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REACTIONS OF PHENYLIMIDOTRICHLOROBIS(TRIPHENYLPHOSPHINE)RHENIUM(V). REACTION WITH TRIMETHYLPHOSPHINE AND REDUCTION OF TRIMETHYLPHOSPHINE COMPLEX TO PHENYLAMIDO COMPLEXES OF RHENIUM(I, III). THE X-RAY CRYSTAL STRUCTURES OF PHENYLAMIDO-(DINITROGEN)TETRAKIS(TRIMETHYLPHOSPHINE)-RHENIUM(I) AND PHENYLAMIDO(BUTA-1,3-DIENE)-TETRAKIS-(TRIMETHYLPHOSPHINE)RHENIUM(I)

KWOK W. CHIU, WAI-KWOK WONG and GEOFFREY WILKINSON*
Chemistry Department, Imperial College, London SW7 2AY, England

and

ANITA M. R. GALAS and MICHAEL B. HURSTHOUSE*
Chemistry Department, Queen Mary College, Mile End Road, London E1 4NS, England

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Abstract—The interaction of $Re(NPh)Cl_3(PPh_3)_2$ with PMe_3 gives $Re(NPh)Cl_3(PMe_3)(PPh_3)$ or $Re(NPh)Cl_3(PMe_3)_2$ depending on conditions. In the presence of excess PMe_3 the phenylimido compounds in tetrahydrofuran are reduced by sodium amalgam giving products whose nature depends on the atmosphere (Ar, N_2, H_2 CO, butadiene) used. The following compounds have been characterised: $Re(NHPh)(N_2)(PMe_3)_4$, $ReH(NHPh)(\eta'\text{-}CH_2PMe_2)(PMe_3)_4$, $Re(H)_2(NHPh)(PMe_3)_4$, $Re(NHPh)(CO)_2(PMe_3)_3$, $Re(NHPh)(CO)_3(PMe_3)_2$, $Re(NHPh)(\eta^4\text{-}C_4H_6)(PMe_3)_3$ and $Re(NPh)Cl_2(PMe_3)_3$. The structures of $Re(NHPh)(N_2)(PMe_3)_4$ (3) and $Re(NHPh)(C_4H_6)(PMe_3)_3$, (8) have been confirmed by single-crystal X-ray diffraction studies. (3) is monoclinic, space group $P2_1/n$ with $a = 9.574(2)$, $b = 19.528(3)$, $c = 14.385(3)$ Å and $\beta = 99.06(2)°$; (8) is orthorhombic, space group $Pbc2_1$, with $a = 12.207(2)$, $b = 13.884(2)$, $c = 14.242(2)$ Å. The structures were solved via the heavy atom method and refined by least squares to R values of 0.065 and 0.062 for 3249 and 2009 observed diffractometer data, respectively. In the dinitrogen complex the N_2 and NHPh ligands adopt a *cis* configuration with Re–N bond lengths of 1.955(13) and 2.200(14) Å, respectively. In the butadiene complex, whose structure is not well defined due to disorder and/or pseudo symmetry correlation effects, the Re–N (amido) distance is 2.13(3) Å.

INTRODUCTION

It has been noted[1] that although alkyl or arylimido complexes of rhenium have long been known few of their reactions have been studied. Reactions of $Re(NR)Cl_3(PPh_3)_2$ with sulphur and oxygen have been studied, the latter reaction generating arylnitroso species $ReCl_3(RNO)(OPPh_3)$. *t*-Butylimido alcoxo complexes, e.g. $Re(OSiMe_3)(NBu^t)_3$, have also been recently described.[2]

We now report the synthesis of trimethylphosphine phenylimido compounds and of species obtained from the sodium amalgam reduction of $Re(NPh)Cl_3(PPh_3)_2$ in the presence of PMe_3 and/or $Re(NPh)Cl_3(PMe_3)_2$ under atmospheres of Ar, N_2, H_2 and CO.

In Table 1 are collected the ^1H NMR data for new compounds; ^{31}P data is given in the text and experimental section.

RESULTS AND DISCUSSION

(1) *Interaction of phenylimidotrichlorobis(triphenylphosphine)rhenium(V) with trimethylphosphine*

Interaction of PMe_3 and $Re(NPh)Cl_3(PPh_3)_2$ in toluene at room temperature (20–25°C) leads to replacement of only one PPh_3 ligand and formation of the green crystalline solvate $Re(NPh)Cl_3(PMe_3)(PPh_3)$. C_7H_8 (**1**) in high yield. At 80–90°C the *bis*-trimethylphosphine complex $Re(NPh)Cl_3(PMe_3)_2$ (**2**) is obtained; the similar triethylphosphine complex is known.[3]

The IR spectrum of **1** shows a strong band at 760 cm^{-1} (Re=NPh) while the ^1H NMR spectrum has a PMe_3 doublet (δ 1.59 ppm, $^2J_{P\text{-}H} = 10$ Hz) indicating *cis* phosphorus atoms as in the *fac* structure (**1**). In the compound **2**, there is a similar band at 769 cm^{-1} in the IR for Re=NPh but the ^1H NMR is a triplet (δ 1.48 ppm, $^2J_{P\text{-}H} = 4$ Hz), indicating *trans* phosphines as in (**2**).

(2) *Reductions by sodium amalgam*

The reduction of either $Re(NPh)Cl_3(PPh_3)_2$ or $Re(NPh)Cl_3(PMe_3)_2$ in the presence of excess PMe_3 gives similar products in all cases when Ar, N_2, H_2 and CO atmospheres are used and, except in one case, leads to phenylamido (NHPh) complexes since tetrahydrofuran as solvent can also act as a source of hydrogen.

(a) *Phenylamido(dinitrogen)tetrakis(trimethylphosphine) rhenium(I).*

The reduction using excess sodium amalgam leads to $Re(NHPh)(N_2)(PMe_3)_4$ (**3**) whose IR spectrum shows a weak band at 3390 cm^{-1} for the N–H stretch and a very strong band at 2000 cm^{-1} for coordinated N_2. The ^1H NMR spectrum has a broad resonance at δ 2.3 ppm

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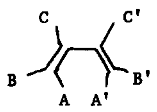
*Authors to whom correspondence should be addressed.

Table 1. ^{1}H nuclear magnetic resonance spectra[a]

Compound	^{1}H δ ppm	Assignment
1. $Re(NPh)Cl_3(PMe_3)(PPh_3)C_7H_8$	7.0-7.9 m (20)	$P\underline{Ph_3}$, $\underline{Ph}N$
	7.1 s (6)	$\underline{Ph}CH_3$
	2.3 s (3)	$PhC\underline{H_3}$
	1.59 d (9) ($^2\underline{J}_{P-H}$ = 10 Hz)	$P\underline{Me_3}$
2. $Re(NPh)Cl_3(PMe_3)_2$	7.0-7.9 m (5)	$\underline{Ph}N$
	1.48 t (18) ($^2\underline{J}_{P-H}$ = 4 Hz)	$P\underline{Me_3}$
3. $Re(NHPh)(N_2)(PMe_3)_4$	6.4-7.5 m (5)	$\underline{Ph}NH$
	2.30 br,s (1)	$N\underline{H}$
	1.22-1.40 m (18)	$P\underline{Me_3}$
	0.98-1.10 m (18)	
4. $Re(NHPh)(H)_2(PMe_3)_4$	6.4-7.5 m (5)	$\underline{Ph}NH$
	2.85 br,s (1)	$N\underline{H}$
	1.56 t ($^2\underline{J}_{P-H}$ = 2 Hz)	$P\underline{Me}_3$
	1.45 d ($^2\underline{J}_{P-H}$ = 4 Hz)	
	-8.8 q of d (1)	$Re-\underline{H}_A$
	($^2\underline{J}_{P-H}$ = 21.0; $^2\underline{J}_{H-H}$ = 2.4 Hz)	
	-7.8 q (1) ($^2\underline{J}_{P-H}$ = 21.3 Hz)	$Re-\underline{H}_B$
5. $Re(NHPh)(H)(CH_2PMe_2)(PMe_3)_4$	6.4-7.5 m (5)	$\underline{Ph}$ NH
	3.0 br,s (1)	$N\underline{H}$
	2,3 d (9) ($^2\underline{J}_{P-H}$ = 26.5 Hz)	PMe_3
	2.14-2,6 m (17)	$P\underline{Me_3}$ $C\underline{H_2}P\underline{Me_2}$
	1,22 br,s (9)	$P\underline{Me_3}$
	-3,30 br,s (1)	$Re-\underline{H}$
6. $Re(NHPh)(CO)_2(PMe_3)_3$	6.4-7.5 m (5)	$\underline{Ph}NH$
	2.80 br,s (1)	$N\underline{H}$
	1.35 d ($^2\underline{J}_{P-H}$ = 4.0 Hz)	$P\underline{Me_3}$
	1.14 m	
7. $Re(NHPh)(CO)_3(PMe_3)_2$	6.4-7.5 m (5)	$\underline{Ph}N$
	2.72 br,s (1)	N-H
	1.28 d ($^2\underline{J}_{P-H}$ = 7.7 Hz)	PMe_3
	1.33 d ($^2\underline{J}_{P-H}$ = 8 Hz)	
8. $Re(NHPh)(\eta^4-C_4H_6)(PMe_3)_3$	7.3-6.4 br,m (5)	$N-\underline{Ph}$
 	4.53 br,s (2)	CC'
	1.50 br,s (2)	BB'
	-0.35 br,s (2)	AA'
	1.21 d ($^2\underline{J}_{P-H}$ = 6.6 Hz)	PMe_3
	1.15 d ($^2\underline{J}_{P-H}$ = 5.9 Hz)	
	0.92 d ($^2\underline{J}_{P-H}$ = 5.2 Hz)	
	2.74 br, s	$N-\underline{H}$

[a] In $^2[H]_6$ benzene at 90 MHz, 35°C; Me_4Si δ 0.0. Relative areas in parenthesis.

(N-*H*) together with complex multiplets between δ 1.0–1.7 ppm for the PMe_3 groups. This complexity suggests different environments for the PMe_3 groups in solution similar to those confirmed in the solid state by X-ray diffraction study described below. The complex reacts with hydrogen and with carbon monoxide to displace dinitrogen as described later. Other rhenium(I) dinitrogen complexes, $ReX(N_2)(PR_3)_4$, and $ReX(N_2)(diphos)_2$, X = Cl, Br, are known.[4,5]

A diagram of the molecule is shown in Fig. 1 and some of the more important bond-lengths and angles are listed in Table 2. The compound is a direct relative of the Re^I chloro derivative $ReCl(N_2)(PMe_2Ph)_4$.[5] However, the two structures are significantly different in that in the chloro compound, the chlorine and dinitrogen ligands are *trans* (and, in fact, mutually disordered) whereas in our compound, the phenylamido and dinitrogen groups are *cis*.

Detailed comparison of the structures is quite revealing. In the chloro complex, the four "equatorial" Re–P bond lengths lie in the narrow range 2.413(4)–2.435(4)—the small differences being ascribed to steric crowding. In our complex we have three structurally different phosphines, and the Re–P distances vary accordingly. Two of the phosphines are mutually *trans* with equal Re–P distances [2.405(4), 2.408(4)Å], which are similar to those in the chloro complex. The phosphine *trans* to the N_2 ligand has an Re–P length of 2.397(3)Å—only slightly shorter than the first two, suggesting little if any *trans* influence for the dinitrogen ligand. This is understandable since, like two *trans* phosphines, we have in this situation, two *trans* π-acceptor ligands competing for *d* electron density. On the other hand, the phosphine *trans* to the phenylamido group has a very short Re–P bond, of length 2.334(4)Å. This again is understandable since *trans* to this phosphine we have the NHPh ligand, and repulsion of the metal *d* electrons by the nitrogen lone pair would tend to enhance the drift of *d* electron density from the metal to the phosphorus.

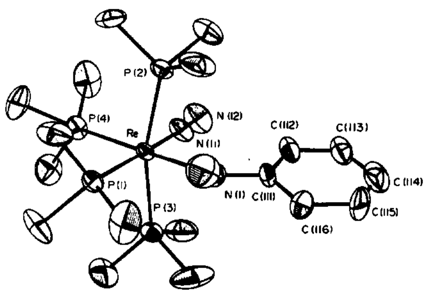


Fig. 1. The molecular structure of $Re(NHPh)(N_2)(PMe_3)_4$.

It may be noted that the metal achieves an 18-electron configuration without $N \rightleftarrows Re$ electron donation and this accounts for the relatively long Re–N(amide) bond length of 2.20(1)Å. Additionally, the nitrogen atom deviates significantly from planarity with the sum of the angles being 353°.

(b) *Phenylamido dihydridotetrakis(trimethylphosphine)-rhenium(III)*

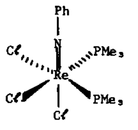
The extremely air-sensitive complex $Re(NHPh)(H)_2 \cdot (PMe_3)_4$ (**4**) can be obtained directly by reduction of $Re(NPh)Cl_3(PMe_3)_2$ in the presence of excess PMe_3 under hydrogen or by oxidative addition of hydrogen from compound (**3**). This reaction is reversible at room temperature

$$Re(NHPh)(N_2)(PMe_3)_4 + H_2 \rightleftharpoons Re(NHPh)(H)_2(PMe_3)_4 + N_2.$$

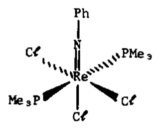
The complex has bands in the IR spectrum at 3382 (N–H str) and medium broad bands at 1925 and 1885 cm^{-1} (Re–H str). The ^1H NMR spectrum again confirms the N–$\underline{H}$ (δ 2.85 ppm) and in addition to PMe_3 resonances there are two Re–H resonances; H_A at δ −8.8 ppm, quintet of doublets ($^2J_{P\text{–}H}$ = 21 Hz, $^2J_{H\text{–}H}$ = 2.4 Hz), H_B at 7.8 ppm, a poorly resolved quintet ($^2J_{P\text{–}H}$ = 21 Hz). There is no change in these high field resonances between −100 and +90°C. The $^{31}P\{^1H\}$ spectrum has two broad singlets at δ −41.63 and −45.37 ppm. This seven-coordinate rhenium(III) complex can have isomers 4a, b; for 4a, the ^1H NMR spectrum should show two pseudo quintets of equal intensity for H_A and H_B provided $J_{H\text{–}Re\text{–}H}$ is very small. For 5b, the two hydrides are equivalent giving a pseudo quintet. The observed spectrum is consistent with a mixture of isomers.

Table 2. Selected bond lengths and angles for $Re(NHPh)(N_2)(PMe_3)_4$

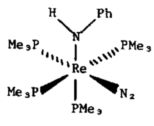
a) Bond Lengths (Å)		b) Bond Angles (°)	
Re-N(11)	1.955(13)	N(1)-Re-N(11)	94.9(6)
Re-N(1)	2.200(14)	N(11)-Re-P(1)	178.3(4)
Re-P(1)	2.397(5)	N(11)-Re-P(cis)	85.9-87.6(5)
Re-P(2)	2.405(6)		
Re-P(3)	2.408(6)	N(1)-Re-P(4)	178.8(4)
Re-P(4)	2.334(6)	N(1)-Re-P(cis)	83.4-86.8(5)
N(11)-N(12)	1.101(18)		
		Re-N(11)-N(12)	176.5(15)
P-C	1.79(2)-1.88(2)		
N(1)-C(111)	1.36(2)	Re-P-C	115-127(1)
C-C(Ph)	1.33(4)-1.47(3)	Re-N(1)-C(111)	141(1)



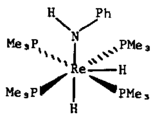
(1)



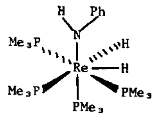
(2)



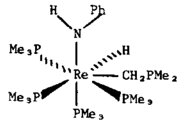
(3)



(4a)



(4b)



(5)

(c) *Reduction under argon*

Reduction of $Re(NPh)Cl_3(PMe_3)_3$ with excess sodium amalgam under argon leads to a pale yellow extremely air sensitive crystalline complex that we must formulate as $Re(NHPh)(H)(\eta^1\text{-}CH_2PMe_2)(PMe_3)_4$ (**5**).

The IR spectrum shows a weak band at 3386 cm^{-1} for the N–H stretch and a weak broad band at 1900 cm^{-1} for the Re–H stretch. The ^1H NMR spectrum confirms the Re–H (δ −3.3 ppm) and also shows a singlet at δ 1.22 ppm, a doublet at δ 2.30 ppm ($^2J_{P-H}$ = 26.5 Hz) and a complex multiplet between δ 2.14–2.60 ppm for PMe_3. The $^{31}P\{^1H\}$ NMR spectrum shows a broad multiplet at δ −39.8 ppm that can be assigned to the $\eta^1\text{-}Me_2PCH_2$ group formed by hydride transfer from the methyl group of PMe_3. Although previously only $\eta^2\text{-}CH_2PMe_2$ groups have been formed in such reactions,[6] there is a precedent for an $\eta^1\text{-}CH_2PR_2$ group (as contrasted with the numerous examples of $\eta^1\text{-}CH_2PR_3$ groups) namely, the complex $(\eta^5\text{-}C_5H_5)_2ZrCl(\eta^1\text{-}CHPPh_2)$ whose structure has been determined by X-ray diffraction.[7] The compound **5** so formulated is thus a 7-coordinate complex of rhenium(III) and is an 18e species.

On passing nitrogen through a tetrahydrofuran solution of the complex a new intense IR band appears at 2000 cm^{-1} and when this reaction is done in an NMR tube the Re–H resonance disappears, suggesting that in solution $Re(NHPh)(N_2)(PMe_3)_4$ is formed. On passing hydrogen through a thf solution, two new IR bands at 1930 and 1890 cm^{-1} appear while the NMR spectrum shows high field lines, characteristic of the above dihydride.

We, therefore, appear to have the reactions shown in Scheme 1.

(d) *Carbon monoxide complexes*

Two carbonyl complexes have been obtained, one by the reaction

$$Re(NHPh)(N_2)(PMe_3)_4 + 2CO = Re(NHPh)(CO)_2(PMe_3)_3$$

and the other, $Re(NHPh)(CO)_3(PMe_3)_2$, by reduction of $Re(NPh)Cl_3(PMe_3)_2$ under CO atmosphere.

The complex $Re(NHPh)(CO)_2(PMe_3)_3$ (**6**) forms air-sensitive orange crystals. The solution (toluene) IR spectrum shows the N–H stretch at 3360 cm^{-1} and terminal CO stretches at 1891 and 1940 cm^{-1} for *cis* CO groups.

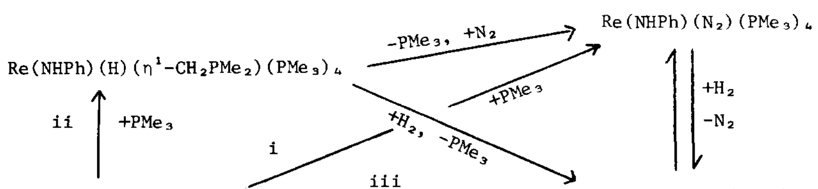
The ^1H NMR spectrum has a pseudo quintet centred at δ 1.14 ppm and a doublet (J = 4.0 Hz) centred at δ 1.35 ppm for the PMe_3 groups. The $^{31}P\{^1H\}$ NMR spectrum shows a doublet (J_{P-P} = 24.4 Hz) and triplet (J_{P-P} = 24.4 Hz) with relative intensity 2:1 at δ −64.97 and −70.94 ppm, respectively.

There are two possible isomers 6a, b. The *fac- cis* isomer should show either two doublets of relative intensity 2:1 or three doublets of relative intensity 1:1:1 for the ^1H NMR spectrum of the PMe_3 groups, whereas 6b should show either a triplet and a doublet of relative intensity 2:1 or two triplets and a doublet of relative intensity 1:1:1. The observed spectrum can be considered as having two overlapping triplets and a doublet suggesting a *mer* configuration of PMe_3 groups. Thus, the spectroscopic data fits best for the *mer- cis* isomer 6b.

The reduction of $Re(NPh)Cl_3(PMe_3)_2$ under carbon monoxide either at room temperature or in presence of two equivalents of PMe_3 at 60°C leads to the tricarbonyl complex $Re(NHPh)(CO)_3(PMe_3)_2$ (**7**) as air-sensitive orange crystals. The solution IR spectrum (benzene) shows the N–H stretch at 3360 cm^{-1} and terminal CO stretches (2006w, 1910m, 1850s). The ^1H NMR spectrum shows the N–H singlet (δ 2.72), two doublets at δ 1.28 ($^2J_{P-H}$ = 7.7 Hz) and δ 1.33 ppm ($^2J_{P-H}$ = 8 Hz) indicating non-equivalent PMe_3 groups as in (**7**) although the $^{31}P\{^1H\}$ spectrum has a broad singlet at δ −73.77 and some free PMe_3 at −62.8 ppm.

(e) *Phenylamido(buta-1,3-diene)tris(trimethylphosphine) rhenium(I)*

The reduction of $Re(NPh)Cl_3(PMe_3)_2$ by excess



Scheme. Reduction by Na/Hg under (i) N_2, (ii) Ar, (iii) H_2.

sodium amalgam under an atmosphere of butadiene in tetrahydrofuran leads to pale yellow crystals of $Re(NHPh)(\eta^4\text{-}C_4H_6)(PMe_3)_3$ (**8**). The IR spectrum has the N-H stretch at 3423 cm^{-1} in addition to PMe_3 and butadiene bands. The ^1H NMR spectrum has the N-$\underline{H}$ resonance at δ 2.74 ppm, resonances for $\eta^4\text{-}C_4H_6$ at δ 4.53, 1.50 and −0.35 ppm, plus three doublets for PMe_3 groups. The ^{31}P NMR has a triplet and two doublets. The spectra are in accord with the structure (**8**) which has been confirmed by X-ray diffraction study.

The gross structural features of the compound are shown in Fig. 2, and although we experienced some problems in the refinement of this structure, there is no doubt in our minds that the complex is correctly identified. In view of the uncertainties in some atomic positions (see Experimental) the bond-lengths and angles in Table 3, must be regarded with some suspicion and where relevant the esd's have been artifically increased.

Accordingly, the discussion of the structure can only be in general terms. One of the main points of note is that the $[Re(NHPh)(PMe_3)_3]$ unit has a very approximate mirror plane, defined by the NHPh group and containing P(3), so that P(1) and P(2) are ψ-mirror related. As far as we can tell, however, the butadiene group is *not* oriented symmetrically with respect to this approximate plane, even though the P(1), P(2) PMe_3 groups are pushed back towards the (NHPh) group almost equally [P(1)-Re-N = 77°, P(2)-Re-N = 76°].

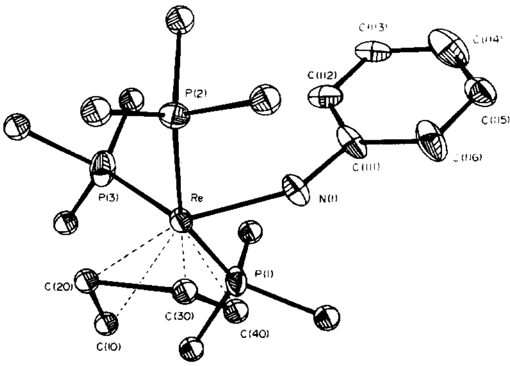
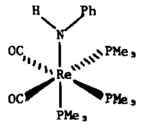
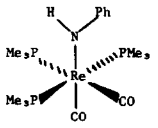


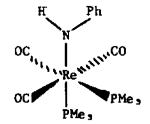
Fig. 2. The molecular structure of $Re(NHPh)(C_4H_6)(PMe_3)_3$.



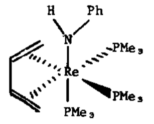
(6a)
fac-cis



(6b)
mer-cis



(7)



(8)

A second point of interest is that if the butadiene group is acting as a 4e donor, then, as in compound **3**, the Re atom achieves and 18e configuration without the need for any amido $p\pi$ donation; although the Re-N distance of 2.13(4)Å is smaller than the value found in compound **3**. The symmetrical orientation of the NHPh group may therefore be explained by intramolecular packing effects.

There are only few phosphine alkene complexes of rhenium. The complex $Re(H)_3(\eta^4\text{-}C_4H_6)(PPh_3)_2$ has been made from $ReH_7(PPh_3)_2$[8] while the latter complex in presence of 3,3-dimethylbut-1-ene dehydrogenates cyclopentane to $Re(H)_2(\eta^5\text{-}C_5H_5)(PPh_3)_2$.[9]

(f) *Phenylimido dichlorotris(trimethylphosphine)rhenium(IV)*

The only case where a phenylamido group is not formed is when $Re(NPh)Cl_3(PMe_3)_2$ in tetrahydrofuran is reduced with exactly one equivalent of sodium amalgam. The air sensitive dark red crystalline rhenium(IV) complex $Re(NPh)Cl_2(PMe_3)_3$ has no N-H stretch in the IR

Table 3. Bond lengths and angles for $Re(NHPh)(\eta^4\text{-}C_4H_6)(PMe_3)_3$

a) Bond Lengths (Å)		b) Bond Angles (°)	
Re-N(1)	2.13(4)	N(1)-Re-P(1)	77(1)
Re-P(1)	2.404(10)	N(1)-Re-P(2)	76(1)
Re-P(2)	2.432(8)	N(1)-Re-P(3)	128(1)
Re-P(3)	2.205(14)	P(1)-Re-P(2)	152(1)
Re-C(10)	2.31(6)	P(1)-Re-P(3)	97(1)
Re-C(20)	2.28(6)	P(2)-Re-P(3)	95(1)
Re-C(30)	2.26(15)		
Re-C(40)	2.28(12)	Re-N(1)-C(111)	140(3)
C(10)-C(20)	1.46(10)		
C(20)-C(30)	1.72(20)		
C(30)-C(40)	1.18(20)		

P-Me - fixed at 1.84 ± 0.01Å

spectrum but shows a Re=NPh band at 739 cm^{-1}. It is also paramagnetic but the magnetic moment (1.66 BM) is low. No EPR signal was observed at room temperature but a frozen benzene solution gave a single broad line centred on $g = 1.74$ with a line width between points of maximum slope of 80 mT. These observations are consistent with a low spin rhenium(IV) species with a ligand field of low symmetry.

EXPERIMENTAL

Microanalyses were by Pascher (Bonn) and Imperial College.

Spectrometers: IR: Perkin-Elmer 597, NMR: Perkin-Elmer R32 (^{1}H 90 MHz), Bruker WM-250 (^{1}H 250 MHz and ^{31}P 101.2 MHz, 28°C). ^{1}H data referenced to Me_4Si, ^{31}P to external 85% H_3PO_4: epr Varian E12 (X-band).

All operations were performed under oxygen-free nitrogen or argon or *in vacuo* and all solvents were dried over sodium and distilled from sodium/benzophenone under nitrogen immediately before use. Light petroleum had b.p. 40–60°C. Melting points were determined in sealed tubes under nitrogen (uncorrected). Analytical data is collected in Table 4.

$Re(NPh)Cl_3(PPh_3)_2$ was prepared according to the literature.[10]

IR spectra were obtained in Nujol mulls, except where stated otherwise.

1. *Phenylimidotrichloro(trimethylphosphine) (triphenylphosphine)rhenium(V)-toluene* (1)

To $Re(NPh)Cl_3(PPh_3)_2$ (2.0 g, 2.2 mmol) suspended in toluene (50 cm^3) was added excess trimethylphosphine (2 cm^3, 20 mmol) and the suspension stirred overnight at room temperature. The green solution was filtered, concentrated to *ca.* 5 cm^3 and cooled at −20°C to give green crystals which were collected, washed with diethyl ether and recrystallised from toluene. Yield 1.5 g, 82%: m.p., 210°C with loss of toluene.

IR cm^{-1}: 3060w, 1480m, 1448m, 1434s, 1410m, 1302w, 1284m, 1278m, 1090s, 1024m, 990w, 947vs, 846m, 760s, 743s, 727s, 692vs, 626s, 560m, 521vs, 514s, 492s.

2. *Phenylimidotrichlorobis(trimethylphosphine) rhenium(V)*, (2)

A suspension of $Re(NPh)Cl_3(PPh_3)_2$ (20.0 g, 22 mmol) and excess trimethylphosphine (8.0 cm^3, 80 mmol) in toluene (100 cm^3) were placed in a pressure bottle and the solution heated at 80–90°C for 18 hr. The green solution was cooled and filtered and the volatile materials removed under vacuum. The residue was extracted with hot toluene (*ca.* 100 cm^3), filtered, concentrated to *ca.* 30 cm^3 and cooled at −20°C. The green crystals were collected and washed with diethylether (50 cm^3) and dried *in vacuo*. Yield 9.4 g (80%); m.p., 239–241°C.

IR (KBr disc), cm^{-1}: 2978w, 2908m, 1408s, 1382m, 1284s, 1260m, 1110br, m, 1026m, 948vs, 860w, 850w, 769s, 748s, 554m.

NMR: $^{31}P\{^1H\}$, δ-40.87 *s* (PMe_3).

3. *Phenylamido(dinitrogen)tetrakis(trimethylphosphine) rhenium(I)*, (3)

A suspension of $Re(NPh)Cl_3(PPh_3)_2$ (2.0 g, 2.20 mmol) in thf (50 cm^3) was added to a solution of trimethylphosphine (3 cm^3, 30 mmol) in thf (50 cm^3) containing excess sodium amalgam (0.78 g, Na in 5 cm^3 Hg) at −78°C under dinitrogen. The solution was allowed to warm slowly and was stirred at ambient temperature for 18 hr. The red solution was filtered, evaporated to dryness under reduced pressure and the residue washed with petroleum (2 × 40 cm^3), then extracted into toluene (*ca.* 30 cm^3), filtered, concentrated (*ca.* 15 cm^3) and cooled at −20°C to give yellow crystals. Yield 1.1 g, 80%: m.p., 98°C (decomp.)

IR cm^{-1}: 3390w, 2000vs, 1590s, 1556m, 1490s, 1340s, 1320m, 1302m, 1284m, 1276m, 1225w, 1174w, 1020w, 980m, 965m, 938s, 856m, 828w, 734s, 710m, 692s, 660s, 518m, 506m.

NMR: $^{31}P\{^1H\}$, δ −67.92 *d* ($^2J_{P-P} = 42.72$ Hz), −70.72 br, s, −74.7br, s and −77.95br, s.

4. *Dihydrido(phenylamido)tetrakis(trimethylphosphine) rhenium(III)*, (4)

Method A. A suspension of $Re(NPh)Cl_3(PPh_3)_2$ (2.0 g, 2.2 mmol) in thf (50 cm^3) was added to excess trimethylphosphine (3.0 cm^3, 30 mmol) in thf (30 cm^3) with sodium amalgam (1.2 g Na in 5 cm^3 Hg) in a pressure bottle at −78°C. After pressurisation with hydrogen (3 atm) the solution was allowed to warm slowly; the bottle was repressurised and the solution stirred for 18 hr at room temperature. The solution was filtered, evaporated under reduced pressure and the residue was extracted with petroleum (40 cm^3), the solution filtered, concentrated to *ca.* 10 cm^3 and cooled to −20°C to give yellow crystals. Yield 0.83 g, 65%; m.p., 125–126°C (decomp.)

Method B. The complex $Re(NHPh)(N_2)(PMe_3)_4$ (0.85 g, 1.4 mmol) in toluene (50 cm^3) was stirred at room temperature for 12 hr under hydrogen (3 atm) with periodic repressurisation. The solution was filtered, evaporated in vacuum and the residue extracted into petroleum (25 cm^3). This solution was filtered, concentrated to *ca.* 10 cm^3 and cooled at −20°C to yield yellow crystals. Yield: 0.73 g, 90%.

IR cm^{-1}: 3380w, 1925br,w, 1885br,w, 1592s, 1487m, 1420w, 1335w, 1320w, 1298w, 1260s, 1085br,s, 1020br,s, 940vs, 851w, 800s, 732w, 700m, 658m.

NMR: $^{31}P\{^1H\}$, δ −41.63br, s; −45.39br,s (PMe_3).

Table 4. Analytical data

Compound	Analysis %[a]					M[b]
	C	H	N	P	Cℓ	
1. $Re(NPh)C\ell_3(PMe_3)(PPh_3).C_7H_8$	50.3 (50.2)	4.6 (4.6)	1.7 (1.7)	7.6 (7.6)	13.0 (13.1)	
2. $Re(NPh)C\ell_3(PMe_3)_2$	27.0 (26.9)	4.3 (4.3)	2.6 (2.6)	11.7 (11.6)	19.5 (19.9)	
3. $Re(NHPh)(N_2)(PMe_3)_4$	35.2 (35.4)	6.9 (6.9)	6.5 (6.9)	20.2 (20.3)		580 (610)
4. $Re(NHPh)(H)_2(PMe_3)_4$	36.9 (37.0)	7.5 (7.6)	2.4 (2.4)	20.4 (21.0)		550 (584)
5. $Re(NHPh)(H)(CH_2PMe_2)(PMe_3)_4$	38.3 (38.3)	7.9 (7.8)	2.3 (2.1)	23.5 (23.5)		620 (658)
6. $Re(NHPh)(CO)_2(PMe_2)_3$	36.2 (36.3)	5.9 (5.9)	2.7 (2.5)	16.5 (16.6)	[c]	530 (563)
7. $Re(NHPh)(CO)_3(PMe_3)_2$	35.4 (35.0)	4.8 (4.7)	2.6 (2.7)	12.1 (12.1)	[d]	510 (514)
8. $Re(NHPh)(C_4H_6)(PMe_3)_3$	40.4 (40.8)	7.0 (6.8)	2.6 (2.5)		16.5 (16.6)	540 (559)
9. $Re(NPh)C\ell_2(PMe_3)_3$	31.9 (31.0)	5.4 (5.5)	1.9 (2.4)	16.3 (16.0)	11.9 (12.2)	600 (576)

[a] Calculated values in parenthesis

[b] Cryoscopically in benzene

[c] O, 6.1 (5.7)%

[d] O, 9.5 (9.3)%

5. *Phenylamidohydrido(η^1 - dimethylphosphidomethyl)tetrakis-(trimethylphosphine) rhenium(III)*, (5)

Excess trimethylphosphine (2.0 cm^3, 20 mmol) and a suspension of $Re(NPh)Cl_3(PPh_3)_2$ (2.0 g, 2.2 mmol) in thf (100 cm^3) was stirred with sodium amalgam (0.7 g, Na in 5 cm^3 Hg) under argon at −78°C. The solution was allowed to warm slowly and stirred at ambient temperature for 18 hr. The deep red solution was filtered, evaporated to dryness under reduced pressure and the residue extracted with toluene (50 cm^3) which was filtered, concentrated *ca.* 15 cm^3, and cooled at −20°C to give yellow crystals. Yield 1.15 g, 85%; m.p., 124–126°C (decomp.).

IR cm^{-1}: 3386w, 1980m, 1590s, 1550m, 1485s, 1430s, 1338s, 1330s, 1272s, 1265s, 1225w, 1162m, 1140m, 1062w, 1015w, 980m, 946vs, 850s, 828s, 725m, 690s, 640s.

NMR: $^{31}P\{^1H\}$, δ −39.8br,m; −43.89br, s; −52.70br,s.

6. *Phenylamidobis(carbon monoxide)tris(trimethylphosphine) rhenium(I)*, (6)

A solution of $Re(NHPh)(N_2)(PMe_3)_4$ (0.72 g, 1.18 mmol) in toluene (50 cm^3) was pressurised with CO (3 atm) in a pressure bottle and stirred at room temperature for 12 hr with occasional repressurisation.

The solution was filtered, evaporated and the residue extracted into toluene (35 cm^3). After filtering the solution was concentrated to *ca.* 20 cm^3 and cooled to −20°C to yield orange crystals which were washed with petroleum and dried. Yield 0.6 g, 90%; m.p., 172–173°C.

IR cm^{-1}: 3360w, 1908s, 1825s, 1590m, 1485m, 1422w, 1330m, 1312m, 1309m, 1287w, 1280w, 1171w, 1025w, 980w, 948s, 860w, 845w, 740m, 728m, 722m, 690m, 670m.

NMR: $^{31}P\{^1H\}$, δ −64.97 *d* ($^2J_{P-P}$ = 24.4 Hz); −70.94 t ($^2J_{P-P}$ = 24.4 Hz).

7. *Phenylamidotris(carbon monoxide)bis(trimethylphosphine) rhenium(I)*, (7)

To a solution of $Re(NPh)Cl_3(PMe_3)_2$ (0.6 g, 1.1 mmol) in thf (50 ml) was added sodium amalgam (1.1 g, Na in 5 ml Hg) in thf (50 ml) in a pressure bottle. After pressurising with carbon monoxide (2 atm) the solution was stirred at ambient temperature for 18 hr. The bottle was repressurised periodically. The solution was filtered and evaporated to dryness under reduced pressure. The residue was extracted with petroleum (2 × 40 cm^3), filtered, concentrated to *ca.* 50 cm^3 and cooled to −20°C to yield orange crystals which were washed with petroleum and dried. Yield 0.42 g (75%); m.p., 143–145°C.

IR cm^{-1}: 3360w, 1950w, 1874s, 1855s, 1590m, 1485m, 1335w, 1320w, 1312w, 1304w, 1285m, 1252w, 1160br,w, 1090br,w, 1020w, 982w, 964w, 948s, 858m, 804m, 739m, 724m, 692w, 672m, 630w, 600m.

IR (benzene) cm^{-1}. 3360w, 2006w, 1910m, 1850vs.

8. *Phenylamido(η^4 - buta - 1,3 - diene)tris(trimethylphosphine) rhenium(V)* (8)

The solution of $Re(NPh)Cl_3(PMe_3)_2$ (0.8 g, 1.5 mmol) in thf (50 cm^3) and excess sodium amalgam [0.8 g, 35 mmol in Hg (5 cm^3)] in a pressure bottle was pressurised with buta-1,3-diene slightly over atmospheric pressure and stirred overnight at room temperature. The solution was filtered and taken to dryness under vacuo. The residue was extracted into petroleum (2 × 30 cm^3), filtered, concentrated to *ca.* 10 cm^3 and cooled to −20°C, to give yellow crystals. Yield 0.5 g, 60%; m.p. 162–164°C (decomp.)

IR cm^{-1}: 3423w, 1588m, 1557w, 1487m, 1437m, 1418w, 1332w, 1320w, 1295m, 1280w, 1270w, 1209w, 1163w, 1141w, 1064w, 1040w, 1020w, 984m, 945s, 850m, 810m, 760m, 715m, 692m, 665m, 650m.

$^{31}P\{^1H\}$, δ −43.83 *t* ($^2J_{P-P}$ = 24.4 Hz), −39.98 d ($^2J_{P-P}$ = 24.4 Hz); −40.36 *d* ($^2J_{P-P}$ = 30.5 Hz) plus weak free PMe_3 at δ −61.85 ppm.

9. *Phenylimidodichlorotris(trimethylphosphine)rhenium(IV)*, (9)

A solution of $Re(NPh)Cl_3(PMe_3)_2$ (1.0 g, 1.87 mmol) in thf (70 cm^3) was added to a solution of trimethylphosphine (2 cm^3, 20 mmol) in thf (50 cm^3) containing exactly 1 equivalent of sodium amalgam (0.043 g in 2 cm^3 Hg) at room temperature. The mixture was stirred for 18 hr at ambient temperature. The red solution was filtered, evaporated to dryness under reduced pressure and the residue extracted with toluene (2 × 35 cm^3), filtered, concentrated to *ca.* 30 cm^3 and cooled to −20°C to give dark red crystals. Yield 0.87 g, 81%; m.p., 179–180°C.

IR cm^{-1}: 3032w, 3022w, 1560m, 1525w, 1475s, 1430m, 1415m, 1390w, 1340w, 1300m, 1280s, 1160w, 1148w, 1068w, 945vs, 856w, 800w, 739s, 722m, 680m, 665w, 650w, 500w.

10. *Crystallographic studies*

Crystal data. Compound 3. $C_{18}H_{42}N_3P_4Re$, $M = 610.65$, monoclinic, $a = 9.574(2)$, $b = 19.528(3)$, $c = 14.385(3)$Å, $\beta = 99.06(2)°$, $U = 2655.9$ Å; space group $P2_1/n$, $Z = 4$ $D_c = 1.53$ g cm^{-1}, D_M not measured, $F(000) = 1224$, μ(Mo–Kα) = 48.5 cm^{-1}.

Compound 8. $C_{18}H_{39}NP_3Re$, $M = 548.64$ orthorhombic, $a = 12.207(2)$, $b = 13.884(2)$, $c = 14.242(2)$Å, $U = 2413.7$ Å^3; space group $Pbc2_1$, $Z = 4$, $D_c = 1.509$ g cm^{-3}, D_M not measured, $F(000) = 1096$, μ(Mo–$K\alpha$) = 50.0 cm^{-1}.

Data collection.[11] CAD4 diffractometer, Mo–$K\alpha$ radiation, ($\lambda = 0.71069$ Å graphite monochromator), $\theta/2\theta$ scan mode.

Compound 3. $1.5 \leqslant \theta \leqslant 25.0$, 4662 data measured, 3249 observed [$I > 1.5\sigma(I)$]; uncorrected for absorption (crystal encapsulated by vacuum grease).

Compound 8. $1.5 \leqslant \theta \leqslant 25.0$, 3066 data measured, 2009 observed [$I > 1.5\sigma(I)$]; corrected for absorption and decay.

Structure solution and refinement

Heavy atom method, full matrix least squares. The structure of compound 3 was refined without problems to final R values of $R = \Sigma|\Delta F|/\Sigma|F_0| = 0.065$, $R_W = [\Sigma(\omega\Delta F_0)^2/\Sigma\omega F_0^2]^{\frac{1}{2}} = 0.064$ with $\omega = 1/[\sigma^2(F_0) + 0.006F_0^2]$. Non-hydrogen atoms were assigned anisotropic thermal parameters, hydrogen atoms were added in idealised positions but allowed to shift according to the movement of the parent C or N atoms and assigned a refineable overall isotropic thermal parameter. The structure of compound **8** was easily solved for the heavy atom position but developed with difficulty due to pseudo-symmetry correlation effects. Eventually enough of the structure was defined to confirm the adoption of the chosen space group, rather than the centrosymmetric alternative, *Pbcm*, but it was found impossible to select an acceptable model for the positions of the butadiene carbon atoms. Additionally, free refinement gave some rather abnormal parameters in the PMe_3 groups (e.g. Re–P(3) = 2.19(1) Å, P–C = 1.66(4) – 1.90(3) Å, although the R value was quite low (0.058). Close analysis of the structure showed that in fact some of the P(3) methyl groups were pseudo-mirror related (i.e. across $Z = 0.25$) to atoms thought to constitute the butadiene group. Unsure of how the Re–P distances may vary in this structure we felt only partially able to tackle the problem by fixing the P–Me bond lengths to well established values. This failed to remove the uncertainty surrounding the detailed identification of the butadiene unit and we can only presume that this group is affected not only by pseudo-symmetry correlation but also perhaps disorder. Attempts to refine using an idealised C_4 group were unsuccessful. The final model presented, therefore contains some residual uncertainties, and the esd's in the coordinates have been adjusted to signify this. The final R, R_W values (see above) are 0.0615 and 0.0583, respectively. Only the rhenium, phosphorus and phenyl amido group atoms were refined anisotropically, and the amido phenyl group was treated as an ideal C_6 hexagon.

Final atomic coordinates for both compounds, tables of anisotropic thermal parameters and lists of F_0/F_c have been deposited with the Editor as supplementary material.† Computers, programs and sources of scattering factor data are given in Ref. 11.

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†Atomic co-ordinates for these structures have also been deposited with the Cambridge Crystallographic Data Centre for inclusion in their Data Base. Copies are also available on request from the Editor at Queen Mary College.

REFERENCES

[1] G. La Monica and S. Cenini, *J. Chem. Soc. Dalton Trans.* 1980, 1145.

[2] W. A. Nugent and R. L. Harlow, *J. Chem. Soc. Chem. Commun.* 1979, 1105.

[3] J. Chatt, J. D. Garforth, N. P. Johnson and G. A. Rowe, *J. Chem. Soc. Dalton Trans.* 1964, 1012.

[4] J. Chatt, J. R. Dilworth and G. J. Leigh, *J. Chem. Soc. Dalton Trans.* 1973, 612.

[5] B. R. Davis and J. A. Ibers, *Inorg. Chem.* 1971, **10**, 578.

[6] H. Schmidbauer and G. Blaschke, *Z. Naturforsch. Teil B* 1980, **35**, 584; H. Werner and R. Werner, *J. Organomet. Chem.* 1981, **209**, C60.

[7] N. E. Schore and H. Hope, *J. Am. Chem. Soc.* 1980, **102**, 4251.

[8] D. Baudry and M. Ephritikhine, *J. Chem. Soc., Chem. Commun.* 1980, 249.

[9] D. Baudry, M. Ephritikhine, H. Felkin, Y. Jeannin and F. Robert, *J. Organomet. Chem.*, 1980, **220**, C7; see also M. A. Green, J. C. Huffman, K. G. Caulton, W. K. Rybak and J. F. Ziółkówski, *J. Organomet. Chem.* 1981, **218**, C39.

[10] J. Chatt, J. R. Dilworth and G. J. Leigh, *J. Chem. Soc.* (*A*) 1970, 2239.

[11] M. B. Hursthouse, R. A. Jones, K. M. A. Malik and G. Wilkinson, *J. Am. Chem. Soc.* 1979, **101**, 4128.