

Dinitrile complexes with a rare *cis*-diphosphine rhenium(I) centre: syntheses, properties and *cis*- to *trans*-isomerization

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Abstract

Complexes *cis*-[Re(NCR)₂(dppe)₂]X **1** (R = Et, ⁱPr, ^tBu, CH₂C₆H₄Cl-4, C₆H₄NEt₂-4, C₆H₄OH-4, C₆H₄OMe-4, C₆H₄Me-4, Ph, C₆H₄F-4, C₆H₄Cl-4 or C₆H₄NO₂-4; dppe = Ph₂PCH₂CH₂PPh₂; X = BF₄ or BPh₄), with a very rare *cis*-diphosphinic rhenium centre, have been prepared, at ambient temperature, by treatment of a tetrahydrofuran (thf) solution of *trans*-[ReCl(N₂)(dppe)₂] with the appropriate nitrile in the presence of Ti[BF₄] or Na[BPh₄]. In the absence of any of these salts, the corresponding chlorides *cis*-[Re(NCR)₂(dppe)₂]Cl are obtained. Those complexes, upon heating (refluxing thf), are converted into the corresponding and novel *trans*-isomers which, alternatively, can be prepared more directly (but in lower yields) from the reaction of *trans*-[ReCl(N₂)(dppe)₂] with the corresponding nitrile, in the presence of the halide abstractor salt, in refluxing thf; the complex double salts *trans*-[Re(NCR)₂(dppe)₂][BF₄]·*trans*-[ReF₂(dppe)₂][BF₄] (R = C₆H₄OMe-4 or C₆H₄Me-4) are also obtained upon a rather unusual double metal fluorination by BF₄⁻. The properties of both series of isomers are compared and criteria to distinguish between the *trans*- and *cis*-(dppe)₂ arrangements are proposed based on the ¹³C NMR patterns of the methylene carbons or of the phenyl carbons bonded to the phosphorus atoms of dppe, or on the low frequency IR spectra of these ligands. No nucleophilic or electrophilic addition was detected for complexes **1** which, upon attempted reaction with [Et₃O][PF₆] or Li[BEt₃H], simply undergo counter-ion exchange.

Keywords: Rhenium complexes; Nitrile complexes; Geometrical isomers; Isomerization; *cis*-Diphosphine complexes

1. Introduction

The study of the relative stabilities of the *trans* and *cis* geometrical isomers of closed shell octahedral-type phosphine complexes has been a matter of recognized interest, namely for Group 6 transition metal complexes with π -acceptor ligands. In particular, MO theoretical studies [1] on models of complexes of the types [ML₂P₄] (M = Cr, Mo or W; L = CO or N₂; P = monophosphine or 1/2 chelating diphosphine) indicate that the *cis*-isomers of such compounds should be thermodynamically more stable than the corresponding *trans*-isomers, although the reverse could result from oxidation of the complexes, a subject which has also been investigated by electrochemical studies for a number of such complexes [2] and related rhenium [3] complexes.

In spite of those expectations, the *trans* geometry has been almost the only one reported for 18-electron Re or

Tc phosphinic complexes, such as [MLL'(dppe)₂] (M = Re [4–6] or Tc [7,8]; L and/or L' = CO, CNR or NCR; dppe = Ph₂PCH₂CH₂PPh₂), [MX(L)(dppe)₂] (M = Re [9–11], X = Cl, L = CO, N₂, CNR, NCR, phenylallene or vinylidene; M = Tc [8,12] X = H, L = CO, N₂ or CNR), as well as those derived from their reactions [11,13–15]. However, such complexes have usually been prepared in refluxing solvents, but by using milder experimental conditions (particularly operating at room temperature) we have already succeeded in the synthesis [16] of a series of mononitrile complexes with the *cis* geometry, of the type *cis*-[ReCl(NCR)(dppe)₂] (R = alkyl or aryl). These *cis* complexes have also been investigated electrochemically [3] and shown to be thermodynamically more stable than the corresponding *trans*-isomers, although the former can convert into the latter isomers, slowly in sunlight [16] or rapidly upon oxidation [3].

We now extend the chemical study to the related dinitrile complexes *cis*-[Re(NCR)₂(dppe)₂]⁺ and their derived *trans*-isomers, the former providing, with the

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above-mentioned cis -[ReCl(NCR)(dppe)₂] complexes, the only known examples of cis -isomers of octahedral rhenium(I) tetraphosphine compounds. Moreover, the complexes of this study constitute very rare examples [7,8] of species with more than one nitrile ligating an electron-rich metal centre without the stabilization by a stronger π -acceptor (such as CO [17]). In addition, the study should also provide a contribution towards the development of the coordination chemistry of nitriles at electron-rich dinitrogen binding metal sites, a still underdeveloped area of research [18].

We have already briefly reported, in a preliminary way, the formation of the particular cis - or $trans$ -[Re(NCC₆H₄Me-4)₂(dppe)₂]⁺ species, with indication of the single crystal diffraction analyses of cis -[Re(NCC₆H₄Me-4)₂(dppe)₂][BF₄] [19] and of the complex double salt $trans$ -[Re(NCC₆H₄Me-4)₂(dppe)₂][BF₄] · $trans$ -[ReF₂(dppe)₂][BF₄] [5].

2. Results and discussion

2.1. Complexes 1, cis -[Re(NCR)₂(dppe)₂]X (X = BF₄, BPh₄ or Cl)

Treatment of a tetrahydrofuran (thf) solution of the dinitrogen complex $trans$ -[ReCl(N₂)(dppe)₂], at room temperature, with the appropriate organonitrile (in approximately a twofold molar ratio) and Ti[BF₄] (in an equivalent amount) under an inert atmosphere and for ca. 24 h usually gives, in high yield (ca. 80%), the corresponding dinitrile complex cis -[Re(NCR)₂(dppe)₂][BF₄] **1** (R = Et, ¹Pr, ¹Bu, CH₂C₆H₄Cl-4, C₆H₄NEt₂-4, C₆H₄OH-4, C₆H₄OMe-4, C₆H₄Me-4, Ph, C₆H₄F-4, C₆H₄Cl-4 or C₆H₄NO₂-4) (Eq. (1) in Scheme 1). Tight control of the experimental conditions in these and in the other reactions of this work is usually required to avoid side reactions and the formation of complex mixtures. In particular, for the synthesis of **1**, the use of more drastic experimental conditions — longer reaction time, exposure to sunlight or refluxing

solvent — lead to different products, in particular the corresponding $trans$ -isomers (see below).

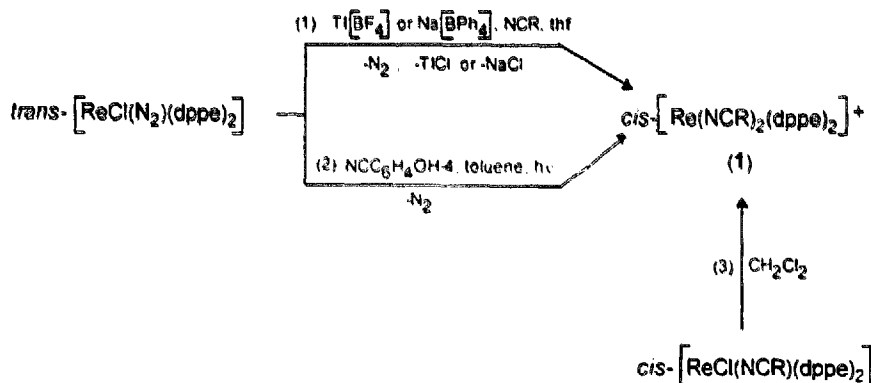
The analogous complexes with BPh₄⁻ as the counterion are prepared by using Na[BPh₄] instead of Ti[BF₄]. Moreover, the identical chloride compounds, i.e. cis -[Re(NCR)₂(dppe)₂]Cl, can also be obtained, although less conveniently, from the aforementioned dinitrogen complex but without the presence of the halide abstractor and using more severe experimental conditions (depending on the R group). Hence, in the case of NCC₆H₄OH-4, the cis -dinitrile complex was obtained by carrying out the reaction in toluene, in sunlight, for 2 days (Eq. (2) in Scheme 1), thus following an elongation of the reaction time in the general procedure [16] for the syntheses of the mononitrile complexes cis -[ReCl(NCR)(dppe)₂] which usually require ca. 4 h.

In addition, the cis -dinitrile species can also be obtained (reaction (3) in Scheme 1) from the decomposition of the corresponding cis -[ReCl(NCR)(dppe)₂] complexes in CH₂Cl₂ (or in thf, although more slowly), conceivably involving a metathesis process; the cis -dinitrile complex was isolated but the other product was not identified, although it was shown, by ¹H NMR, to be a paramagnetic species. This conversion of the cis -chloro-mononitrile into the cis -dinitrile complexes was monitored by IR and ¹H NMR.

2.1.1. Physical data

Complexes **1** have been isolated as yellow or orange solids (greenish-yellow for R = C₆H₄NEt₂-4 and dark red for R = C₆H₄NO₂-4) in ca. 80% yields, and their IR spectra (KBr pellets) show strong bands in the 2240–2150 cm⁻¹ range which are assigned to the N≡C stretching mode of the nitrile ligands. In most of the cases the observation of two ν (NC) bands is indicative of the cis geometry of complexes **1**. Exceptionally, only one band is detected for **1** for R = Et and ¹Pr, and no band was observed for **1** with R = C₆H₄NEt₂-4; the lack of detection of ν (NC) bands in nitrile ligands is known to occur [20] in a number of complexes.

The lowering of ν (NC) of the NCR species upon



Scheme 1.

coordination, $\Delta\nu = -2$ to -65 cm^{-1}) is indicative of a significant π -acceptance of the nitrile from the Re(I) metal centre. However, these shifts are lower than those observed for the corresponding mononitrile complexes *cis*-[ReCl(NCR)(dppe)₂] ($\Delta\nu = -15$ to -100 cm^{-1}) [10,11] in accordance with the expected weaker electron-richness of the cationic binding metal site in the former complexes compared with the metal centre in the latter case. As expected, the aryl nitrile ligands present $\nu(\text{NC})$ at lower values than those observed for the weaker π -acceptor ligating alkyl nitriles and, within the former, the lowering of $\nu(\text{NC})$ upon coordination follows the electron-withdrawing ability of the phenyl substituent.

Other features of the IR spectra which enable us to distinguish between the *cis*- and *trans*-isomers are discussed below.

The molecular structure of *cis*-[Re(NCC₆H₄Me-4)₂(dppe)₂][BF₄], as determined by a single-crystal diffraction analysis, has already been reported [19] confirming its *cis* geometry. The complex cation presents a distorted octahedral coordination with the two linear nitrile ligands (N–C–C angles of 177(2) and 178(2)^o) forming an N–Re–N angle of 81.6(6)^o. The average Re–N bond length, 2.065(16) Å [19], is significantly longer than that exhibited by *trans*-[ReCl(NCMe)(dppe)₂], 1.978(5) Å [21], in agreement with the expected weaker π -electron releasing ability of the cationic binding metal centre in the former complex compared with that in the latter compound (see above). The average N–C multiple bond and Re–P bond lengths for that *cis*-dinitrile complex are 1.125(24) Å and 2.374(6) Å respectively [19] (see also below).

2.1.2. ¹H, ³¹P-¹H and ¹⁹F NMR spectra

In the ¹H NMR spectra (Table 1) the presence of dppe-phenyl signals slightly upfield from the bulk of the phenyl resonances are diagnostic [22,23] of a *cis* arrangement of the two diphosphine ligands. They usually appear either as two distinct triplets (R = Et, ¹Bu, CH₂C₆H₄Cl-4, C₆H₄F-4, C₆H₄Cl-4 and C₆H₄NO₂-4 (Fig. 1(a))) or as two partially overlapped triplets (R = ¹Pr, C₆H₄NEt₂-4, C₆H₄OH-4 and C₆H₄OMe-4 (Fig. 1(b)), although their resonances can also overlap with those of the aromatic protons of the nitrile ring (R = Ph and C₆H₄Me-4 (Fig. 1(c)), and commonly integrate for eight protons. The upfield shifts are believed [22,23] to result from interactions between four *ortho*-protons of two phenyl rings of the diphosphines and the nitrile ligands in *cis* position, and their multiplicity is due to coupling to the adjacent *meta*-protons as well as to the phosphorus nucleus (³J(HH) ≈ ³J(PH) ≈ 8–9 Hz).

The aromatic nitrile proton resonances of complexes 1 are partially observed as doublets, also upfield from the bulk dppe-phenyl region. They are part of an AA'BB'-spin system (AA' and BB' corresponding to the

pairs of *ortho*- and *meta*-protons) or of an AB-type pattern (if the rotation around the Re–NCR or the ReNC–R bond is not hampered), the remaining being buried under the phenyl multiplets of the diphosphine ligands. A related resonance pattern was detected for aromatic isocyanide ligands, e.g. in *trans*-[Re(CNR)₂(dppe)₂][BF₄] [4]. In complex 1 with R = CH₂C₆H₄Cl-4 the methylene protons of the nitrile ligands appear as two doublets (²J(HH) = 18.0 Hz, centred at δ 4.30 and δ 3.32), thus indicating their non-equivalence. The coupling between these protons was confirmed by spin decoupling experiments. The alkyl groups of the other ligating nitriles exhibit expected patterns, as quoted in Table 1.

The ³¹P-¹H NMR spectra present two broad and equally intense resonances, at δ in the range -101 to -109 ppm relative to P(OMe)₃, in accord with two pairs of non-equivalent phosphorus nuclei resulting from the *cis* geometry. They did not resolve on lowering the temperature down to -95°C (in CD₂Cl₂).

The ¹⁹F NMR spectra of the complexes with BF₄⁻ as the counter ion exhibit the expected singlet resonance of this anion at $\delta -151.5$ relative to CFCl₃, whereas for 1 (R = C₆H₄F-4) the aromatic fluoro resonance is observed as a 1:2:3:4:3:2:1 heptet at $\delta -99.10$ which was analysed as a partially overlapping triplet (³J(FH) = 8.8 Hz) of triplets (⁴J(FH) = 4.5 Hz).

2.1.3. ¹³C-¹H and ¹³C NMR spectra

In the ¹³C-¹H NMR spectra (Table 2) the nitrile-carbon N≡CR resonance is observed as a singlet in the range δ 126.8–123.2, which corresponds to a downfield shift (by ca. 8.2 to 2.8) upon coordination (except for R = ¹Bu with an upfield shift of -2.57 ppm). In some cases, this resonance was not clearly established, conceivably being buried under the phenyl multiplets. The resonances of the other carbon nuclei of the nitrile ligands usually have been detected as singlets which, in the ¹H-coupled spectra, split into the expected multiplets in which the fine ²J(CH) coupling is, in some cases, observed (Table 2). For 1 (R = C₆H₄F-4), the resonances of the *para*- and the *meta*-aromatic carbons appear as doublets at δ 165.1 and 117.2, in the ¹³C-¹H NMR spectra, due to coupling to ¹⁹F (¹J(CF) = 257.1 Hz and ²J(CF) = 23.1 Hz respectively).

One of the most interesting features of the ¹H-decoupled ¹³C NMR spectra is the low field resonances of the diphosphine phenyl carbons directly attached to the phosphorus atoms, C_{ipso}, which appear as a pair of triplets ($J = 16.5$ – 18.0 Hz) and a pair of doublets ($J = 30.9$ – 43.0 Hz), the former probably due to the virtual coupling to two phosphorus nuclei and the latter to a simple ¹J(CP) coupling (Fig. 2(a)). Such a pattern is not observed in the *trans* complexes (see below).

Virtual coupling to phosphorus nuclei is also observed with the methylene dppe carbons whose ¹³C-¹H

Table 1
 ^1H and ^{31}P - $\{^1\text{H}\}$ NMR data for the nitrile complexes *cis*- $[\text{Re}(\text{NCR})_2(\text{dppe})_2][\text{BF}_4]$ 1

R	^1H ^a			^{31}P - $\{^1\text{H}\}$ ^b
	δ (ppm)	$J(\text{HH})$ (Hz)	Assignment	
Et	7.33–7.03 (m,br, 32H)	—	Ph (dppe)	– 101.5
	6.71 (t, 4H)	$^3J[\approx ^3J(\text{PH})] = 8.4$	H_o (dppe)	– 104.6
	6.58 (t, 4H)	$^3J[\approx ^3J(\text{PH})] = 7.9$		
	2.77–2.41 (m,br, 8H)	—	CH_2 (dppe)	
	2.23–2.03 (m,br, 4H)	—	CH_2 (nitrile)	
	0.85 (t, 6H)	$^3J = 7.9$	Me (nitrile)	
^iPr ^c	7.43–7.01 (m,br, 32H)	—	Ph (dppe)	– 103.4
	6.69 (t, 4H) ^d	$^3J[\approx ^3J(\text{PH})] = 8.1$	H_o (dppe)	– 108.1
	6.63 (t, 4H) ^d	$^3J[\approx ^3J(\text{PH})] = 8.4$		— ^c
	2.78–2.40 (m,br, 8H)	—	CH_2 (dppe)	
	2.40 (hp, 2H)	$^3J = 7.0$	CH (nitrile)	
	0.92 (d, 6H) ^e	$^3J = 6.9$	Me (nitrile)	
0.90 (d, 6H) ^e	$^3J = 6.9$			
^iBu ^c	7.20–6.75 (m,br, 32H)	—	Ph (dppe)	– 103.4
	6.66 (t, 4H)	$^3J = 8.3$	H_o (dppe)	– 106.8
	6.43 (t, 4H)	$^3J = 7.4$		
	2.75–2.37 (m,br, 8H)	—	CH_2 (dppe)	
	0.85 (s, 18H)	—	Me (nitrile)	
	$\text{CH}_2\text{C}_6\text{H}_4\text{Cl}$ -4	7.55–6.83 (m,br, 40H)	—	Ph (dppe + nitrile)
6.66 (t, 4H)		$^3J[\approx ^3J(\text{PH})] = 8.2$	H_o (dppe)	– 105.4
6.55 (t, 4H)		$^3J[\approx ^3J(\text{PH})] = 8.4$		
4.30 (d, 2H)		$^2J = 18.0$	CH_2 (nitrile)	
3.32 (d, 2H)		$^2J = 18.0$		
2.75–2.26 (m,br, 6H)		—	CH_2 (dppe)	
1.95–1.77 (m,br, 2H)	—			
$\text{C}_6\text{H}_4\text{NEt}_2$ -4	7.55–7.00 (m,br, 40H)	—	Ph (dppe + nitrile)	– 102.5
	6.85–6.74 (m,br, 2H)	—	H_o (dppe)	– 106.4
	6.74–6.66 (m,br, 2H)	—		
	6.65 (d, 2H)	$^3J = 9.2$	H_A (aromatic nitrile)	
	6.53 (d, 2H)	$^3J = 9.2$	H_B (aromatic nitrile)	
	3.44 (q, 8H)	$^3J = 6.9$	CH_2 (nitrile)	
	2.80–2.53 (m,br, 6H)	—	CH_3 (dppe)	
	1.95–1.75 (m,br, 2H)	—		
	1.23 (t, 12H)	$^3J = 6.9$	Me (nitrile)	
$\text{C}_6\text{H}_4\text{OH}$ -4	7.60–6.90 (m,br, 38H)	—	Ph (dppe + nitrile)	– 102.7
	6.85–6.65 (m, 8H)	—	H_o (dppe)	– 107.3
	6.58 (d, 2H)	$^3J = 8.7$	H_B (aromatic nitrile)	
	2.80–2.47 (m,br, 8H)	—	CH_2 (dppe)	
$\text{C}_6\text{H}_4\text{OMe}$ -4	7.65–7.00 (m,br, 36H)	—	Ph (dppe + nitrile)	– 102.3
	6.97 (d, 2H)	$^3J = 8.9$	H_A (aromatic nitrile)	– 106.4
	6.78 (d, 2H)	$^3J = 8.9$	H_B (aromatic nitrile)	
	6.75–6.71 (m, 8H)	—	H_o (dppe)	
	3.92 (s, 6H)	—	Me (nitrile)	
	2.68–1.92 (m,br, 8H)	—	CH_2 (dppe)	
$\text{C}_6\text{H}_4\text{Me}$ -4	7.49–7.02 (m,br, 38H)	—	Ph (dppe + nitrile)	– 102.4
	6.79–6.75 (m, 8H)	—	H_o (dppe)	– 106.7
	6.71 (d, 2H)	$^3J = 7.8$	H_B (aromatic nitrile)	
	2.86–2.60 (m,br, 6H)	—	CH_2 (dppe)	
	2.02–1.86 (m,br, 2H)	—		
	2.44 (s, 6H)	—	Me (nitrile)	
Ph	7.61–6.99 (m, 40H)	—	Ph (dppe + nitrile)	– 102.3
	6.80–6.71 (m, 10H)	—	H_o (dppe) + + H_B (aromatic nitrile)	– 106.6
	2.92–2.51 (m,br, 6H)	—		
	2.05–1.85 (m,br, 2H)	—	CH_2 (dppe)	

Table 1 (continued)

R	¹ H ^a			³¹ P-{ ¹ H} ^b
	δ (ppm)	J(HH) (Hz)	Assignment	
C ₆ H ₄ F-4 ^f	7.40–7.05 (m,br, 36H)	—	Ph (dppe + nitrile)	– 102.2
	6.93 (d, 2H)	³ J = 5.1	H _A (aromatic nitrile)	– 107.9
	6.90 (d, 2H)	³ J = 5.1	H _B (aromatic nitrile)	
	6.76 (t, 4H)	³ J[≈ ³ J(PH)] = 8.7	H _o (dppe)	
	6.70 (t, 4H)	³ J[≈ ³ J(PH)] = 9.5		
	2.88–2.06 (m,br, 6H)	—	CH ₂ (dppe)	
	2.10–1.93 (m,br, 2H)	—		
C ₆ H ₄ Cl-4	7.44–6.95 (m, 38H)	—	Ph (dppe + nitrile)	– 103.0
	6.76 (d, 2H)	³ J = 8.4	H _B (aromatic nitrile)	– 107.3
	6.74 (t, 4H)	³ J[≈ ³ J(PH)] = 9.3	H _o (dppe)	
	6.65 (t, 4H)	³ J[≈ ³ J(PH)] = 8.4		
	2.81–2.45 (m,br, 6H)	—	CH ₂ (dppe)	
	2.60–1.90 (m,br, 2H)	—		
C ₆ H ₄ NO ₂ -4	7.60–6.94 (m,br, 40H)	—	Ph (dppe + nitrile)	– 104.1
	6.84 (t, 4H)	³ J[≈ ³ J(PH)] = 8.4	H _o (dppe)	– 108.8
	6.64 (t, 4H)	³ J[≈ ³ J(PH)] = 9.0		
	2.85–2.50 (m,br, 8H)	—	CH ₂ (dppe)	

^a In CDCl₃ unless stated otherwise. δ values relative to internal SiMe₄; s = singlet, d = doublet, t = triplet, q = quartet, hp = heptet, m = multiplet, br = broad; subscripts *o*, *m* and *p* denote the aromatic ortho, meta and para phosphinic protons, respectively; subscripts *A* and *B* refer to the aromatic nitrile protons (see text). ^b In (CD₃)₂CO unless stated otherwise. δ values relative to internal P(OMe)₃. The observed resonances are all broad "singlets". ^c In CD₂Cl₂. ^d 1:2:2:2:1 quintet due to two partially overlapped triplets (Fig. 1). ^e In CDCl₃ the two doublets are partially overlapped resulting in an apparent triplet at δ = 0.91. ^f In the ¹⁹F NMR spectra a 1:2:3:4:3:2:1 heptet at δ = –99.10 (relative to CFC1₃) was observed which was analysed as a partially overlapping triplet (³J(FH) = 8.8 Hz) of triplets (⁴J(FH) = 4.5 Hz).

NMR spectra exhibit two close triplets (apparent *J* between 10 and 20 Hz) at δ ca. 34–36, and a higher field broad multiplet at δ ca. 25 ppm (Fig. 2(b)). The particular structure of the diphosphine CH₂ resonances may also be diagnostic of a *cis* geometry. In fact, in the

related mononitrile complexes *cis*-[ReCl(NCR)(dppe)₂] [16], these resonances appear as two unresolved multiplets at those chemical shifts; on the contrary, in complexes with a *trans* geometry, such as the related trans-isomers of the dinitrile complexes under study (see

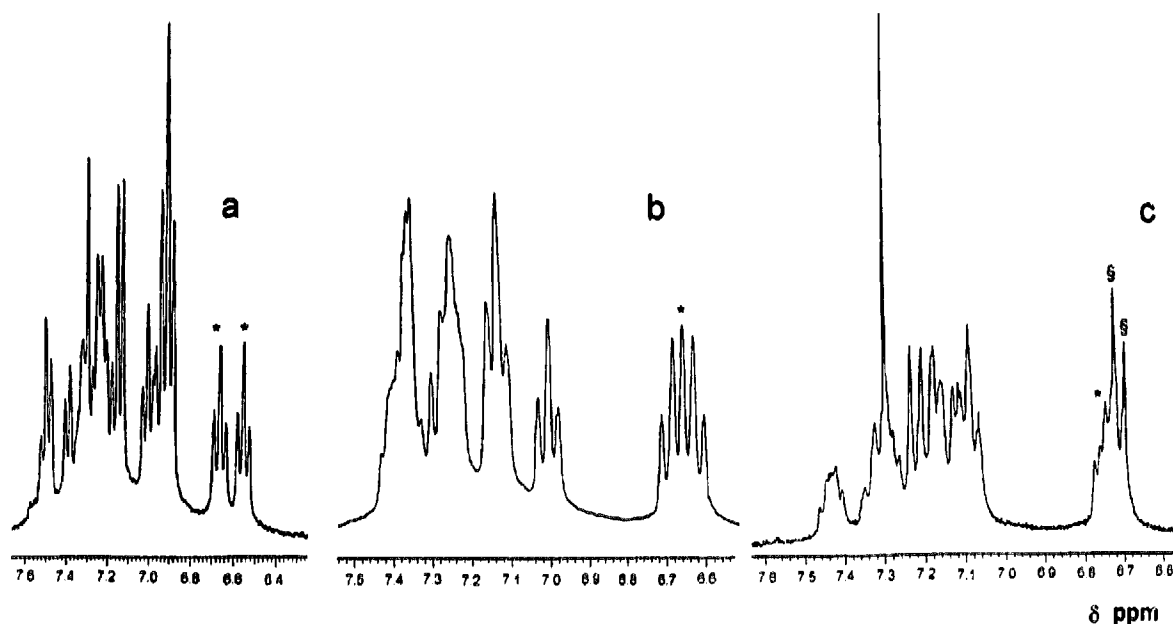


Fig. 1. ¹H NMR spectra (partial phenyl region) of *cis*-[Re(NCR)₂(dppe)₂]⁺: (a) R = CH₂C₆H₄Cl-4, in CD₂Cl₂; (b) R = ¹Pr, in CD₂Cl₂; (c) R = C₆H₄Me-4, in CDCl₃. (*) Resonances of the *ortho*-protons of dppe-phenyls. (§) High field protons of the nitrile ring.

below) or *trans*-[ReCl(=C=CHR)(dppe)₂] [24], the resonances of the CH₂ carbons are observed either as a broad signal or as a quintet due to virtual coupling to the four equivalent phosphorus nuclei [25].

2.1.4. Reactivity

Attempted reactions of the nitrile ligands in complexes **1** in CH₂Cl₂ either with electrophiles — such as protic acids (e.g. HBF₄) or alkylating agents, e.g.

Table 2
¹³C-(¹H) and ¹³C NMR data for the nitrile complexes *cis*-[Re(NCR)₂(dppe)₂][BF₄] **1**

R	δ ^a (ppm)	¹³ C-(¹ H)	J(CP) [¹ J] ^b (Hz)	¹³ C	¹ J(CH) [² J] ^c (Hz)	Assignment	
Et	141.1	t	18.6	m,br	—	C _i (dppe)	
	138.5	d	[41.6]	m,br	—		
	138.1	d,br	[43.0]	m,br	—		
	136.7	t	17.4	m,br	—		
	134.0–126.8	m	—	m	—	Ph (dppe)	
	123.2	s	—	s,br	—		NCR
	34.4	t	9.9	tm	ca. 114	CH ₂ (dppe)	
	33.9	t	10.6	tm	ca. 114		
	25.2	m,br	—	tm	ca. 136	CH ₂ (nitrile)	
	13.5	s	—	t	136.5		
	10.5	s	—	q	130.9		Me (nitrile)
^t Pr	141.2	t	18.6	m,br	—	C _i (dppe)	
	138.2	d	[32.9]	m,br	—		
	138.1	d	[41.6]	m,br	—		
	137.3	t	17.1	m,br	—		
	134.1–126.7	m	—	m,br	—	Ph (dppe)	
	34.8	t	10.4	tm	ca. 129		CH ₂ (dppe)
	34.2 ^c	t	10.4	tm	ca. 129		
	25.2	m	—	tm	ca. 129	CH (nitrile)	
	22.5	s	—	dd	136.5 [3.4]		
	20.3	s	—	qd	130.3 [4.7]		
	19.7	s	—	qd	130.3 [5.0]		
^t Bu ^d	150.0	s	—	d	161.3	Ph (dppe)	
	143.3	t	16.5	m	—		
	142.8	d	[31.6]	m	161.9	NCR	
	141.1	t	16.5	m	—		
	139.6	d	[31.0]	m	—	CH ₂ (dppe) ^e	
	138.2	s	—	m	—		
	135.2–127.5	m	—	m	—	CH ₂ (dppe) ^e	
	123.8	s	—	—	—		
	35.7	t	ca. 12	tm,br	ca. 126	CH ₂ (dppe) ^e	
	35.3	t	ca. 12	tm,br	ca. 126		
	28.3	s	—	q	131.9	CH ₃ (nitrile)	
25.4	s	—	s	—	NCCMe ₃		
C ₆ H ₄ NEt ₂ -4	150.6	s	—	s,br	—	C _p (nitrile)	
	142.0–135.4	m	—	m,br	—		
	135.4–137.2	m	—	m,br	—	Ph (dppe + nitrile)	
	111.2	s	—	dd	160.1 [4.6]		
	96.6	s	—	t	[9.0]	C _i (nitrile)	
	44.8	s	—	tq	135.9 [4.2]		
	34.8	m	—	tm	ca. 148	CH ₂ (dppe)	
	25.0	m,br	—	tm	ca. 134		
	12.5	s	—	qm	ca. 125.6	Me (nitrile)	
	C ₆ H ₄ OMe-4	143.6	s	—	s,br	—	C _p (nitrile)
		141.9	s	—	d	161.3	
140.2–126.1		m	—	m	—	Ph (dppe)	
125.8		s,br	—	s	—		
122.5		s	—	d	158.9	C _m (nitrile)	
109.1		s	—	s,br	—		
34.0		m,br	—	tm	ca. 134	CH ₂ (dppe)	
24.8		m,br	—	tm	ca. 124		
21.8		s	—	q	126.5	Me (nitrile)	

Table 2 (continued)

R	δ^a (ppm)	$^{13}\text{C}\{-^1\text{H}\}$	$J(\text{CP}) [^1J]^b$ (Hz)	^{13}C	$^1J(\text{CH}) [^2J]^c$ (Hz)	Assignment	
$\text{C}_6\text{H}_4\text{Me-4}$	144.2	s	—	s,br	—	C_p (nitrile)	
	140.9	t	18.6	m,br	—	C_i (nitrile)	
	138.2	d	[34.1]	m,br	—		
	137.5	d	[41.6]	m,br	—		
	136.5	t	17.4	m,br	—		
	135.1–127.3	m,br	—	m,br	—	Ph (dppe + nitrile)	
	126.3	m,br	—	m,br	—	NCR	
	109.8	s	—	t	[9.1]	C_i (nitrile)	
	34.5	t	9.6	tm	ca. 116	CH_2 (dppe)	
	34.0	t	11.5	tm	ca. 116		
	25.1	m,br	—	tm	ca. 139		
	22.0	s	—	q	127.5	Me (nitrile)	
	$\text{C}_6\text{H}_4\text{F-4}$	165.1	d ^f	—	dm	—	C_p (nitrile)
		140.5	t	18.9	m,br	—	C_i (dppe)
137.7		d	[30.9]	m,br	—		
137.2		d	[36.5]	m,br	—		
136.3		t	17.9	m,br	—		
135.0–127.8		m	—	m,br	—	Ph (dppe) + C_p (nitrile)	
126.1		s	—	s,br	—	NCR	
117.2		d ^g	—	dd	166.9	C_m (nitrile)	
109.1		s	—	s,br	—	C_i (nitrile)	
34.4		t	10.3	tm	ca. 129	CH_2 (dppe)	
33.9		t	10.3	tm	ca. 129		
25.2		m	—	tm	ca. 146		
$\text{C}_6\text{H}_4\text{NO}_2\text{-4}$	149.1	—	—	s,br	—	C_p (nitrile)	
	139.8–127.6	—	—	m	—	Ph (dppe + nitrile)	
	124.7	—	—	d	170.5	C_m (nitrile)	
	124.3	—	—	s	—	NCR	
	118.5	—	—	t	[10.7]	C_i (nitrile)	
	33.5	—	—	tm,br	ca. 129	CH_2 (dppe)	
	25.2	—	—	tm,br	ca. 141		

^a In CD_2Cl_2 unless stated otherwise; δ values relative to internal SiMe_4 ; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dm = doublet of multiplets, tm = triplet of multiplets, qm = quartet of multiplets, tq = triplet of quartets; subscripts *i*, *o*, *m* and *p* denote the aromatic ipso (C-1), ortho (C-2,6), meta (C-3,5) and para (C-4) aromatic carbons (positions relative to the P atom or to the cyano group). ^b Apparent coupling constant due to virtual coupling; ¹*J* values in square brackets. ^c ²*J* values in square brackets. ^d In $(\text{CD}_3)_2\text{CO}$. ^e Partially overlapped with the acetone resonance. ^f ¹*J*(CF) = 257.1 Hz. ^g ²*J*(CF) = 23.1 Hz.

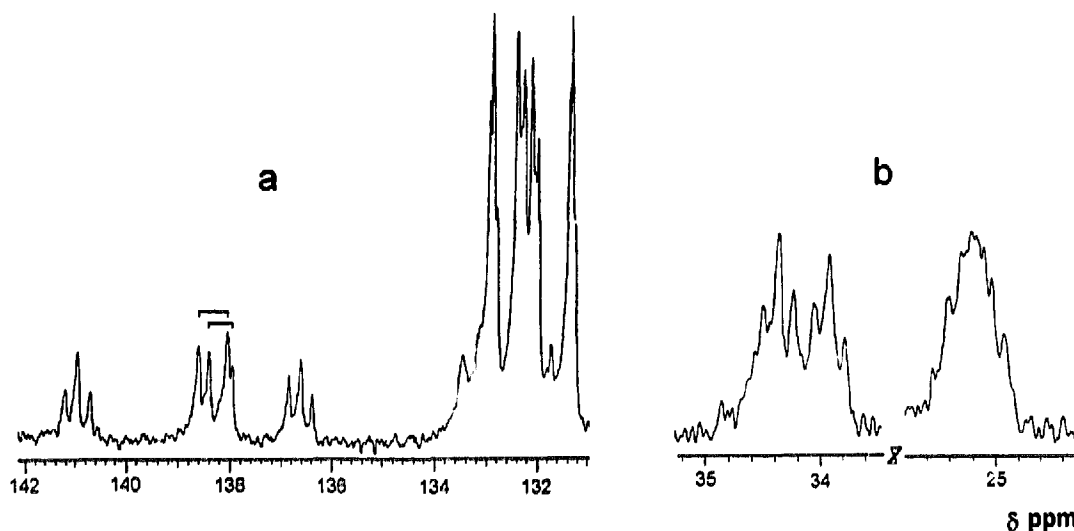


Fig. 2. $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of $\text{cis-}[\text{Re}(\text{NCEt})_2(\text{dppe})_2]^+$ in CD_2Cl_2 . (a) Phenyl; (b) methylene carbons of dppe (intensity scale expanded by a factor of 2.3 relative to (a)).

$[\text{Et}_3\text{O}]\text{X}$ ($\text{X} = \text{PF}_6$ or BF_4) — or with nucleophiles, e.g. $\text{Li}[\text{BEt}_3\text{H}]$, have failed. Only exchange of the counterion by $[\text{PF}_6]^-$ or $[\text{BEt}_3\text{H}]^-$ was observed in the case of $[\text{Et}_3\text{O}][\text{PF}_6]$ or $\text{Li}[\text{BEt}_3\text{H}]$ respectively.

Hence, the products *cis*- $[\text{Re}(\text{NCC}_6\text{H}_4\text{Me-4})_2(\text{dppe})_2][\text{PF}_6]$ and *cis*- $[\text{Re}(\text{NCC}_6\text{H}_4\text{OMe-4})_2(\text{dppe})_2][\text{BEt}_3\text{H}]$ respectively, were isolated and the unreacted complex cations recognized by IR and ^1H and ^{31}P NMR spectroscopies, whereas the corresponding counter-ions were unambiguously identified by IR (e.g. strong band at 835 cm^{-1} for $[\text{PF}_6]^-$) or, in the case of $[\text{BEt}_3\text{H}]^-$, by comparison of its ^1H NMR spectrum with that of a sample of $\text{Li}[\text{BEt}_3\text{H}]$ (in thf). The methylene protons multiplet centred at $\delta -0.19$ (in CD_2Cl_2) was analysed as a quartet ($^2J(\text{BH}) = 4.05\text{ Hz}$) of overlapping quartets ($^3J(\text{HH}) = 7.95\text{ Hz}$), due to coupling to ^{11}B (with nuclear spin of $3/2$) and to the methyl protons respectively; the assignment was confirmed by ^1H -decoupling experiments (the multiplet converted into the expected quartet, due to the former coupling, upon irradiation at the methyl protons resonance). In addition, the methyl protons multiplet centred at $\delta 0.65$ and analysed as a quartet ($^3J(\text{BH}) = 2.70\text{ Hz}$) of overlapping triplets ($^3J(\text{HH}) = 7.95\text{ Hz}$) transformed into the expected quartet upon irradiation at the methylene protons resonance. The BH resonance was not detected, possibly being buried under other complex resonances.

Moreover, the presence of the $[\text{BEt}_3\text{H}]^-$ counter-ion was also confirmed by cyclic voltammetry of a solution of *cis*- $[\text{Re}(\text{NCC}_6\text{H}_4\text{OMe-4})_2(\text{dppe})_2][\text{BEt}_3\text{H}]$ in 0.2 mol dm^{-3} $[\text{N}^n\text{Bu}_4][\text{BF}_4]/\text{CH}_2\text{Cl}_2$ at a Pt disc electrode. Apart from the reversible anodic wave at $E_p^{ox} = 0.45\text{ V}$ due to the $\text{Re(I)} \Rightarrow \text{Re(II)}$ oxidation, an irreversible anodic wave was observed at $E_p^{ox} = 0.39\text{ V}$ vs. a saturated calomel electrode (SCE) (measured at a scan rate of 200 mV s^{-1}) and ascribed to the oxidation of the anion; this was confirmed by comparing the cyclic voltammogram with that of a sample of the corresponding lithium salt, $\text{Li}[\text{BEt}_3\text{H}]$, run in identical experimental conditions.

The lack of reactivity of complexes **1** towards electrophiles or nucleophiles parallels the observed behaviour for the related diisocyanide complexes *trans*- $[\text{Re}(\text{CNR})_2(\text{dppe})_2][\text{BF}_4]$. This agrees with the expected much weaker possible activation towards electrophilic addition of the unsaturated nitrile or isocyanide ligands

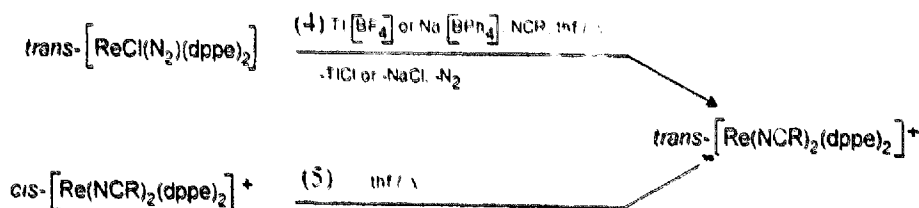
by the cationic $\{\text{Re}(\text{dppe})_2\}^+$ centre compared with the electron-rich neutral $\{\text{ReCl}(\text{dppe})_2\}$ or related $\{\text{M}(\text{dppe})_2\}$ ($\text{M} = \text{Mo}$ or W) sites. In fact, much more pronounced $\nu(\text{N}\equiv\text{C})$ shifts to lower wavenumbers are observed upon coordination of such substrates to these neutral metal centres, compared with the cationic one of the present study (see above), and electrophilic addition (commonly protonation) is then known to occur either at the β -position of the unsaturated ligand (to form methyleneamide or aminocarbene species, derived from ligating nitriles [11] or isocyanides [13] respectively) or at the metal to give hydride complexes [26,27].

The present study indicates that the cationic metal centre is not sufficiently electron releasing to induce such a type of reactivity. However, complexes **1** undergo isomerization to the corresponding *trans* complexes whose synthesis and characterization are described below.

2.2. Complexes **2**, *trans*- $[\text{Re}(\text{NCR})_2(\text{dppe})_2]\text{X}$ ($\text{X} = \text{BF}_4$ or BPh_4)

The dinitrile complexes *trans*- $[\text{Re}(\text{NCR})_2(\text{dppe})_2]\text{X}$ ($\text{R} = ^i\text{Bu}$, $\text{C}_6\text{H}_4\text{OMe-4}$, $\text{C}_6\text{H}_4\text{F-4}$ or $\text{C}_6\text{H}_4\text{Cl-4}$, $\text{X} = \text{BF}_4$; $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$, $\text{X} = \text{BPh}_4$) with the *trans* geometry may be synthesized in refluxing thf conditions (Scheme 2) for ca. 3 days, either from the dinitrogen complex *trans*- $[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$, in the presence of a twofold molar ratio of the appropriate NCR and of a halide abstractor (Eq. (4) in Scheme 2) (ca. 25% yield), or from the corresponding previously described *cis*-isomers (Eq. (5) in Scheme 2) (70–40% yield, the higher value corresponding to $\text{X} = \text{BPh}_4$ and the lower one to $\text{X} = \text{BF}_4$). Even if we take into consideration the observed yields (ca. 80%) for the preparation of the *cis*-isomers from the dinitrogen complex, the overall yields of the syntheses of the *trans*-compounds, involving the isolation of the other isomers as intermediate species, are higher than those of the direct route from the dinitrogen complex.

Side reactions have also been detected in some cases and, e.g., on the attempted synthesis of *trans*- $[\text{Re}(\text{NCC}_6\text{H}_4\text{Me-4})_2(\text{dppe})_2][\text{BF}_4]$ according to the reaction (4) in Scheme 2, in the presence of $\text{Ti}[\text{BF}_4]$, the isolated product was shown, by single-crystal diffraction analysis [5], to contain also discrete moieties of



Scheme 2.

trans-[ReF₂(dppe)₂]⁺ in which the fluoride ligands have originated from [BF₄]⁻, and which constitutes a rare example of a mononuclear rhenium compound with only halide and phosphine ligands [28]. Therefore, the species was formulated [5] as the complex double salt *trans*-[Re(NCC₆H₄Me-4)₂(dppe)₂][BF₄] · *trans*-[ReF₂(dppe)₂][BF₄] (the similar product but with the NCC₆H₄OMe-4 ligand was obtained from the analogous reaction of this nitrile). The double metal fluorination by [BF₄]⁻, despite the presence of the nitrile substrate, is surprising, although the ability of this anion to mono-fluorinate the rhenium centre has been documented [15].

Both complex cations present a distorted octahedral coordination, and the Re–N and N–C multiple bond lengths of the virtually linear nitrile ligands (average 2.063(7) Å and 1.102(13) Å respectively) [5] are similar to those shown by the *cis*-isomer *cis*-[Re(NCC₆H₄Me-4)₂(dppe)₂]⁺ (average 2.065(16) Å and 1.125(24) Å respectively) [19] (see above). However, the average Re–P distance in the *trans*-isomer, 2.401(3) Å [5], is slightly longer than that in the *cis*-isomer, 2.374(6) Å, suggesting a weaker π-electron release from the metal to the phosphines in the former isomer.

Complexes **2** were isolated as orange or yellow (R = ^tBu) solids, giving satisfactory elemental analyses,

and their multinuclear NMR spectroscopic properties are given in Tables 3 and 4.

2.2.1. IR spectroscopy

In their IR spectra, complexes **2** show a strong band in the 2180–2125 cm⁻¹ range (KBr pellets) assigned to N≡C stretching of the nitrile ligand. These values are lower than those exhibited by the corresponding free nitriles and of those observed for the previously described *cis*-isomers, as well as those reported [16] for the analogous *cis*-mononitrile complexes. The observation of a single IR band associated with the stretching mode of the two unsaturated N≡C groups indicates the *trans* geometry of complexes **2**, which is also confirmed by ³¹P NMR data (see below).

Comparing the low frequency pattern (in the 550–450 cm⁻¹ range, in which some CC vibration modes of the phenyl rings are expected [29]) of the IR spectra of the diphosphine region of the *cis*- and *trans*-dinitrile complexes of this study, one recognizes some diagnostic features which are indicative of the type of arrangement of the two diphosphines, in particular the number and broadness of the observed bands. Indeed, whereas the *cis*-[Re(NCR)₂(dppe)₂]⁺ complexes present only two partially overlapping bands (one of them with a predominant intensity), the *trans* compounds exhibit

Table 3
¹H and ³¹P-{¹H} NMR data ^a for complexes *trans*-[Re(NCR)₂(dppe)₂]**2** (X = BF₄ or BPh₄)

R	¹ H ^b		³¹ P-{ ¹ H} ^c
	δ (ppm)	Assignment	
^t Bu	7.32 (s,br, 8H)	Ph (dppe)	- 107.5 (s)
	7.27–7.07 (m, 32H)		
	2.50 (s,br, 8H)	CH ₂ (dppe)	
	0.57 (s,br, 18H)	CH ₃ (nitrile)	
C ₆ H ₄ OMe-4 ^d	7.35–6.78 (m, 48H)	Ph (dppe + nitrile)	- 113.7 (s)
	2.44 (s,br, 8H)	CH ₂ (dppe)	
	1.53 (s,br, 6H)	CH ₃ (nitrile)	
C ₆ H ₄ Me-4	7.27 (m, 8H)	Ph (dppe + nitrile + BPh ₄)	- 112.7 (s)
	7.11–7.03 (m, 56H)		
	6.34 (d,br, 4H)		
	2.52 (s,br, 8H)	CH ₂ (dppe)	
	2.41 (s,br, 6H) ^e	CH ₃ (nitrile)	
C ₆ H ₄ F-4 ^f	7.29 (t, 8H) ^g	Ph (dppe + nitrile)	- 112.8 (s)
	7.26–7.00 (m, 36H)		
	6.79 (m,br, 4H)	CH ₂ (dppe)	
	2.54 (s,br, 8H)		
C ₆ H ₄ Cl-4	7.40–7.00 (m, 68H)	Ph (dppe + nitrile + BPh ₄)	- 115.2 (s, br)
	2.70 (s,br, 4H)	CH ₂ (dppe)	
	2.54 (s,r, 4H)		

^a With BF₄⁻ as the counter-ion, except for R = C₆H₄Me-4 and R = C₆H₄Cl-4 when X = BPh₄. ^b In CD₂Cl₂. δ values relative to internal SiMe₄; s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. ^c In CD₂Cl₂. δ values relative to internal P(OMe)₃. ^d Corresponds to the dinitrile complex of the double salt *trans*-[Re(NCR)₂(dppe)₂][BF₄] · *trans*-[ReF₂(dppe)₂][BF₄]. The resonances due to the paramagnetic difluoro complex were not established, except the very broad ³¹P-{¹H} resonance at δ ca. 113.0–111.5. ^e In CDCl₃ the Me resonances are observed at δ 2.70 (s, 3H) and δ 1.89 (s, 3H). ^f In the ¹⁹F NMR spectra the unresolved singlet at δ -105.03 (relative to CFCl₃) was attributed to the C₆H₄F-4 resonance. ^g Apparent coupling constant ³J = 6.8 Hz (see text).

Table 4
 ^{13}C -(^1H) and ^{13}C NMR data for complexes **2**, $\text{trans-}[\text{Re}(\text{NCR})_2(\text{dppe})_2][\text{BF}_4]$

R	δ^a (ppm)	^{13}C -(^1H)	^{13}C	$J(\text{CH}) [^2J]^b$ (Hz)	Assignment
$\text{C}_6\text{H}_4\text{Me-4}$	142.69	s	s,br	—	C_p (nitrile)
	135.17	qt ^c	m,br	—	C_i (dppe)
	132.79	s	d	160.7	C_p (dppe)
	132.00	s	d	169.9	C_m or C_o (nitrile)
	129.91	d ^d	dd	157.6	C_o (dppe)
	128.91	s	d	162.5	C_m (dppe)
	121.33	s	s,br	—	NCR
	110.78	s	t	[9.0]	C_i (nitrile)
	30.63	qt ^c	tm	132.3	CH_2 (dppe)
	21.87	s	q	127.2	CH_3 (nitrile)
$\text{C}_6\text{H}_4\text{F-4}^f$	134.80	m	m	—	C_i (dppe)
	134.52	d ^f	dd	157.4	C_o (nitrile)
	132.74	s	d	160.0	C_p (dppe)
	130.12	s	d	162.6	C_o (dppe)
	129.01	s	d	162.5	C_m (dppe)
	120.04	s	s,br	—	NCR
	116.85	d ^g	dd	166.8	C_m (nitrile)
	110.07	s,br	s,br	—	C_i (nitrile)
	30.47	m	tm	127.5	CH_2 (dppe)
$\text{C}_6\text{H}_4\text{Cl-4}^h$	134.51	m	m,br	—	C_i (dppe)
	132.66	s	d	160.6	C_p (nitrile)
	131.29	s	—	—	— ⁱ
	130.15	s	d	163.2	C_o (dppe)
	129.10	s	d	156.9	C_m (dppe)
	112.02	s,br	s,br	—	C_i (nitrile)
	30.27	m,br	tm	139.9	CH_2 (dppe)

^a In CD_2Cl_2 ; δ values relative to internal SiMe_4 ; s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet, br = broad, dd = doublet of doublets, tm = triplet of multiplets. ^b 2J values in square brackets. ^c Apparent coupling constant $|J(\text{CP})| = 10.1$ Hz. ^d $^2J(\text{CP}) = 3.8$ Hz. ^e Apparent coupling constant $|J(\text{CP})| = 10.8$ Hz. ^f $^3J(\text{CF}) = 10.0$ Hz. ^g $^2J(\text{CF}) = 22.9$ Hz. ^h The δ value for the NCR ligands could not be unambiguously assigned. ⁱ Unassigned resonance.

four clearly defined bands (Fig. 3). Moreover, similar features are also evident in both the *cis*- and *trans*-mononitrile complexes $[\text{ReCl}(\text{NCR})(\text{dppe})_2]$ and in related carbonyl compounds which will be described separately. The use of IR criteria for the assignment of stereochemistry in other phosphine complexes has been reported in a few cases [30], in particular for bis(triphenylphosphine) complexes of Pt(II) in which a sharp

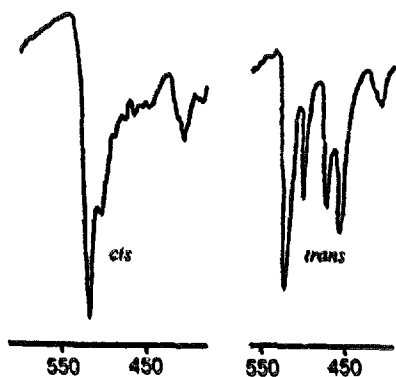


Fig. 3. IR spectra (low frequency phosphine region) (KBr pellets) of *cis*- and *trans*- $[\text{Re}(\text{NCC}_6\text{H}_4\text{Me-4})_2(\text{dppe})_2][\text{BF}_4]$. Frequency in wavenumbers (cm^{-1}).

and strong band at ca. 550cm^{-1} , probably due to ligand (phosphine) internal modes, split or activated by complexation [30], is indicative of a *cis* geometry.

2.2.2. Multinuclear NMR spectroscopy

In the ^1H NMR spectra of complexes **2** (Table 3) the resonance pattern of the diphosphine ligands presents a considerable simplicity. Hence, the methylene protons commonly exhibit an unresolved broad singlet resonance at δ ca. 2.5, whereas eight phenyl protons usually resonate at a slightly lower field (δ ca. 7.3) than the bulk phenyl resonance. In one case ($\text{R} = \text{C}_6\text{H}_4\text{F-4}$) this low field resonance appears as a triplet (apparent $J = 6.8$ Hz) but it cannot be unambiguously assigned, since it can be attributed to the phenyl protons either in *ortho* (coupling to both the *meta*-proton and the phosphorus nucleus, $^3J(\text{HH}) \approx ^3J(\text{HP}) = 6.8$ Hz), in *meta* (coupling to the *ortho*- and *para*-protons), or in *para* position (coupling to the *meta*-protons).

For all the complexes **2** a singlet is observed in their ^{31}P -(^1H) NMR spectra in agreement with the *trans* geometry. In addition, in the case of the double salt $\text{trans-}[\text{Re}(\text{NCC}_6\text{H}_4\text{OMe-4})_2(\text{dppe})_2][\text{BF}_4] \cdot \text{trans-}[\text{ReF}_2(\text{dppe})_2][\text{BF}_4]$, a very broad resonance at δ ca.

113.0–111.5 is also observed, being assigned to the paramagnetic difluoro-Re(III) compound.

In the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra of some of the complexes **2** (Table 4) the resonance of the cyano group has been detected as a broad singlet at δ ca. 121.3–120.0, i.e. at a slightly higher field than that of the corresponding *cis*-isomers, conceivably in agreement with the expected higher electronic density at the nitrile carbon in the former complexes (lower $\nu(\text{NC})$, as shown above). The resonances of the phenyl *ipso*-carbons of the chelated diphosphines are much simpler than in the case of the *cis*-isomers **1** (see above), being observed as an unresolved low field multiplet at δ ca. 135; in one case it appears as a quintet due to virtual coupling to the four phosphorus nuclei ($J(\text{CP}) = 10.1$ Hz). The remaining phenyl phosphine carbons appear as singlets which convert into the expected doublets in the ^1H -coupled spectra. Although some of the coordinated nitrile phenyl carbon resonances are buried under those of the phosphines, the assignment of those observed was possible on the basis of the similarity of the δ values with those of the free NCR species.

In contrast with the complex pattern observed for the *cis*-isomers **1** (see above), the methylene carbons resonance of the diphosphines appears as a broad signal at δ ca. 30 which for **2** ($\text{R} = \text{C}_6\text{H}_4\text{Me}$ -4) is resolved into a quintet (10.8 Hz) due to virtual coupling to the four phosphorus nuclei.

3. Final comments

In this work we have succeeded in selecting the conditions favourable to the synthesis of complexes with the rather unusual *cis*-diphosphine geometry and we have proposed spectroscopic diagnostic criteria for its identification. The use of relatively mild experimental conditions allowed the isolation of nitrile complexes with the *cis*- $\{\text{Re}(\text{dppe})_2\}^+$ centre, in particular of the types *cis*- $\{\text{Re}(\text{NCR})_2(\text{dppe})_2\}^+$ or *cis*- $\{\text{ReCl}(\text{NCR})(\text{dppe})_2\}$ which are the only known *cis*-isomers of octahedral Re(I) tetraphosphine complexes. However, they convert into the corresponding *trans*-isomers upon activation by sunlight or by heating, and the use of such conditions in the synthesis experiments leads to the isolation of the latter species as the final products.

The starting material is a *trans* complex, *trans*- $\{\text{ReCl}(\text{N}_2)(\text{dppe})_2\}$, and thus the geometrical flexibility of the $\{\text{Re}(\text{dppe})_2\}^+$ centre is evident, depending on both the electronic properties of the substrates and the applied experimental conditions. Nitriles appear to promote such a flexibility (compared with isocyanides or dinitrogen for which only the *trans*-isomers are known). Moreover, their coordination lability or further reactivity allows the occurrence of side reactions involving the halogenation of the metal centre, conceivably by

metathesis of $\{\text{ReCl}(\text{dppe})_2\}$ or upon fluorination by $[\text{BF}_4]^-$. Moreover, the $\{\text{Re}(\text{NCR})(\text{dppe})_2\}^+$ centres are significantly less basic than $\{\text{ReCl}(\text{dppe})_2\}$ and, in contrast to the latter and under identical experimental conditions, they are neither susceptible to electrophilic addition (e.g. by H^+ or R^+) nor able to activate a substrate (nitrile or isocyanide) towards such a reaction.

The syntheses of series of both types of geometrical isomer also allowed the recognition of typical IR and ^{13}C NMR spectroscopic patterns which can be of diagnostic value to establish the geometrical arrangement of the two diphosphine ligands in complexes with metal centres of the type $\{\text{M}(\text{dppe})_2\}$.

In addition, the compounds prepared also provide very rare examples of nitrile complexes with an electron-rich metal centre without stabilization by a stronger π -acceptor.

4. Experimental

All the manipulations and reactions were carried out in the absence of air using standard inert-gas flow and vacuum techniques. Solvents were purified by standard procedures, *trans*- $\{\text{ReCl}(\text{N}_2)(\text{dppe})_2\}$ was prepared by a published method [9] and the organonitriles (Fluka, Aldrich or Lancaster Synthesis), $\text{Li}[\text{BEt}_3\text{H}]$ (Aldrich; 1 mol dm $^{-3}$ in thf) and $[\text{Et}_3\text{O}][\text{PF}_6]$ (Aldrich) were commercially available. IR measurements were carried out on a Perkin–Elmer 683 spectrophotometer, and ^1H , ^{19}F , ^{31}P and ^{13}C NMR spectra on a Varian Unity 300 spectrometer.

The electrochemical experiments were performed on an EG & G PARC 173 potentiostat and an EG & G PARC 175 universal programmer. A two-compartment three-electrode cell, with a platinum-wire working electrode, probed by a Luggin capillary connected to a silver wire pseudo-reference electrode and a platinum or tungsten auxiliary electrode, was employed. The potentials were measured in 0.2 mol dm $^{-3}$ $[\text{N}^n\text{Bu}_4][\text{BF}_4]-\text{CH}_2\text{Cl}_2$ and are quoted relative to the SCE by using the *trans*- $\{\text{ReCl}(\text{N}_2)(\text{dppe})_2\}^{0/+}$ couple ($E_{1/2}^{0/+} = 0.28$ V vs. SCE) as internal reference.

4.1. Syntheses of *cis*- $\{\text{Re}(\text{NCR})_2(\text{dppe})_2\}[\text{BF}_4]$ **1 ($\text{R} = \text{Et}$, ^iPr , ^tBu , $\text{CH}_2\text{C}_6\text{H}_4\text{Cl}$ -4, $\text{C}_6\text{H}_4\text{NEt}_2$ -4, $\text{C}_6\text{H}_4\text{OH}$ -4, $\text{C}_6\text{H}_4\text{OMe}$ -4, $\text{C}_6\text{H}_4\text{Me}$ -4, Ph , $\text{C}_6\text{H}_4\text{F}$ -4, $\text{C}_6\text{H}_4\text{Cl}$ -4 or $\text{C}_6\text{H}_4\text{NO}_2$ -4)**

The complexes **1** were prepared under dinitrogen by adding the appropriate nitrile, in a 2.2-fold molar ratio, to a thf solution of *trans*- $\{\text{ReCl}(\text{N}_2)(\text{dppe})_2\}$ with $\text{Tl}[\text{BF}_4]$ and the mixture left stirring at room temperature for ca. 24 h. The white precipitate of thallium salts was then filtered off and the filtrate was taken to dryness. The

resulting solid was dissolved in CH_2Cl_2 and the solution was filtered again. Addition of diethyl ether led to the precipitation of the corresponding complex which was filtered off, washed with CH_2Cl_2 - Et_2O and dried in vacuo (typically ca. 80% yield). IR (KBr pellet) ($\nu(\text{NC})$): 2240 (s) (R = Et); 2210 (s,br) (R = ^iPr); 2215 (s), 2205 (s) (R = ^tBu); 2230 (sh), 2220 (s) (R = $\text{CH}_2\text{C}_6\text{H}_4\text{Cl-4}$); not observed for (R = $\text{C}_6\text{H}_4\text{NEt}_2\text{-4}$); 2210 (sh), 2200 (s) (R = $\text{C}_6\text{H}_4\text{OH-4}$); 2200 (s), 2190 (s) (R = $\text{C}_6\text{H}_4\text{OMe-4}$); 2205 (s), 2190 (s) (R = $\text{C}_6\text{H}_4\text{Me-4}$); 2200 (m), 2170 (s) (R = Ph); 2205 (w), 2190 (s) (R = $\text{C}_6\text{H}_4\text{F-4}$); 2200 (sh), 2185 (s) (R = $\text{C}_6\text{H}_4\text{Cl-4}$); 2180 (m), 2150 (s) (R = $\text{C}_6\text{H}_4\text{NO}_2\text{-4}$).

As a typical example, $\text{cis-}[\text{Re}(\text{NCC}_6\text{H}_4\text{Me-4})_2(\text{dppe})_2][\text{BF}_4]$ was prepared as follows: thf (200 cm^3) was added to a mixture of $\text{trans-}[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$ (0.30 g, 0.29 mmol), $\text{Ti}[\text{BF}_4]$ (0.13 g, 0.43 mmol) and $\text{NCC}_6\text{H}_4\text{Me-4}$ (0.075 g, 0.64 mmol) and the system was stirred under dinitrogen for 24 h. The solution was then concentrated, the undissolved thallium salts were filtered off, and the filtrate was taken to dryness. The solid residue was partially dissolved in a small volume (10 cm^3) of CH_2Cl_2 , the solution filtered and on addition of Et_2O the desired product precipitated as a yellow crystalline solid which was filtered off, washed with CH_2Cl_2 - Et_2O (1:3) and dried in vacuo.

4.2. Synthesis of $\text{cis-}[\text{Re}(\text{NCC}_6\text{H}_4\text{Me-4})_2(\text{dppe})_2][\text{BPh}_4]$

This complex was prepared in a similar way to that described above for the corresponding $\text{cis-}[\text{Re}(\text{NCR})_2(\text{dppe})_2][\text{BF}_4]$ species, but using $\text{Na}[\text{BPh}_4]$ instead of $\text{Ti}[\text{BF}_4]$.

4.3. Synthesis of $\text{cis-}[\text{Re}(\text{NCC}_6\text{H}_4\text{OH-4})_2(\text{dppe})_2]\text{Cl}$

Elongation of the reaction time in the general procedure followed [16] in the synthesis of the mononitrile complexes $\text{cis-}[\text{ReCl}(\text{NCR})(\text{dppe})_2]$ led to the isolation of this cationic species in the following way. A suspension of $\text{trans-}[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$ (0.30 g, 0.29 mmol) and $\text{NCC}_6\text{H}_4\text{OH-4}$ (0.070 g, 0.55 mmol) in toluene (250 cm^3) was stirred for 48 h (substantially smaller reaction times result in mixtures of the dinitrile complex with the starting dinitrogen compound) under dinitrogen and in sunlight. The yellow solid formed was filtered off, washed with small portions of toluene (1 cm^3) and dried in vacuo. Further crops were obtained by successive concentrations of the solution followed by filtrations (ca. 85% yield).

4.4. Synthesis of $\text{cis-}[\text{Re}(\text{NCC}_6\text{H}_4\text{Me-4})_2(\text{dppe})_2][\text{PF}_6]$

$[\text{Et}_3\text{O}][\text{PF}_6]$ (0.040 g, 0.18 mmol) was added to a solution of $\text{cis-}[\text{Re}(\text{NCC}_6\text{H}_4\text{Me-4})_2(\text{dppe})_2][\text{BF}_4]$

(0.040 g, 0.030 mmol) in CH_2Cl_2 (5 cm^3) and the system was left stirring overnight. Upon addition of Et_2O , yellow crystals were formed which were filtered off, washed with CH_2Cl_2 - Et_2O (1:3), then with Et_2O and dried in vacuo (85% yield).

4.5. Synthesis of $\text{cis-}[\text{Re}(\text{NCC}_6\text{H}_4\text{OMe-4})_2(\text{dppe})_2][\text{BEt}_3\text{H}]$

To a CH_2Cl_2 solution (20 cm^3) of $\text{cis-}[\text{Re}(\text{NCC}_6\text{H}_4\text{OMe-4})_2(\text{dppe})_2][\text{BF}_4]$ (0.26 g, 0.20 mmol), an excess of $\text{Li}[\text{BEt}_3\text{H}]$ (0.80 cm^3 of a 1 mol dm^{-3} thf solution, 0.80 mmol) was added dropwise and the mixture was left stirring for ca. 0.5 h. The white precipitate containing $\text{Li}[\text{BF}_4]$ was then filtered off and addition of Et_2O led to the precipitation of a bright yellow solid which was isolated by filtration and whose IR analysis indicated to be the starting complex. The mother solution was left standing and orange crystals of the title complex formed which were separated by decantation of the solution, washed with CH_2Cl_2 - Et_2O (1:3) and dried in vacuo (40% yield).

4.6. Syntheses of $\text{trans-}[\text{Re}(\text{NCR})_2(\text{dppe})_2][\text{BF}_4]$ 2 (R = ^iBu , $\text{C}_6\text{H}_4\text{OMe-4}$, $\text{C}_6\text{H}_4\text{Me-4}$, $\text{C}_6\text{H}_4\text{F-4}$ or $\text{C}_6\text{H}_4\text{Cl-4}$)

These complexes are preferably obtained: (i) from the corresponding cis- isomers, although in some cases (R = ^iBu or $\text{C}_6\text{H}_4\text{F-4}$) could also be prepared, in lower yields; (ii) from the reactions of $\text{trans-}[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$ with the appropriate nitrile in the presence of $\text{Ti}[\text{BF}_4]$.

The former route (i) is exemplified for 2 (R = $\text{C}_6\text{H}_4\text{OMe-4}$) as follows: $\text{cis-}[\text{Re}(\text{NCC}_6\text{H}_4\text{OMe-4})_2(\text{dppe})_2][\text{BF}_4]$ (0.16 g, 0.12 mmol) was dissolved in thf (20 cm^3) and the system was left refluxing under dinitrogen. The orange suspension which was present in the mixture after 3 days of reaction was the trans- dinitrile complex. Filtration of the cooled solution allowed the isolation of this compound as an orange crystalline solid which was washed with small portions of thf and dried in vacuo (43% yield). Further crops, obtained by successive concentrations of the mother-solution and filtrations, consisted of a mixture of the two isomers.

Route (ii), from the dinitrogen complex, is exemplified for 2 (R = ^iBu) in the following way: NC^iBu (0.063 cm^3 , 0.57 mmol) was added to a mixture of $\text{trans-}[\text{ReCl}(\text{N}_2)(\text{dppe})_2]$ (0.20 g, 0.19 mmol) and $\text{Ti}[\text{BF}_4]$ (0.083 g, 0.28 mmol) in thf (40 cm^3) and the system was left refluxing under dinitrogen for 3 days. During this period no change of colour (yellow) was observed, but a dark-yellow precipitate was formed. Concentration of the solution in vacuo followed by filtration allowed the isolation of $\text{trans-}[\text{Re}(\text{NC}^i\text{Bu})_2(\text{dppe})_2][\text{BF}_4]$ which was washed with thf,

then with water and dried in vacuo (ca. 20% yield). Further crops from the mother solution consisted of mixtures of the *cis*- and the *trans*-dinitrile complexes. IR (KBr pellet) ($\nu(\text{NC})$): 2180 (s) (R = ^tBu); 2140 (s) (R = C₆H₄OMe-4); 2140 (s) (R = C₆H₄Me-4); 2130 (s) (R = C₆H₄F-4); 2125 (s) (R = C₆H₄Cl-4).

4.7. Syntheses of *trans*-[Re(NCR)₂(dppe)₂][BPh₄] (R = C₆H₄Me-4 or C₆H₄Cl-4)

These complexes are also more conveniently prepared (i) from the corresponding *cis*-isomers, although they can also be obtained (ii) from the reaction of *trans*-[ReCl(N₂)(dppe)₂] with the appropriate nitrile in the presence of Na[BPh₄].

Route (i) is exemplified for **2** (R = C₆H₄Me) as follows: refluxing a thf (or CH₂Cl₂) solution (20 cm³) of *cis*-[Re(NCC₆H₄Me-4)₂(dppe)₂][BPh₄] (0.050 g, 0.03 mmol) for a period of 3 days, followed by addition of Et₂O, led to the precipitation of the red, crystalline, *trans*-dinitrile complex which was filtered off, washed with thf (or CH₂Cl₂)-Et₂O (1:3) and dried in vacuo (ca. 70% yield).

Route (ii) is exemplified for **2** (R = C₆H₄Me-4) in the following way: thf (40 cm³) was added to a mixture of *trans*-[ReCl(N₂)(dppe)₂] (0.20 g, 0.19 mmol) with NCC₆H₄Me-4 (0.060 g, 0.42 mmol) and Na[BPh₄] (0.13 g, 0.38 mmol) and the system was left refluxing under dinitrogen for 3 days. The initially yellow solution turned to red. The system was taken to dryness, 5 cm³ of CH₂Cl₂ were added and the white precipitate of sodium salts was filtered off. The analysis of the first two crops, obtained upon addition of Et₂O to the mother-solution, indicated the presence of a mixture of the desired complex with the starting compound. The third fraction, however, was the red crystalline *trans*-dinitrile complex which was isolated by filtration, washed with CH₂Cl₂-Et₂O (1:3) and dried in vacuo (25% yield).

4.8. Syntheses of *trans*-[Re(NCR)₂(dppe)₂][BF₄] · *trans*-[ReF₂(dppe)₂][BF₄] (R = C₆H₄OMe-4 or C₆H₄Me-4)

These complex double-salts were prepared following the procedure [5] previously outlined, and now detailed as follows for the former compound: thf (15 cm³) was added to a mixture of *trans*-[ReCl(N₂)(dppe)₂] (0.20 g, 0.19 mmol), NCC₆H₄OMe-4 (0.080 g, 0.57 mmol) and Tl[BF₄] (0.080 g, 0.28 mmol) and the system was left refluxing for 3 days. The solution was taken to dryness and CH₂Cl₂ was added to the final residue. The white precipitate of thallium salts was filtered off and addition of Et₂O led to the precipitation of orange needle crystals which were isolated, washed with Et₂O and dried in vacuo (ca. 45% yield). Further crops contain the *cis*-di-

nitrile complex, which can be separated from the *trans* double salt by recrystallization from CH₂Cl₂-Et₂O.

5. Supplementary material

Tables of analytical and IR spectroscopic data for complexes **1** and **2** are available.

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