, *Inorg. Chem.*, (*a*) 1990, **29**, 1271; (*b*) 1991, **30**, 1980.

24 J. Chatt, C. T. Kan, G. J. Leigh, C. J. Pickett and D. R. Stanley, *J. Chem. Soc.*, *Dalton Trans.*, 1980, 2032.

25 S. Lochschmidt, F. Mathey and A. Schmidpeter, *Tetrahedron Lett.*, 1986, **27**, 2365.

Paper 9/06238F