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Proton addition and hydrogen-bond formation in reactions of the dicyano-complex $[NBu_4]$[*trans*-$Re(CN)_2(dppe)_2$] with protic reagents

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$[NBu_4]$[*trans*-$Re(CN)_2(dppe)_2$] (**1**, dppe = $Ph_2PCH_2CH_2PPh_2$) reacted with protic acids (HA = HBF_4, CH_3CO_2H or $[Et_3NH][BPh_4]$, added in stoichiometric amounts) to give, on protonation of one of the cyano-ligands, the isocyanide complex *trans*-$[Re(CN)(CNH)(dppe)_2]$ **3a**, whereas the hydrogen-bonded cyano-adducts *trans*-$[Re(CN{\cdot}HO_2CCF_3)_2(dppe)_2]$ **4**, *trans*-$[Re(CN{\cdot}HOMe)_2(dppe)_2]$ **5** and *trans*-$[Re(CN{\cdot}HNEt_3)_2(dppe)_2][BPh_4]$ **6** were obtained on treatment of **3a** with an excess of CF_3CO_2H or of **1** with an excess of MeOH or $[Et_3NH][BPh_4]$, respectively. However, solvent or other molecules can be trapped in the crystal lattice without hydrogen-bond interaction and *trans*-$[Re(CN)_2(dppe)_2]{\cdot}2L$ (L = MeOH **2a** or Me_2CO **2b**) or *trans*-$[Re(CN)_2(dppe)_2]{\cdot}NEt_3$ **7** are formed on attempted recrystallization of **1** from MeOH or Me_2CO, or as a side product in the reaction of **1** with $[Et_3NH][BPh_4]$, respectively. The crystal structures of **2b**, **4**, **5** and partially that of **2a** were also determined and the anodic cyclic voltammetric behaviour (which is shown to distinguish between the CN–H and the hydrogen-bond CN $\cdots$ H formations) of the above complexes is described as well as an interpretative theoretical study (by extended Hückel and *ab initio* methods) of the CN and CNH complexes.

Introduction

There has been a recent growth of interest in the development of an C≡NH/C≡N based organometallic chemistry,[1–4] and we have addressed this field by investigating the activation of these unsaturated species by electron-rich N_2-binding metal centres, as well as their interconversion in view of its significance[5,6] within the biological reduction of aqueous cyanide by nitrogenase. Hence, we have already reported the syntheses of *trans*-$[ReCl(CNH_n)(dppe)_2]^{n-1}$ ($n = 0$,[7] 1[8–11] or 2;[8–11] dppe = $Ph_2PCH_2CH_2PPh_2$) as well as the chemical and electrochemical interconversions[9–11] of the cyano ($C{\equiv}N^-$), isocyano (C≡NH) and aminocarbyne (CNH_2^+) species, and the synthetic application of the complexes with the cyano-protonated ligands in the preparation of the cyano-compounds *trans*-$[Re(CN)L(dppe)_2]$ (L = NCR, N_2, CO or vinylidene).[10] The CN/CNH interconversion was also recently investigated at *trans*-$[FeH(CNH_n)(dppe)_2]$ ($n = 0$ or 1)[4,12] and at *trans*-$[M(H_2)(CNH_n)(LL)_2]^{n+1}$ ($n = 0$ or 1; M = Fe, Ru or Os; LL = bidentate diphosphine).[2,3] The acidity of the CNH_n ($n = 1$[2,3,9–11] or 2[9–11]) ligands and their possible involvement in hydrogen-bonding[2,3,8] have also been recognized.

In the current study we extended the investigation of the coordination chemistry of the CN/CNH couple to the rhenium(I) dicyano-complex $[NBu_4]$[*trans*-$Re(CN)_2(dppe)_2$] **1** in which the cyanide ligands are known to be prone to electrophilic attack by an alkylating agent, RI (R = Me, Et or Pr) or $[Et_3O][PF_6]$,[13,14] or by a Lewis acid metal ion ($M^+ = Li^+$, Na^+, Tl^+ or Ag^+)[13] to give the corresponding diisocyanide complexes *trans*-$[Re(CNR)_2(dppe)_2]^+$ or the adducts *trans*-$[Re(CN)(CNM)(dppe)_2]$, respectively. We have now observed that the ligating CN in **1** can also undergo ready protonation to give CNH or hydrogen-bond formation (mainly detected for its oxidized derivative *trans*-$[Re(CN)_2(dppe)_2]$ **2**) with a variety of protic species including Brönsted acids (HBF_4, CH_3CO_2H, CF_3CO_2H or $[Et_3NH][BPh_4]$) or methanol. This double propensity of the cyano-ligand is examined by various techniques and methods (spectroscopic, X-ray structural, electrochemical and theoretical) and can clearly be exhibited in the current systems, although the ability of the crystal lattice to trap (even without the formation of hydrogen bonds) polar molecules (MeOH, Me_2CO or NEt_3) was also shown for **2** by X-ray diffraction.

Results and discussion

Formation of CNH and hydrogen-bonded cyano-complexes

Treatment of a THF solution of $[NBu_4]$[*trans*-$Re(CN)_2(dppe)_2$] **1** with a stoichiometric amount of $[Et_3NH][BPh_4]$ or $[Et_3ND][BPh_4]$ affords whitish products of low solubility in common solvents which are formulated as the isocyanide complexes *trans*-$[Re(CN)(CNE)(dppe)_2]$ (E = H **3a** or D **3b**, respectively) [Scheme 1(a)] on the basis of their spectroscopic and analytical data (Experimental section). Complex **3a** is also obtained on reaction of **1** with CH_3CO_2H or $HBF_4{\cdot}Et_2O$, added also in stoichiometric amounts. The use of an excess of acid leads to the formation of a mixture of unidentified products, conceivably due, at least in part, to the competition of various sites for the protons and/or to side reactions (see below) of the cyanide ligand with the BF_4^- or BPh_4^- anions. In the related complexes *trans*-$[M(H)(CN)(LL)_2]^+$ (M = Fe, Ru or Os, LL = bidentate diphosphine)[2] protonation can occur at the cyanide, hydride or metal to afford a variety of products.

The IR spectra of *trans*-$[Re(CN)(CNE)(dppe)_2]$ (E = H **3a** or D **3b**) display two stretching frequencies in the CN region at 1895 **3a** (1890, **3b**) and 2049 **3a** (2050, **3b**) cm^{-1} which are attributed to ν(CN) of the CNH (or CND) and CN ligands, respectively, but no clear signals were observed for ν(NH) or ν(ND). The isocyanide (CNH) displays a ν(CN) value higher than that of the related chloro-complex *trans*-$[ReCl(CNH)(dppe)_2]$ (1725, 1685 cm^{-1})[8] (in accord with the weaker π-electron releasing ability of the $\{Re(CN)(dppe)_2\}$ centre compared to $\{ReCl(dppe)_2\}$), but well in the range

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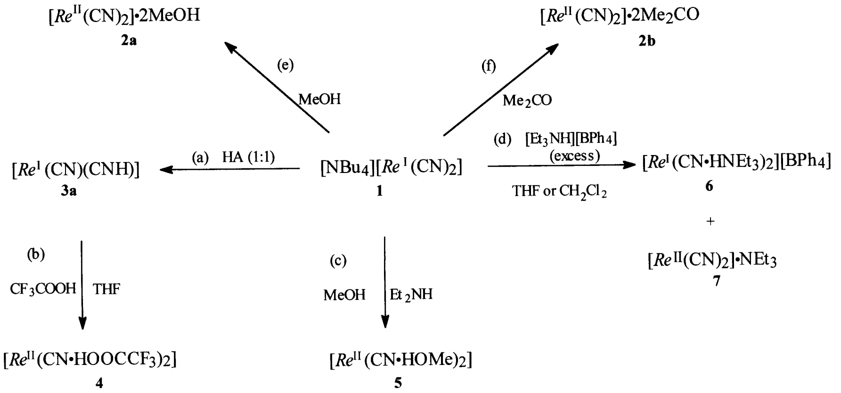


Scheme 1 Reactions of $[NBu_4][\mathit{Re}(CN)_2]$ **1**. *Re* = *trans*-{Re(dppe)$_2$}. (a) HA = $[Et_3NH][BPh_4]$ (THF), CH_3CO_2H (CH_2Cl_2) or $HBF_4{\cdot}Et_2O$ (CH_2Cl_2).

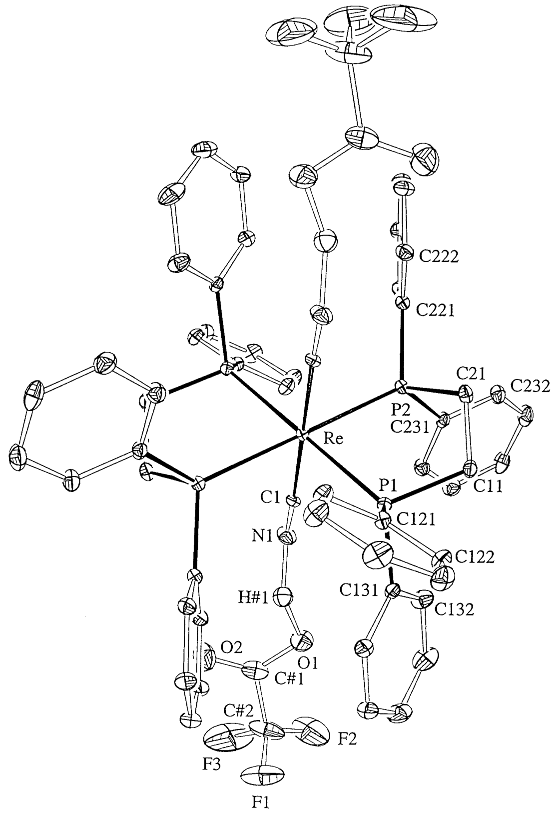


Fig. 1 Molecular structure of *trans*-$[Re(CN{\cdot}HO_2CCF_3)_2(dppe)_2]$ **4**, showing the atom labeling scheme.

of the alkyl isocyanide complexes *trans*-$[ReCl(CNR)(dppe)_2]$ (R = alkyl).[15] The cyanide ligand in **3a** or **3b** displays ν(CN) at a value that is identical to that of free CN^-, *e.g.* in $[NBu_4]CN$ (2050 cm^{-1}), and considerably higher than that observed for its precursor **1** (1995 cm^{-1}). This indicates that it is not behaving as an extensive π-electron acceptor in spite of the expected π-electron releasing ability of the electron-rich rhenium(I) site or, alternatively, is involved in a hydrogen bridge with an isocyanide ligand of another molecule. It is generally accepted that bridging cyanides display higher stretching frequencies than terminal ones,[16,17] and a hydrogen bridge could also account for the absence of a clearly observable ν(NH) band in the IR spectrum and for the low solubility of the complexes in usual solvents.

On dissolution in common solvents (*e.g.* CH_2Cl_2 or THF), complexes **3a** or **3b** undergo ready decomposition to paramagnetic species, mostly *trans*-$[Re(CN)_2(dppe)_2]$ **2**, a red product that is also formed in the solid state even under dinitrogen. Hence, attempts at recrystallization resulted in the isolation of **2**.

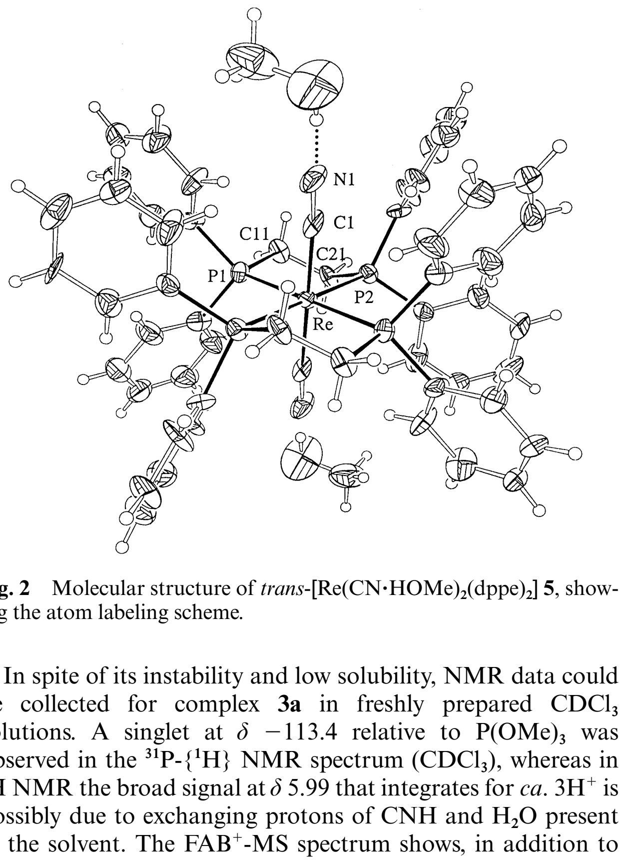


Fig. 2 Molecular structure of *trans*-$[Re(CN{\cdot}HOMe)_2(dppe)_2]$ **5**, showing the atom labeling scheme.

In spite of its instability and low solubility, NMR data could be collected for complex **3a** in freshly prepared $CDCl_3$ solutions. A singlet at δ −113.4 relative to $P(OMe)_3$ was observed in the ^{31}P-{^1H} NMR spectrum ($CDCl_3$), whereas in ^1H NMR the broad signal at δ 5.99 that integrates for *ca.* $3H^+$ is possibly due to exchanging protons of CNH and H_2O present in the solvent. The FAB^+-MS spectrum shows, in addition to the molecular ion, a signal (m/z = 1053) assigned to the H_2O adduct.

In order to get further insight on the interaction of rhenium cyanide species with acids, a THF solution of *trans*-$[Re(CN)(CNH)(dppe)_2]$ **3a** was treated with a large excess (up to a twenty-fold molar ratio) of CF_3CO_2H (Scheme 1(b)). The violet product **4** exhibits, in the IR spectrum, ν(C≡N) bands at 2045s and 1949m cm^{-1}, as well as a strong ν(C=O) band at 1702 cm^{-1} and two weak bands at 2916 and 2852 cm^{-1} assigned to hydrogen-bonded ν(NH). By X-ray diffraction analysis, **4** was identified as the diadduct *trans*-$[Re(CN{\cdot}HO_2CCF_3)_2(dppe)_2]$ and therefore its formation involved oxidation of the metal. Liberation of H_2 gas was not observed and the hydrogen atom acceptor has not been identified. The molecular structure of **4** is depicted in Fig. 1, showing one hydrogen-bonded acid molecule per cyanide ligand. The short N···O distance (2.61(2) Å) is comparable to that (2.616(4) Å) reported for $[Ru(OTf)(CNH)(dppe)_2]OTf$[2] (OTf = O_3SCF_3) and indicates a strong N···H···O interaction.

Hydrogen bonding was also detected by X-rays (see below for details) in the red MeOH diadduct *trans*-$[Re(CN{\cdot}HOMe)_2(dppe)_2]$ **5** (Fig. 2) formed from complex **1** in MeOH in the presence of Et_2NH, with involvement of metal oxidation (Scheme 1 (c)) as in the previous case. In **5** the solvent molecules point to the cyanide ligands at short $N\cdots O$ distances (2.74(5) Å), consistent with hydrogen bridging.[3,4,18–20] The IR spectroscopic evidence for a hydrogen bond is provided by the detection of two broad and weak ν(NH) bands at 2927 and 2808 cm^{-1}, in addition to a strong one at 3303 cm^{-1}.

The related diadduct, although of Re^I, *trans*-$[Re(CN\cdot H\text{-}NEt_3)_2(dppe)_2][BPh_4]$ **6** was obtained (Scheme 1 (d)) by treatment of a THF or CH_2Cl_2 solution of $[NBu_4]$[*trans*-$Re(CN)_2(dppe)_2$] **1** with an excess (higher than threefold) of $[Et_3NH][BPh_4]$. It is yellow in colour and the presence of hydrogen-bonded Et_3NH^+ is indicated by IR (2678, 2492 cm^{-1}). ν(CN), 1989 cm^{-1}, is slightly lower than that reported for **1** (1995 cm^{-1}),[14] as would be expected for the partial isocyanide character of the ligand in **6**. The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows a singlet at δ −108.6 and the elemental analysis supports the formulation. Moreover, the low oxidation potential of **6** (see below) corroborates the rhenium(I) oxidation state.

These results indicate that the cyanide ligands at the electron-rich rhenium–diphosphine centre are prone to establish hydrogen-bond interactions with proton donors (such as MeOH, CF_3CO_2H or Et_3NH^+) and, to a lesser extent, can also form a N–H covalent bond giving the ligating isocyanide CNH in *trans*-[Re(CN)(CNH)$(dppe)_2$] **3a** whose very low solubility possibly constitutes a driving force for its isolation. The tendency of the cyanide ligand for hydrogen bonding is known[2–4,18–20] in other cases and in particular the cyanide–hydrogen isocyanide bridge that we have postulated above for **3a** was established[19] by X-ray diffraction in $[Cr(CO)_5\{CN\cdot H\cdot NC\}Cr(CO_5)]^-$. Moreover, the ability of the cyanide ligands in complex **1** to form adducts with metal ions was detected before in its reactions with $Ag[BF_4]$,[14] $Tl[BF_4]$, NaI or LiI[13] to give $[Re(CN)(CNM)(dppe)_2]$ ($M = Ag^+$, Tl^+, Na^+ or Li^+). These adducts display very low solubility in solvents such as CH_2Cl_2 or THF, as observed for **3a**. The formulation of adducts with 2 NaI was also proposed on the basis of a kinetic study[13] of the alkylation of **1**. In the case of the reactions of **1** with protic acids, diadducts with hydrogen-bonded acids to the two cyanide ligands can be formed (complexes **4**–**6**), but no complex with two protonated cyanide ligands was detected.

In the protonation reactions [(a) and (d), Scheme 1] described above with HBF_4 or $[Et_3NH][BPh_4]$ we did not get any evidence for the possibility of conversion of the CN^- (or CNH) ligand into ligated $CNBPh_3^-$ or $CNBF_3^-$, which has been reported[12,21–23] in other systems with $Na[BPh_4]$ or HBF_4, respectively. Such possibilities are ruled out in our case by (i) the recognition that the same cyano-product **3a** is obtained in reaction (a) (Scheme 1) when using an acid like CH_3CO_2H that could not behave as a source of BF_3 or BPh_3, (ii) IR data that show ν(CN) in **6** at a lower wavenumber, 1989 cm^{-1}, than the expected one for the $CNBPh_3^-$ ligand which should be higher[12,23] than that, 1995 cm^{-1}, of the corresponding cyano-complex **1**, (iii) elemental analyses, and (iv) FAB^+-MS. Metal fluorination by HBF_4, known[24–26] to occur in other systems, was also not detected in our reactions (the diamagnetic products exhibit a singlet resonance in the $^{31}P\text{-}\{^1H\}$ NMR spectra without any splitting due to $^{31}P\cdots{}^{19}F$ coupling).

Other cyano-complexes

The capacity of *trans*-$[Re(CN)_2(dppe)_2]$ **1** to accommodate solvent molecules in the lattice, without any hydrogen-bond stabilizing effect, was clearly shown by the X-ray analyses (see below for details) of *trans*-$[Re(CN)_2(dppe)_2]\cdot 2MeOH$ **2a** (Fig. 3a) and *trans*-$[Re(CN)_2(dppe)_2]\cdot 2Me_2CO$ **2b** (Fig. 3b) obtained [Scheme 1 (e) and (f)] from slow recrystallization of **1** from methanol or acetone, respectively. They display non-interacting ordered solvent molecules. In particular the structures of **5** and **2a** show that MeOH can occupy a vacant space in the lattice either at a bridging (**5**) or at a non-bridging (**2a**) distance of the cyanide ligand.

Table 1 Selected bond lengths (Å) and angles (°) of complexes **2b**, **4** and **5**

	2b	4	5
Re(1)–C(1)	2.13(1)	2.068(6)	2.05(2)
Re(1)–P(1)	2.415(3)	2.4225(13)	2.437(4)
Re(1)–P(2)	2.417(3)	2.4357(14)	2.418(4)
P–C(av.)	1.82	1.84	1.83
N(1)–C(1)	1.12(2)	1.154(7)	1.17(2)
C(11)–C(21)	1.51(2)	1.522(8)	1.50(2)
C(1)–Re(1)–P(1)	95.4(4)	91.2(2)	95.5(5)
C(1)–Re(1)–P(2)	82.6(4)	82.1(2)	86.6(4)
P(1)–Re(1)–P(2)[a]	100.2(1)	99.98(5)	98.4(1)
N(1)–C(1)–Re(1)	174(1)	177.8(5)	175(2)

[a] Open face.

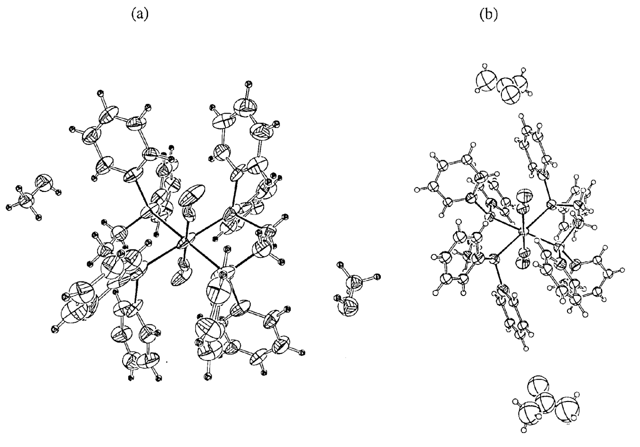


Fig. 3 Molecular structures of *trans*-$[Re(CN)_2(dppe)_2]\cdot 2MeOH$ **2a** (a) and *trans*-$[Re(CN)_2(dppe)_2]\cdot 2Me_2CO$ **2b** (b).

Complexes **2a** and **2b** are red, as other rhenium(II) complexes, and display a common ν(CN) value (2030 cm^{-1}) which is also identical to that of **5** (2033 cm^{-1}) indicating that the value of ν(CN) does not allow one to distinguish between those cyano-complexes and their cyano-adducts with solvent. Nevertheless, the presence in **2a** or **2b** of solvent of crystallization is indicated by a medium intensity band (1710 cm^{-1}) attributed to ν(CO) of the acetone molecule (**2b**) or by a band at 1036 cm^{-1} assigned to MeOH (**2a**). A red compound related to these, formulated as *trans*-$[Re(CN)_2(dppe)_2]\cdot NEt_3$ **7** on the basis of elemental analysis, IR and FAB^+-MS, was obtained as a secondary product in the reaction of **1** with $[Et_3NH][BPh_4]$ that gives mainly (see above) *trans*-$[Re(CN\cdot HNEt_3)_2(dppe)_2][BPh_4]$ **6**. Its formation involves oxidation of Re^I in solution and deprotonation of triethylammonium.

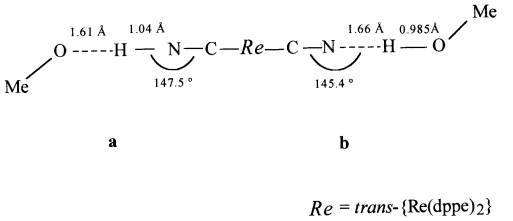
Crystal structures of the hydrogen-bonded cyano-complexes and solvent adducts

The crystal structures of the dicyano-complexes $[NBu_4]$[*trans*-$Re(CN)_2(dppe)_2$] **1** and *trans*-$[Re(CN)_2(dppe)_2]$ **2** were previously established,[13] and now we report the single crystal X-ray diffraction analyses of *trans*-$[Re(CN\cdot HO_2CCF_3)_2(dppe)_2]$ **4**, *trans*-$[Re(CN\cdot HOMe)_2(dppe)_2]$ **5** and *trans*-$[Re(CN)_2(dppe)_2]\cdot 2Me_2CO$ **2b** whose molecular structures are shown in Figs. 1–3, selected bond lengths and angles being given in Table 1. The structure of *trans*-$[Re(CN)_2(dppe)_2]\cdot 2MeOH$ **2a**, Fig. 3(a), is depicted for comparative purposes, although the low quality of the crystal did not allow a full determination of the structure.[27] All the complexes display a pseudo-octahedral geometry similar to that reported[13] for **2**, and two solvent or acid molecules per rhenium atom have been located. In **2b** the cavity that hosts the solvent is directed towards the P–Re–P face that has one P atom of each phosphine, while in **2a**, **4** or **5** it is oriented to the P–C–C–P face containing the methylene groups of dppe.

Compound **4** is triclinic, whereas **2a**, **2b** and **5** are monoclinic. Compounds **4** and **5** crystallize in the $P\bar{1}$ and $P2_1/a$ space group, respectively, and **2a** and **2b** in the $P2_1/c$ group. Since the crystallographic space group has an inversion centre at the metal, the H#1 atom (Fig. 1) is at an average position between the added protic molecule and the protonated cyanide.

From the crystallographic data we conclude that the structure of the dicyanide complexes can allocate the molecules of the solvent or acid in two different types of cavity: one that surrounds the diphosphine ligands and has no intermolecular contacts with the metal or the cyanide ligands, and another one close to the latter ligands. The former type of cavity can accommodate either a non-protic (acetone in **2b**) or a protic (methanol in **2a**), whereas the latter can host a species (MeOH or CF_3CO_2H, in **5** or **4**, respectively) that can form a hydrogen bond with the cyanide ligand.

In view of the hydrogen bonds present in complexes **4** and **5**, each axial ligand can be considered to exhibit a partial cyanide (CN^-) and a partial isocyanide (CNH) character, the hydrogen atom of the latter being shared by the acid or the solvent and the ligated cyano group. It may even be that the relative CNH/CN character differs for the two *trans* ligands, as suggested by the two distinct *ν*(CN) bands shown by the IR spectrum of **4**. The band at the lower wavenumber (1949 cm^{-1}) is consistent with a predominant isocyanide character and consequently with a significant covalent N–H interaction, whereas that at a higher value (2045 cm^{-1}) is well in the range of the cyanide ligand frequencies for cyano-complexes, thus suggesting a weaker N···H interaction. Unrestricted Hartree–Fock *ab initio* calculations performed on the model complex *trans*-[Re(CNH·OMe)$_2$(PH$_3$)$_4$] confirm this interpretation. The distance between the nitrogen atom of one of the cyanide ligands (**a**, Scheme 2) and the hydrogen atom of MeOH, 1.04 Å, is in the range expected for a covalent bond, whereas that between the O and the H atoms, 1.61 Å, corresponds to a bridging interaction. In contrast, the distance (1.66 Å) of the hydrogen to the nitrogen atom of the other cyanide ligand (**b**, Scheme 2) is longer and that between the O and the H atoms, 0.985 Å, is shorter. Hence the calculations suggest that the complex should be better formulated as *trans*-[Re(CNH···OMe)(CN···HOMe)(PH$_3$)$_4$]. Similar axial bond descriptions can be expected for complexes **4** and **6** with CF_3CO_2H or Et_3NH^+ instead of MeOH.



Scheme 2 Relevant axial bond distances and angles for the model complex *trans*-[Re(CNH·OMe)$_2$(PH$_3$)$_4$] obtained by *ab initio* calculations.

The CNH angles on both sides of the molecule are similar and considerably bent. The conceivable different structural properties of the two axial ligands of the molecule are not evident from the X-ray structural analyses of complexes **4** or **5**, possibly due to the expected[28] disorder of those ligands in the two positions with equal occupancy factor, thus becoming crystallographically equivalent. However, comparison between the species with and without hydrogen bridges indicate that the Re–C bond lengths appear to be slightly shorter in the former, *i.e.* 2.068(6) and 2.05(2) Å, in **4** and **5**, respectively, while in **2a** or **2b** they are 2.10(3) and 2.13(1) Å. The C–N bond length is less sensitive to the CN or CNH nature of the ligand and no trend is detected, the values being in the range (1.14–1.83 Å) of those reported for other complexes.[2–4,18–20]

Table 2 Cyclic voltammetric data[a] for complexes **2**–**7**

	$E^{\text{ox}}_{1/2}$/V	
Complex	Re$^{\text{I/II}}$	Re$^{\text{II/III}}$
3a *trans*-[Re(CN)(CNH)(dppe)$_2$]	(0.26)	0.76[b]
4[c] *trans*-[Re(CN·HO$_2$CCF$_3$)$_2$(dppe)$_2$]		0.90
5[d] *trans*-[Re(CN·HOMe)$_2$(dppe)$_2$]		0.84
6 *trans*-[Re(CN·HNEt$_3$)$_2$(dppe)$_2$][BPh$_4$]	−0.26	[e]
2a *trans*-[Re(CN)$_2$(dppe)$_2$]·2MeOH		0.75[b]
2b *trans*-[Re(CN)$_2$(dppe)$_2$]·2Me$_2$CO		0.75[b]
7 *trans*-[Re(CN)$_2$(dppe)$_2$]·NEt$_3$		0.75[b,f]

[a] In CH_2Cl_2, $E^{\text{ox}}_{1/2}$ values (measured at 200 mV s^{-1}) in volts (±20 mV) *versus* SCE, using ferrocene ($E^{\text{ox}}_{1/2}$ = 0.54 V *versus* SCE) as internal standard; the values in parentheses corresponds to an irreversible wave (E^{ox}_{p}). [b] Assigned to the oxidation of *trans*-[Re(CN)$_2$(dppe)$_2$] **2** (see text). [c] In the presence of added CF_3CO_2H. [d] In the presence of added MeOH or in MeOH solution; in the absence of MeOH; dissociation occurs to give complex **2** ($E^{\text{ox}}_{1/2}$ = 0.75 V). [e] Anodic waves are observed at 0.71, 0.76 and 0.95 (irrev.) V, the third one being due to oxidation of the counter ion. [f] Another irreversible anodic wave is observed at $E^{\text{ox}}_{\text{p}} - 0.99$ V, due to oxidation of the NEt$_3$ group.

Electrochemical study

The redox properties of the complexes were studied by cyclic voltammetry in 0.2 M [NBu$_4$][BF$_4$]–CH$_2$Cl$_2$ or THF, at a Pt-wire electrode and the relevant electrochemical data are displayed in Table 2. Of particular interest for this study would be the possibility to test the effect of hydrogen bonding on the redox potential of the complexes. This is somehow hampered by the dissociation of the adducts in the electrolyte medium, *i.e.* not only *trans*-[Re(CN)$_2$(dppe)$_2$]·*n*L ($n = 2$; L = MeOH **2a** or Me$_2$CO **2b**; $n = 1$, L = NEt$_3$ **7**) but also *trans*-[Re(CN·HOMe)$_2$(dppe)$_2$] **5**, in CH$_2$Cl$_2$ or THF, exhibit cyclic voltammograms identical to that[7] of *trans*-[Re(CN)$_2$(dppe)$_2$] **2** with a reversible anodic wave at $E^{\text{ox}}_{1/2}$ = 0.75 V. However, addition of MeOH to a CH$_2$Cl$_2$ solution of **5** results in a shift of the anodic wave to $E^{\text{ox}}_{1/2}$ = 0.84 V, a value identical to that observed for the anodic wave of **5** in MeOH, a solvent in which the dissociation of the complex should be hampered. Therefore, an anodic shift of 0.09 V in the oxidation potential of the complex results from the establishment of the hydrogen-bonding interactions of MeOH with the cyano-ligands. Similarly, a CH$_2$Cl$_2$ solution of *trans*-[Re(CN·HO$_2$CCF$_3$)$_2$(dppe)$_2$] **4**, in the presence of added CF$_3$CO$_2$H, exhibits a reversible anodic wave at $E^{\text{ox}}_{1/2}$ = 0.90 V, although in the absence of the free acid the oxidation wave occurs at a potential (0.79 V) that is close to that of **2**. In agreement with this observed anodic shift of the oxidation potential due to hydrogen-bond formation, the rhenium(I) complex *trans*-[Re(CN·HNEt$_3$)$_2$(dppe)$_2$][BPh$_4$] **6** shows an anodic wave at $E^{\text{ox}}_{1/2}$ = −0.26 V, a value significantly higher than that, −0.49 V, known[7] for the Re$^{\text{I}}$–Re$^{\text{II}}$ oxidation of the parent compound [NBu$_4$][*trans*-Re(CN)$_2$(dppe)$_2$]. However, a much higher increase in the oxidation potential is observed upon protonation of the cyano-ligand, *i.e.* its conversion into the isocyanide CNH, as shown by the much more anodic potential of the first anodic wave of the rhenium(I) isocyanide complex *trans*-[Re(CN)(CNH)(dppe)$_2$] **3a**, E^{ox}_{p} = 0.26 V, in comparison with that, $E^{\text{ox}}_{1/2}$ = −0.49 V, of the rhenium(I) dicyano-precursor *trans*-[Re(CN)$_2$(dppe)$_2$]$^-$, consistent with the known[29] much higher net electron π acceptance minus σ donation of the isocyanide relatively to the cyanide ligand.

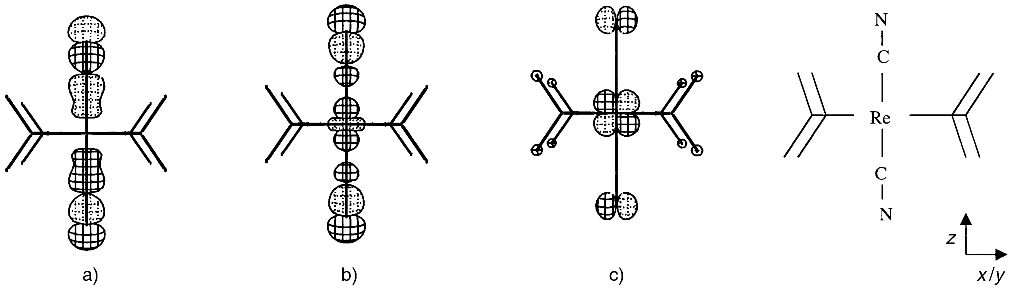


Fig. 4 Frontier molecular orbitals for the model complex *trans*-$[Re(CN)_2(PH_3)_4]^-$ **1′**: (a), (b) σ-donor interactions; (c) back-bonding interactions (involving rhenium d_{xy} and d_{yz} orbitals, highest energy).

Table 3 *Ab inito* optimized parameters for $[ReLL'(PH_3)_4]^x$ ($x = -1$ or 0; L,L′=CN or CNH)

	L=L′=CN		L=CN	L′=CNH
	$x = -1$ (**1′**)	$x = 0$ (**2′**)	$x = 0$ (**3a′**)	
Re–C/Å	2.196	2.130	2.169	2.044
C–N/Å	1.163	1.178	1.162	1.175
HOMO (au)	0.00859	−0.20744	−0.16543	
LUMO (au)	0.4209	0.1626	0.2691	
Charge at N (e)	−0.40	−0.28	−0.34	−0.39
Charge at Re (e)	−0.17	0.21	0.04	

Hence, the hydrogen bond of the cyano-ligands in the latter complex results in a shift of the oxidation potential of *ca.* 0.1–0.2 V, whereas protonation (formation of a covalent N–H bond) leads to a much more significant anodic shift (*ca.* 0.75 V).

The oxidation potential of complex **3a** is similar to that (0.29 V)[7] of the analogous methyl isocyanide complex *trans*-$[Re(CN)(CNMe)(dppe)_2]$. The first anodic wave (I) of a solution of *trans*-$[Re(CN)(CNH)(dppe)_2]$ **3a** at $E_p^{ox} = 0.26$ V is irreversible and is followed by a second one (II, reversible) at $E_{1/2}^{ox} = 0.76$ V. A reversible cathodic wave at $E_{1/2}^{red} = -0.49$ V is observed upon scan reversal following the first anodic wave. The anodic wave II and the cathodic one are assigned to the oxidation and reduction, respectively, of *trans*-$[Re(CN)_2(dppe)_2]$ **2**,[7] formed by anodically induced deprotonation of the isocyanide complex **3a** (eqn. 1), known[9] to occur for the related *trans*-$[ReCl(CNH)(dppe)_2]$ complex. The reduction of the liberated proton is also detected as an irreversible cathodic wave at $E_{1/2}^{red} = -0.76$ V. As mentioned above, the isocyanide complex **3a** is unstable and converts into *trans*-$[Re(CN)_2(dppe)_2]$, and this conversion (that is faster in THF than in CH_2Cl_2) has also been detected by cyclic voltammetry, with the decrease with time of the peak current of the first anodic wave and its concomitant replacement by the waves of the latter complex.

$$\underset{\mathbf{3a}}{trans\text{-}[Re(CN)(CNH)(dppe)_2]} \xrightleftharpoons{-e} trans\text{-}[Re(CN)(CNH)(dppe)_2]^+ \xrightarrow{-H^+} \underset{\mathbf{2}}{trans\text{-}[Re(CN)_2(dppe)_2]} \qquad (1)$$

Theoretical studies

Our theoretical studies on the model complex *trans*-$[Re(CNH{\cdot}OMe)_2(PH_3)_4]$, with hydrogen-bonded methanol, have been presented above, and now we discuss our extended Hückel molecular orbital (EHMO) and *ab initio* (Table 3) calculations carried out using the model complexes *trans*-$[ReLL'(PH_3)_4]^x$ ($x = -1$ or 0; L,L′ = CN or CNH) in order to try to understand the electronic features and reactivity of the cyanide and hydrogen isocyanide complexes.

The analysis of the frontier orbitals for *trans*-$[Re(CN)_2(PH_3)_4]^-$ **1′** shows that two sigma bonds and two back-bonding interactions (at higher energy) are established between the cyanides and the metal orbitals of appropriate symmetry, Fig. 4. A main difference between the rhenium(I) cyanide or isocyanide and the rhenium(II) cyanide compounds is that the HOMO is filled or half filled, respectively. In the former case there is transfer of electron density from the metal d_{xz} or d_{yz} orbitals to the nitrogen atom of the cyanide ligand thus rendering it more negative and enhancing its susceptibility to proton attack which occurs at *trans*-$[Re(CN)_2(dppe)_2]^-$ (see above) whose model *trans*-$[Re(CN)_2(PH_3)_4]^-$ compound **1′** presents the N atoms with the most negative charge (−0.40) and the protonation is charge controlled.

The bond lengths calculated by *ab initio* methods, Table 3, are in good agreement with the experimental data (Table 1). From these results it is evident that the C–N bond lengths for the cyanide (CN) and isocyanide (CNH) complexes are similar. In contrast, the Re–CN distance is longer for the rhenium(I) than for the rhenium(II) complexes, in accord with the antibonding character of the HOMO which is filled in the rhenium(I) complexes. In *trans*-$[Re(CN)_2(PH_3)_4]^-$ **1′** the charge at the Re atom (Table 3) is negative as would be expected for an anionic species, but not so much as at the nitrogen atom of the cyanide group where the proton addition occurs. The charge at the metal atom is positive for the neutral complexes, *trans*-$[Re(CN)(CNH)(PH_3)_4]$ **3′** and *trans*-$[Re(CN)_2(PH_3)_4]$ **2′**, being higher for the rhenium(II) compound. The order follows that of the oxidation potential of the complexes (Table 2) which also parallels the decreasing order of the energy of the HOMO.

Conclusion

At the electron-rich anionic rhenium(I) complex *trans*-$[Re(CN)_2(dppe)_2]^-$ the cyanide ligand is activated towards electrophilic attack by a variety of electrophiles such as protic species, alkylating agents or metals ions. Although stepwise alkylation can occur at the CN ligands to form diisocyanide complexes,[13,14] only single protonation at one of the ligating cyanides was observed in this study to give a mono hydrogen isocyanide (CNH) product. The acidity of the CNH ligand, which would be further enhanced by protonation of the *trans*-CN group, conceivably accounts for the failure to obtain the di-CNH product.

However, both cyano-ligands at the Re^I can establish hydrogen bonds to a protic electrophile such as $[Et_3NH]^+$. Such a propensity was fully demonstrated for the two ligating cyanides in the rhenium(II) complex *trans*-[Re(CN)$_2$(dppe)$_2$], in particular towards CF$_3$CO$_2$H or MeOH, but the lower electron-rich character of the oxidized Re results in a weaker nucleophilic activation of the CN ligands which thus are not able to undergo protonation.

The relative tendency of the cyanide ligand to undergo protonation *versus* that to form an hydrogen bond is not only dependent on the metal oxidation state but is also tuned by the ligand in *trans* position. A strong net electron-donor ability of the latter ligand and a low metal oxidation state promote the CN protonation to form a stable CNH complex such as *trans*-[ReCl(CNH)(dppe)$_2$][9] or *trans*-[FeH(CNH)(dppe)$_2$]$^+$,[12] whereas a weaker net electron-donor capacity and the susceptibility of the *trans* ligand to undergo electrophilic attack, as well as a higher metal oxidation state, discourage protonation of the ligated cyanide although its capacity for hydrogen bond formation can still be present as in *trans*-[Re(CN·HO$_2$CCF$_3$)$_2$(dppe)$_2$] or *trans*-[Re(CN·HOMe)$_2$(dppe)$_2$]. The oxidation potential of the complex is rather sensitive to protonation of the CN ligand (to give CNH), and, to a much lesser extent, to the hydrogen-bond formation, shifting anodically by *ca.* 0.75 or *ca.* 0.1–0.2 V, respectively. Hence, electrochemical methods, in particular cyclic voltammetry, can be of diagnostic value to detect and distinguish such processes.

Experimental

All manipulations were done under dinitrogen or argon. The solvents were purchased from LabScan, pre-dried and distilled immediately before use. HBF$_4$·Et$_2$O, CF$_3$CO$_2$H and CH$_3$CO$_2$H were used as supplied by Aldrich. [NBu$_4$][*trans*-Re(CN)$_2$(dppe)$_2$][7] and [Et$_3$NE][BPh$_4$][30] (E = H or D) were prepared by published methods. ^{1}H and ^{31}P-{^{1}H} NMR spectra were recorded on a Varian Unity 300 MHz instrument and chemical shifts were measured relative to TMS or P(OMe)$_3$, respectively, IR spectra in KBr pellets on a Perkin-Elmer 683 infrared spectrometer or a Bio-Rad FTS 3000 MX (Excalibur Series) FTIR and FAB mass spectra in 3-nitrobenzyl alcohol matrix using a Carlo Erba Instruments Auto/HRGC/Trio 2000 MS Spectrometer at room temperature. Magnetic susceptibility measurements (25 °C) were recorded on a Johnson Mathey (Alfa Products) magnetic susceptibility balance . The electrochemical studies were performed at an EG&G PAR 173 potentiostat/galvanostat and an EG&G PARC 175 universal programmer, in a 0.2 M [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$ or THF solution, using a platinum wire as working electrode. The potential values are quoted *versus* SCE and were measured by using the [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ redox couple ($E = 0.54$ V *versus* SCE) as internal standard.

Syntheses of the complexes

***trans*-[Re(CN)$_2$(dppe)$_2$]·2Me$_2$CO 2b.** [NBu$_4$][*trans*-Re(CN)$_2$(dppe)$_2$] **1** (*ca.* 0.10 g) was dissolved in acetone (*ca.* 10 cm^3) and the solution allowed slowly to evaporate until the beginning of precipitation. The solution was filtered and left at *ca.* −18 °C overnight. The red crystalline product was filtered off and dried under vacuum (*ca.* 0.030 g, 40% yield) (Found: C, 62.0; H, 5.1; N, 2.5. C$_{60}$H$_{60}$N$_2$O$_2$P$_4$Re requires C, 62.6; H, 5.2; N, 2.4%). IR: ν(C≡N) 2030 cm^{-1}.

***trans*-[Re(CN)$_2$(dppe)$_2$]·2MeOH 2a.** This complex (red) was obtained analogously to **2b** but using MeOH as the solvent instead of Me$_2$CO (*ca.* 0.015 g, 20% yield) (Found: C, 61.8; H, 5.2; N, 2.6. C$_{56}$H$_{56}$N$_2$O$_2$P$_4$Re requires C, 61.2; H, 5.1; N, 2.5%). IR: ν(C≡N) 2030 cm^{-1}. $\mu_{\text{eff}} = 1.83\ \mu_{\text{B}}$.

***trans*-[Re(CN)(CNH)(dppe)$_2$] 3a.** A mixture of complex **1** (0.10 g, 0.078 mmol) and [Et$_3$NH][BPh$_4$] (0.033 g, 0.078 mmol) was dissolved in THF (10 cm^3) and stirred. After a few minutes an abundant whitish suspension of complex **3a** formed which was filtered off after *ca.* $\frac{1}{2}$ h and dried under vacuum (0.050 g, 62% yield). FAB$^+$-MS: *m*/*z* 1035, [M − H]$^+$ (Found: C, 62.2; H, 5.0; N, 2.8. C$_{54}$H$_{49}$N$_2$P$_4$Re requires C, 62.6; H, 4.7; N, 2.7%). IR: ν(C≡N) 2049 and 1895 cm^{-1} (CNH). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ −113.4. Attempts at recrystallization or even washing with Et$_2$O afforded *trans*-[Re(CN)$_2$(dppe)$_2$].

Complex **3b** was prepared in a similar way by using [Et$_3$ND][BPh$_4$] instead of the non-deuteriated acid. FAB$^+$-MS: *m*/*z* 1037, [*M*]$^+$ (Found: C, 62.9; H, 4.8; N, 2.6. C$_{54}$H$_{48}$DN$_2$P$_4$Re requires C, 62.6; H, 4.6; N, 2.7%). IR: ν(C≡N) 2050 and 1890 cm^{-1} (CND). Complex **3a** also forms by reaction of **1**, in CH$_2$Cl$_2$, with MeCO$_2$H or HBF$_4$·Et$_2$O in the 1 : 1 molar ratio.

***trans*-[Re(CN·HO$_2$CCF$_3$)$_2$(dppe)$_2$] 4.** CF$_3$CO$_2$H (0.10 cm^3, 1.30 mmol) was added to a solution of *trans*-[Re(CN)(CNH)(dppe)$_2$] **3a** (0.050 g, 0.048 mmol) in THF (10 cm^3) and stirred for 1 h. The solvent was completely evaporated under vacuum and the obtained solid recrystallized from CH$_2$Cl$_2$–n-pentane. The violet crystals that separated were filtered off and dried under vacuum (0.020 g, 33% yield) (Found: C, 54.8; H, 3.8; N, 1.8. C$_{58}$H$_{50}$N$_2$O$_4$P$_4$Re requires C, 55.1; H, 4.0; N, 2.2%). IR: ν(C≡N) 2045 and 1949 cm^{-1}. No NMR spectrum could be obtained due to paramagnetism.

***trans*-[Re(CN·HOMe)$_2$(dppe)$_2$] 5.** Addition of Et$_2$NH (0.010 cm^3, 0.097 mmol) to a solution of complex **1** (0.10 g, 0.078 mmol) in MeOH (10 cm^3) afforded a suspension that was filtered off. The filtered solution was slightly concentrated under vacuum and cooled overnight at *ca.* −18 °C to give red crystals of **5** (0.030 g, 35% yield) (Found: C, 59.5; H, 4.6; N, 2.2. C$_{56}$H$_{56}$N$_2$P$_4$O$_2$Re requires C, 59.5; H, 5.3; N, 2.5%). IR: ν(C≡N) 2033 cm^{-1}.

***trans*-[Re(CN·HNEt$_3$)$_2$(dppe)$_2$][BPh$_4$] 6 and *trans*-[Re(CN)$_2$(dppe)$_2$]·NEt$_3$ 7.** CH$_2$Cl$_2$ (10 cm^3) was added to a mixture of complex **1** (0.087 g, 0.068 mmol) and [Et$_3$NH][BPh$_4$] (0.14 g, 0.33 mmol) and stirred for 3 hours. The yellow solution was then filtered, n-pentane (1 cm^3) added and the resulting solution cooled at *ca.* −18 °C overnight. The red-violet compound *trans*-[Re(CN)$_2$(dppe)$_2$]·NEt$_3$ **7** precipitated and was filtered off, washed with n-pentane and dried under vacuum (0.030 g, 30% yield). FAB$^+$-MS: *m*/*z* 1035, [*M*]$^+$ (Found: C, 63.4; H, 5.5; N, 3.7. C$_{58}$H$_{63}$N$_3$P$_4$Re requires C, 63.3; H, 6.0; N, 3.7%). IR: ν(C≡N) 2038 cm^{-1}. Addition of n-pentane (1 cm^3) to the filtered yellow solution resulted in the precipitation of a yellow powder, *trans*-[Re(CN·HNEt$_3$)$_2$(dppe)$_2$][BPh$_4$] **6** which was filtered off, washed with Et$_2$O and dried under vacuum (0.050 g, 47% yield). FAB$^+$-MS: *m*/*z* 1036, [*M*-HNEt$_3$-NEt$_3$]$^+$ (Found: C, 69.5; H, 7.0; N, 3.3. C$_{90}$H$_{100}$BN$_4$P$_4$Re requires C, 69.4; H, 6.4; N, 3.6%). IR: ν(C≡N) 1989 cm^{-1}. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ −108.6.

Crystal structure determination of complexes 2a, 2b, 4 and 5

The X-ray data were collected from red (**2a**, **2b** and **5**) or violet crystals (**4**) of the complexes, mounted in thin-walled glass capillaries. Data were collected at room temperature on Enraf-Nonius Turbo CAD-4 (**2a** and **2b**) and MACH3 (**4** and **5**) diffractometers with graphite-monochromatized Mo-Kα (**4** and **5**) and Cu-Kα (**2b**) radiation, using an ω − 2θ scan mode. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections. The crystal data are summarized in Table 4. The data were corrected[31] for Lorentz-polarization effects, for linear decay and empirically for absorption. The heavy atom positions were located by Patterson methods using SHELXS 86.[32] The remaining atoms were located in successive Fourier-difference maps and refined by least squares on F^2 using SHELXL 93.[33] Two solvent molecules were also located

Table 4 Crystallographic data for complexes **2b**, **4** and **5**

	2b	**4**	**5**
Formula	$C_{54}H_{48}N_2P_4Re\cdot 2Me_2CO$	$C_{54}H_{48}N_2P_4Re\cdot 2CF_3C_2H$	$C_{54}H_{48}N_2P_4Re\cdot 2MeOH$
M	1151.3	1265.64	1099.22
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/a$
a/Å	11.713(5)	9.5290(10)	13.474(3)
b/Å	13.432(5)	11.251(4)	18.692(2)
c/Å	17.179(6)	12.9660(10)	10.155(3)
β/°	96.48(3)	81.020(10)	107.78(1)
U/Å^3	2686	1324	2436
Z	2	1	2
μ/mm^{-1}	5.344 (Cu-Kα)	2.349 (Mo-Kα)	2.531 (Mo-Kα)
No. reflections measured	5303	5970	4524
No. unique reflections (R_{int})	5085 (0.07)	5676	4266 (0.13)
$R1$ ($I > 2\sigma(I)$)	0.08	0.04	0.08
$wR2$	0.20	0.09	0.12

in the Fourier-difference map in the structures of **2b** (acetone) and **2a** (methanol), although the small dimensions and the poor quality of the **2a** crystal did not allow complete determination of the structure. All the non-hydrogen atoms were refined with anisotropic thermal motion parameters. The hydrogen atoms were included in calculated positions, constrained to ride at fixed distances of the parent carbon (or oxygen) atom. Atomic scattering factors and anomalous dispersion terms were as in SHELXL 93.[33] The ORTEP drawings were made with ORTEX.[34]

CCDC reference number 186/2145.

See http://www.rsc.org/suppdata/dt/b0/b004189k/ for crystallographic files in .cif format.

MO calculations

All extended Hückel and *ab initio* MO calculations were carried out on model complexes with the $Ph_2PCH_2CH_2PPh_2$ ligands replaced by pairs of PH_3 phosphines. Extended Hückel[35] type calculations were carried out with modified H_{ij}.[36] The basis set for the metal atoms consisted of ns, np and $(n - 1)$d orbitals. The s and p orbitals were described by single Slater type wavefunctions, and d orbitals were taken as contracted linear combinations of two such wavefunctions. Standard parameters were used for all atoms. The EHMO calculations were made with CACAO.[37] *Ab initio* calculations were performed at the Hartree–Fock level with a LANL2MB basis set using the GAUSSIAN 94/DFT program.[38]

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