Synthesis and Redox Properties of *cis*-[ReCl(NCR)($Ph_2PCH_2CH_2PPh_2$)$_2$] (R = alkyl or aryl) Complexes with a *cis*-Phosphine Rhenium(I) Centre

M. Fátima C. Guedes da Silva, João J. R. Fraústo da Silva and Armando J. L. Pombeiro*
Centro de Quimica Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais,
1096 Lisbon codex, Portugal

Treatment of a solution of *trans*-[ReCl(N_2)(dppe)$_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) in toluene with the appropriate organonitrile in sunlight afforded *cis*-[ReCl(NCR)(dppe)$_2$] **1** (R = $C_6H_4NEt_2$-4, C_6H_4OMe-4, C_6H_4Me-4, Ph, C_6H_4F-4, C_6H_4Cl-4, $C_6H_4NO_2$-4, $CH_2C_6H_4Cl$-4, Et, Pr^i or Bu^t) the ^{31}P-{^1H} NMR spectra of which have been analysed as ABCD spin systems. Cyclic voltammograms of the complexes, in aprotic medium at a Pt electrode, show a single-electron reversible oxidation at half-wave anodic potentials ($^IE_{\frac{1}{2}}^{ox}$) in the range −0.20 to −0.02 V *vs.* saturated calomel electrode (at −20 °C) which is followed by a second anodic process at a higher potential. For the aromatic nitriles, direct or inverse linear correlations are observed between $^IE_{\frac{1}{2}}^{ox}$ and the Hammett constant, σ_p, of the phenyl substituent or the ν(NC) frequency, respectively.

The co-ordination chemistry of small N- or C-unsaturated molecules, such as dinitrogen,[1] isocyanides[2] or alkynes,[2,3] has been considerably developed for the electron-rich Group 6, 7 or 8 d^6-metal phosphine centres {ML_4} [M = Mo or W, L = tertiary phosphine or L_2 = chelating diphosphine, *e.g.*, $Ph_2PCH_2CH_2PPh_2$ (dppe)], *trans*-{$ReClL_4$}, *trans*-{ReL_4}$^+$ or *trans*-{$FeHL_4$}$^+$. In particular, dinitrogen can undergo electrophilic attack,[4–6] whereas isocyanides[7–11] and alkyne-derived alkynyl,[12] allene[13] or vinylidene[14] ligands are activated towards β-protonation to afford a variety of multiple metal–carbon bonded species, in particular aminoalkylidynes (from isocyanides),[15] η^2-vinyl (from allene)[16] or alkylidynes (from alkylidenes or alkynyls).[12,17]

In contrast, the co-ordination chemistry of nitriles at electron-rich metal centres has been much less developed, in spite of the widespread use of nitrile complexes as starting materials in co-ordination chemistry.[18] This conceivably stems, at least in part, from their relatively poor π-acid character, and they usually ligate such centres only in combination with a stronger π-electron acceptor, in particular in *trans*-[Mo(N_2)(NCR)(dppe)$_2$][19] or *trans*-[ReL(NCR)(dppe)$_2$]$^+$ (L = N_2[20] or CNMe[10]). Nevertheless, we have previously succeeded in the preparation of the nitrile compounds of the types *trans*- or *cis*-[Re(NCR)$_2$(dppe)$_2$]$^+$ [21,22] and *trans*-[ReCl(NCR)(dppe)$_2$],[23,24] as well as of methyleneamido complexes formed upon β-protonation at the nitrile ligand,[23] and now we report the extension of the synthesis to *cis*-[ReCl(NCR)(dppe)$_2$] **1**. Moreover, the complexes reported herein and *cis*-[Re(NCR)$_2$(dppe)$_2$]$^+$ [22] constitute the only known examples of *cis* isomers for octahedral rhenium(I) tetraphosphine compounds; this is also of particular significance to the investigation of the electronic factors determining the relative stabilities of the *cis* and *trans* geometrical isomers of octahedral-type phosphine complexes with π-acceptor or π-donor ligands, which has been the subject of a number of molecular orbital (MO)[25] and electrochemical[26] studies.

Results and Discussion

Treatment of the dinitrogen complex *trans*-[ReCl(N_2)(dppe)$_2$] in toluene with the appropriate organonitrile (NCR, in a twofold molar ratio), under an inert atmosphere, in sunlight, for *ca.* 4 h, usually gives the corresponding mononitrile complex *cis*-[ReCl(NCR)(dppe)$_2$] **1** (R = $C_6H_4NEt_2$-4, C_6H_4OMe-4, C_6H_4Me-4, Ph, C_6H_4F-4, C_6H_4Cl-4, $C_6H_4NO_2$-4, $CH_2C_6H_4Cl$-4, Et, Pr^i or Bu^t) [equation (1)]. The alkyl

$$trans\text{-}[\mathrm{ReCl(N_2)(dppe)_2}] + \mathrm{NCR} \longrightarrow cis\text{-}[\mathrm{ReCl(NCR)(dppe)_2}] + \mathrm{N_2} \quad (1)$$

compounds **1** (R = Bu^t, Pr^i or $CH_2C_6H_4Cl$-4) are quite unstable in solution and were usually obtained contaminated with other species. Different experimental conditions (such as longer reaction time, higher temperature or a greater excess of the nitrile) commonly lead to different products, in particular the corresponding *trans* isomers[23,24] or dinitrile[21,22] compounds, which will be reported in detail separately.

The formation of the *cis* isomers of the nitrile complexes, which occurs under milder conditions than those leading to the *trans* isomers, is noteworthy as previously only *trans* geometry has been found for the two diphosphine ligands in 18-, 17- and 16-electron octahedral Re or Tc complexes, such as the rhenium complexes mentioned above and related technetium species, *trans*-[TcHL(dppe)$_2$] (L = N_2 or CO),[27] as well as the dihalogeno complexes *trans*-[MX_2(L–L)$_2$]$^{n+}$ [M = Re[28] or Tc;[29] X = Cl, Br or F; L–L = chelating bis(tertiary phosphine or arsine); *n* = 0 or 1].

In addition, the complexes **1** contain a π-acceptor (NCR) and a π-donor (Cl) ligand bonded to the {Re(dppe)$_2$}$^+$ core, and therefore represent a combination of ligands (π-acceptor *versus* π-donor) which has not been previously studied. Extended-Hückel MO calculations[25] indicate that for 18-electron octahedral complexes of the types [$ML_2L'_4$] (M = Cr, Mo or W; L = N_2, CO or O; L′ = phosphine) two π-acceptor ligands should stabilize the *cis* geometry, whereas two π-donor ligands are expected to stabilize the *trans* form. The chloro–nitrile compounds reported here represent, in principle, a more complex situation and the overall (net) effect is expected to depend on the relative ability of the two ligands for π-acceptance and π-donation.

The complexes **1** have been isolated as red or orange solids (except for R = $CH_2C_6H_4Cl$-4 or $C_6H_4NO_2$-4, which are green or deep blue, respectively) (Table 1) and the *cis* geometry has been assigned on the basis of ^{31}P NMR (Table 2) spectroscopic data. The IR spectra (KBr pellets) exhibit ν(N≡C) values in the range 2215–2110 cm^{-1} which are considerably lower than those exhibited by the free nitriles (Δν = −15 to −100 cm^{-1}) in agreement with an appreciable π-acceptance of the nitrile ligand

Table 1 Physical data for the nitrile complexes *cis*-[ReCl(NCR)(dppe)$_2$] **1**

				Analysis (%)^c		
R	Colour	ν(NC)^a	Δν(NC)^b	C	H	N
$C_6H_4NEt_2$-4	Orange	2190s (br)	−20	62.9 (63.4)	5.1 (5.3)	2.0 (2.4)
C_6H_4OMe-4^d	Orange	2170 (sh)	−35	63.7 (63.8)	5.1 (5.0)	1.2 (0.9)
		2180s	−25			
C_6H_4Me-4	Orange	2175m (br)	−55	64.5 (63.5)	5.4 (4.9)	1.3 (1.2)
Ph	Red	2165s (br)	−60	61.2 (63.2)	4.7 (4.4)	1.1 (1.3)
C_6H_4F-4^d	Red	2170s (br)	−70	63.5 (63.3)	4.9 (4.8)	1.1 (1.2)
C_6H_4Cl-4	Red	2160s (br)	−60	60.6 (61.3)	4.7 (4.5)	1.1 (1.2)
$C_6H_4NO_2$-4^e	Blue	2110s	−100	62.2 (61.9)	4.8 (4.7)	1.5 (1.3)
		2130s	−85			
$CH_2C_6H_4Cl$-4^d	Green	2210w (br)	−45	62.2 (61.7)	4.7 (4.9)	1.4 (1.2)
Et	Red	2215w (br)	−25		*f*	
Pr^i	Red	2215m	−15		*f*	
		2195m	−35			
Bu^t	Red	2206w (br)	−44		*f*	

^{a} In KBr pellets, except for liquid free nitriles (R = Ph, Et, Pr^i or Bu^t) for which the values were measured in liquid phase (NaCl plates); values in cm^{-1} ±2.5; s = strong, m = medium, w = weak, sh = shoulder, br = broad. ^{b} Δν(NC) = ν(NC)$_{coord}$ − ν(NC)$_{free}$. ^{c} Required values in parentheses. ^{d} With ½ toluene of crystallization. ^{e} Other characteristic C–NO$_2$ bands are observed at 1320 and 1570 cm^{-1}. ^{f} Not analytically pure.

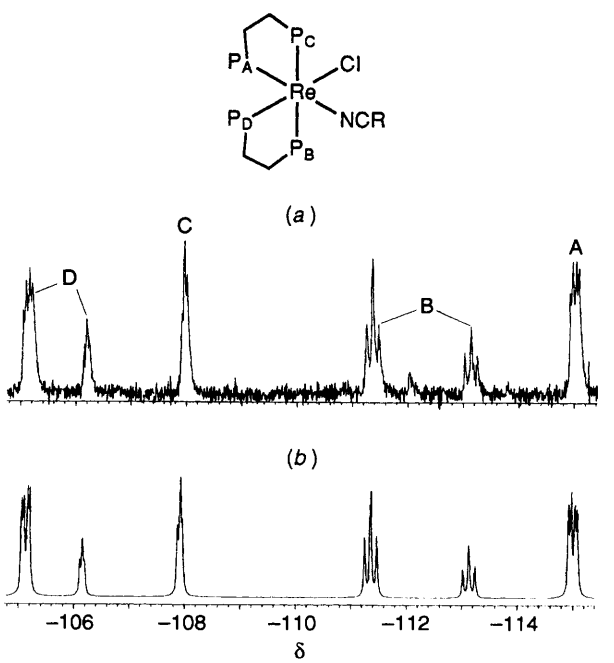

Fig. 1 (*a*) Experimental and (*b*) theoretical ^{31}P-{^{1}H} NMR spectra of *cis*-[ReCl(NCC$_6$H$_4$F-4)(dppe)$_2$] (in C$_6$D$_6$), analysed as an ABCD spin system [δ$_A$ −115.01, δ$_B$ −112.10, δ$_C$ −107.19, δ$_D$ −105.10; *J*(AB) = 13.9, *J*(AC) = 5.5, *J*(AD) = −0.5, *J*(BC) = 215.0, *J*(BD) = 13.1 and *J*(CD) = 5.2 Hz]

from the electron-rich Re^I metal centre; the shift, |Δν|, increases with increasing π-acceptor ability of the nitrile (*e.g.* for the aromatic nitrile complexes, from 20 cm^{-1} for R = C$_6$H$_4$NEt$_2$-4 to *ca.* 100 cm^{-1} for R = C$_6$H$_4$NO$_2$-4). Two ν(N≡C) bands are observed in the spectra of **1** (R = Pr^i, C$_6$H$_4$OMe-4 or C$_6$H$_4$NO$_2$-4), whereas in dichloromethane solution only one band is seen for each species, suggesting that the splitting is due to a solid-state effect. Other characteristic bands can be identified in **1** (R = C$_6$H$_4$NO$_2$-4) at 1570 and 1320 cm^{-1} due to the aromatic nitro group (asymmetric and symmetric stretching, respectively[30]), and in **1** (R = C$_6$H$_4$F-4) where C–F stretching[30] is found at 1235 cm^{-1}.

The ^{31}P-{^{1}H} NMR spectra present a rather complex pattern, in accord with their *cis* geometry, and they have been analysed as ABCD[31] spin systems. The values of the chemical shifts and coupling constants were refined using a LAME iterative program[31] and the computed spectra were in accord with experiment [see Fig. 1 for **1** (R = C$_6$H$_4$F-4)]. Similar patterns (which have also been analysed and refined by computation) are exhibited by the ^{31}P-{^{1}H} NMR spectra of the other aromatic nitrile complexes (Table 2). However, the alkyl nitrile compounds present a distinct ABCD pattern [see Fig. 2 for **1** (R = Pr^i)]; moreover, their P nuclei resonate at higher fields than for the aryl derivatives.

The labelling of the different P nuclei as A, B, C or D and their proposed assignment (see Figs. 1 and 2) was based on their relative δ and *J* values. The mutually *trans* atoms P$_B$ and P$_C$ were assumed to have the highest coupling constant [*J*(BC) ⩾ 215 Hz is always much higher than the others]. Moreover, P$_D$, always *trans* to a chloride ligand, is least affected by the nature of NCR, whereas the remaining nucleus (P$_A$), *trans* to the nitrile, is more significantly affected when R changes from an aromatic to an alkyl group (*cf.* Figs. 1 and 2).

In the ^{13}C NMR spectra (Table 2) the nitrile-carbon N≡*C*R resonance is observed as a singlet in the range δ 125.5–120.9 which corresponds to a downfield shift (by *ca.* 6.5 to 1.9 ppm) upon co-ordination. Moreover, the resonance of the aromatic carbon directly bonded to the cyano group, N≡C–*C*, occurs as a broad singlet in the range δ 121.5–104.2 which [except for **1** (R = C$_6$H$_4$Cl-4)] is also at lower field (by *ca.* 4.1 to 0.2 ppm) than those of the corresponding free nitriles.

The electronic spectra of complexes **1** have been recorded in tetrahydrofuran (thf) and the data are quoted in Table 3. In the region above *ca.* 290 nm there is one dominant band (in the range 344–294 nm), apart from additional absorptions which are detected for the aromatic nitrile complexes (in the range 460–340 nm) probably originating in the aromatic rings.

Although for the related isocyanide complexes *trans*-[ReCl(CNR)(dppe)$_2$][32] the corresponding lower frequency band (in the range *ca.* 330–305 nm, the energy of which is dependent upon the R group) has been assigned to a metal-to-isocyanide charge-transfer transition, in complexes **1** the effect of the R group on the band energy has not been clearly established.

Redox Properties.—Cyclic voltammograms of complexes **1**, in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]–thf, at a Pt electrode, show a single-electron reversible oxidation at $^IE_{\frac{1}{2}}^{ox}$ = −0.20 to −0.02 V *vs.* the saturated calomel electrode (SCE) (Table 4) assigned to the Re^I $\longrightarrow$ Re^{II} oxidation, which is followed, at a higher potential (*ca.* 0.65–0.80 V), by a second one-electron anodic

Table 2 ^{1}H, ^{31}P-{^{1}H} and ^{13}C-{^{1}H} NMR data for the nitrile complexes *cis*-[ReCl(NCR)(dppe)$_2$] **1**

	^{1}H [a,b]		^{31}P-{^{1}H} [a,c]		^{13}C-{^{1}H} [b,d]	
R	δ	Assignment	δ	^{2}J(PP)/Hz	δ	Assignment
$C_6H_4NEt_2$-4	8.10–6.27 (m, 42 H)	Ph [dppe + H$_o$ nitrile]	*g*		*g*	
	5.63 (d, 2 H) [e]	H$_m$ (nitrile)				
	2.24–2.02 (m, br, 12 H)	CH_2 (dppe + nitrile)				
	0.19 (t, 6) [f]	CH_3 (nitrile)				
C_6H_4OMe-4	7.55–6.60 (m, 44 H)	Ph (dppe + nitrile)	δ_A −115.98	*J*(AB) = 13.1	163.0 (s, br)	C$_p$ (nitrile)
	3.08–2.33 (m, br, 8 H)	CH_2 (dppe)	δ_B −113.81	*J*(AC) = 5.0	137.5–123.4 (m)	Ph (dppe) + C$_o$ (nitrile)
	3.84 (s, 3 H)	CH_3 (nitrile)	δ_C −108.41	*J*(AD) = −0.1	122.1 (s)	N*C*R
			δ_D −106.78	*J*(BC) = 217.1	115.0 (s) [h]	C$_m$ (nitrile)
				J(BD) = 14.2	104.2 (s, br)	NC*C*
				J(CD) = 6.2	33.94 (m, br)	CH_2 (dppe)
					24.92 (m, br)	
					0.94 (s) [i]	CH_3 (nitrile)
C_6H_4Me-4	7.87–6.52 (m, 44 H)	Ph (dppe + nitrile)	δ_A −114.80	*J*(AB) = 13.8	134.0–125.6 (m, br)	Ph (dppe + nitrile)
	2.73–2.12 (m, br, 8 H)	CH_2 (dppe)	δ_B −112.53	*J*(AC) = 6.5	120.9 (s)	N*C*R
	2.34 (s, 3 H)	CH_3 (nitrile)	δ_C −107.16	*J*(AD) = 0.5	*j*	NC*C*
			δ_D −105.40	*J*(BC) = 215.3	*j*	CH_2 (dppe)
				J(BD) = 13.9	1.35 (s) [k]	CH_3 (nitrile)
				J(CD) = 6.2		
Ph	8.86–6.40 (m, 45 H)	Ph (dppe + nitrile)	δ_A −115.04	*J*(AB) = 13.7	137.8–123.6 (m)	Ph (dppe + nitrile)
	3.06–1.88 (br, 8 H)	CH_2 (dppe)	δ_B −112.62	*J*(AC) = 4.9	122.3 (s)	N*C*R
			δ_C −107.58	*J*(AD) = 0.5	112.4 (m, br)	NC*C*
			δ_D −105.50	*J*(BC) = 216.5	33.9 (m)	CH_2 (dppe)
				J(BD) = 14.5	24.7 (m)	
				J(CD) = 5.2		
C_6H_4F-4	7.20–6.80 (m, br, 44 H)	Ph (dppe + nitrile)	δ_A −115.01	*J*(AB) = 13.9	164.67 (d) [l]	C$_p$ (nitrile)
	2.85–2.25 (m, br, 8 H)	CH_2 (dppe)	δ_B −112.10	*J*(AC) = 5.5	143.7–121.0 (m)	Ph (dppe) + C$_o$ (nitrile)
			δ_C −107.19	*J*(AD) = −0.5	120.9 (s)	N*C*R
			δ_D −105.10	*J*(BC) = 215.0	117.3 (d) [m]	C$_m$ (nitrile)
				J(BD) = 13.1	108.7 (s)	NC*C*
				J(CD) = 5.2	34.1 (m, br)	CH_2 (dppe)
					24.9 (m, br)	
C_6H_4Cl-4	7.93–6.27 (m, 44 H)	Ph (dppe + nitrile)	δ_A −115.32	*J*(AB) = 14.0	140.0–125.6 (m)	Ph (dppe + nitrile)
	2.10–0.40 (br, 8 H)	CH_2 (dppe)	δ_B −112.31	*J*(AC) = 4.9	121.4 (s)	N*C*R
			δ_C −107.39	*J*(AD) = −0.4	111.2 (s)	NC*C*
			δ_D −105.24	*J*(BC) = 215.1	34.3 (m, br)	CH_2 (dppe)
				J(BD) = 14.3	25.2 (m, br)	
				J(CD) = 6.0		
$C_6H_4NO_2$-4	7.01–6.40 (m, 46.5 H)	Ph (dppe + nitrile + toluene [n])	δ_A −117.49	*J*(AB) = 15.1	138.2–128.4 (m)	Ph (dppe + nitrile)
			δ_B −113.87	*J*(AC) = 4.2	125.5 (s)	N*C*R
	2.42–2.12 (m, br, 8 H)	CH_2 (dppe)	δ_C −109.28	*J*(AD) = 0.2	121.5 (s)	NC*C*
	1.99 (s, 1.5 H)	CH_3 (toluene) [n]	δ_D −106.35	*J*(BC) = 215.3	34.1 (m, br)	CH_2 (dppe)
					21.5 (m, br)	
				J(BD) = 14.05		
				J(CD) = −6 .4		
$CH_2C_6H_4Cl$-4	7.78–6.20 (m, 40 H)	Ph (dppe)	*g*		*g*	
	6.08–5.78 (m, br, 4 H)	C_6H_4 (nitrile)				
	3.25 (q, 2 H) [o]	CH_2 (Et_2O) [p]				
	3.05–1.45 (m, br, 8 H)	CH_2 (dppe)				
	1.13 (t, 3 H) [o]	CH_3 (Et_2O) [p]				
	2.09 (s, 2 H)	CH_2 (nitrile)				
Et [q]	7.72–7.19 (m, 40 H)	Ph (dppe)	δ_A −132	*J*(AB) = 6	*g*	
	2.69–2.53 (m, br, 10 H)	CH_2 (dppe + nitrile)	δ_B −154	*J*(AC) ≈ 0–1		
	1.27 (m, br, 3 H)		δ_C −135	*J*(AD) ≈ 0–1		
		CH_3 (nitrile)	δ_D −109	*J*(BC) = 391		
				J(BD) = 42		
				J(CD) ≈ 0–1		
Bu^t	7.48–6.80 (m, 40 H)	Ph (dppe)	δ_A −133.74	*J*(AB) = 6.1	*g*	
	3.25 (q, 6 H) [r]	CH_2 (Et_2O) [p]	δ_B −156.01	*J*(AC) = 1.1		
	2.19 (t, 8 H) [s]	CH_2 (dppe)	δ_C −137.38	*J*(AD) = −0.4		
	1.54 (s, 9 H)	CH_3 (nitrile)	δ_D −111.23	*J*(BC) = 425.8		
	1.10 (t, 9 H) [r]	CH_3 (Et_2O) [p]		*J*(BD) = 47.4		
				J(CD) = 0.0		
Pr^i [t]	8.7–7.3 (m, br) [u]	Ph (dppe)	δ_A −129.6	*J*(AB) = 6.9	*g*	
	3.2–2.28 (m, br) [u]	CH_2 (dppe) + CH (nitrile)	δ_B −152.4	*J*(AC) = 1.2		
			δ_C −133.2	*J*(AD) = 0.7		
	1.21 (d) [u,v]	CH_3 (nitrile)	δ_D −108.5	*J*(BC) = 426.0		
				J(BD) = 49.9		
				J(CD) = −1.0		

[a] In C_6D_6 unless stated otherwise. [b] δ in ppm relative to internal $SiMe_4$; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. [c] ABCD spin system; δ in ppm relative to external $P(OMe)_3$. [d] In CD_2Cl_2. [e] ^{3}J(HH) = 8.74 Hz. [f] ^{3}J(HH) = 7.06 Hz. [g] No reliable spectrum due to decomposition. [h] A doublet in the ^{13}C-^{1}H undecoupled spectrum with ^{1}J(CH) = 163.6 Hz. [i] A quartet in the ^{13}C-^{1}H undecoupled spectrum with ^{1}J(CH) = 118.5 Hz. [j] Not detected. [k] A quartet in the ^{13}C-^{1}H undecoupled spectrum with ^{1}J(CH) = 117.4 Hz. [l] ^{1}J(CF) = 260.8 Hz. [m] ^{2}J(CF) = 21.15 Hz. [n] Toluene of crystallization. [o] ^{3}J(HH) = 6.72 Hz. [p] Ether of crystallization. [q] ^{31}P values not refined by iteration. [r] ^{3}J(HH) = 6.83 Hz. [s] Due to virtual coupling to ^{31}P nuclei $\frac{1}{2}|^{2}J(HP) + ^{3}J(HP)|$ = 3.9 Hz. [t] In $(CD_3)CO$. [u] No reliable ingration due to decomposition. [v] ^{3}J(HH) = 7.0 Hz.

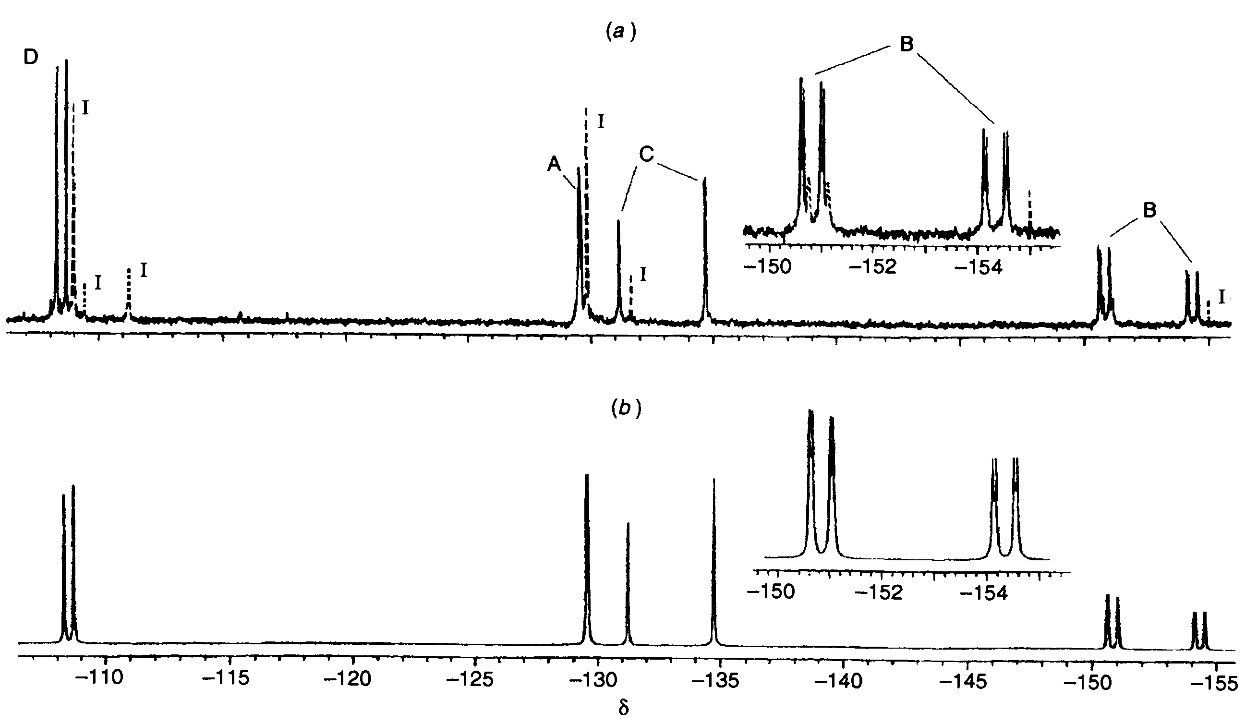

Fig. 2 (*a*) Experimental and (*b*) theoretical $^{31}P-\{^1H\}$ NMR spectra of *cis*-[ReCl(NCPr^i)(dppe)$_2$] [in $(CD_3)_2CO$], analysed as an ABCD spin system [δ_A −129.6, δ_B −152.4, δ_C −133.2, δ_D −108.5; *J*(AB) = 6.9, *J*(AC) = 1.2, *J*(AD) = 0.7, *J*(BC) = 426.0, *J*(BD) = 49.9 and *J*(CD) = −1.0 Hz]. I = decomposition product(s)

Table 3 Electronic spectra[a] of *cis*-[ReCl(NCR)(dppe)$_2$] **1** in thf (260–850 nm)[b]

R	λ_n(log ε_n)	$10^{-2}(1/\lambda_n)$
$C_6H_4NEt_2$-4	266 (4.40)	376
	272 (4.47)	368
	294 (4.72)	340
	ca. 340 (4.02)	294
	ca. 380 (3.92)	263
	ca. 420 (3.73)	250
C_6H_4OMe-4	272 (4.03)	368
	284 (3.74)	352
	328 (3.56)	305
C_6H_4Me-4	265 (4.05)	377
	272 (3.98)	368
	323 (3.56)	310
	ca. 397 (3.22)	252
Ph	**344 (3.36)**	291
	ca. 419 (3.08)	239
C_6H_4F-4	264 (3.92)	379
	271 (3.83)	369
	324 (3.39)	309
	396 (3.18)	253
$CH_2C_6H_4Cl$-4	264 (4.12)	379
	271 (4.04)	369
	ca. **314 (3.89)**	319
Bu^t	264 (4.04)	379
	271 (3.94)	368
	ca. **330 (3.14)**	303

[a] λ Values in nm ±4; 1/λ values in cm^{-1}; values in bold refer to the most significant band above *ca.* 290 nm. [b] For **1** (R = C_6H_4Cl-4, $C_6H_4NO_2$-4, Et or Pr^i), no reliable data were obtained due to decomposition.

Table 4 Cyclic voltammetric data[a] for complexes *cis*-[ReCl(NCR)(dppe)$_2$] **1**[b]

R	$^{I}E_{\frac{1}{2}}^{ox}$	$^{II}E_{\frac{1}{2}}^{ox}$
$C_6H_4NEt_2$-4	−0.20	0.65
C_6H_4OMe-4	−0.16	0.74
C_6H_4Me-4	−0.14	0.76
Ph	−0.13	0.78
C_6H_4F-4	−0.10	0.76
C_6H_4Cl-4	−0.09	0.77
$C_6H_4NO_2$-4[c]	−0.02	0.80
$CH_2C_6H_4Cl$-4	−0.14	0.72
Bu^t	−0.14	0.75

[a] Values in V ±0.01 relative to SCE, measured at a Pt disc electrode (φ = 0.5 mm), by using as internal reference the *trans*-[ReCl(N$_2$)(dppe)$_2$]$^{0/+}$ couple ($E_{\frac{1}{2}}^{ox}$ = 0.28 *vs.* SCE or −0.26(5) V *vs.* the ferrocene–ferrocenium redox couple); scan rate 200 mV s^{-1}; 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]–thf, −20 °C. [b] For **1** (R = Et or Pr^i) no reliable data were collected due to decomposition. [c] Cathodic wave at −0.85 V *vs.* SCE due to reduction of the nitro group.

wave involving an electron-transfer induced *cis* $\longrightarrow$ *trans* isomerization of the dicationic species, the mechanism of which has been established by digital simulation of the cyclic voltammograms and is discussed in detail separately for **1** (R = C_6H_4Me-4).[26b]

The oxidation potentials for the first anodic wave are considerably lower than those reported for the related complexes *trans*-[ReCl(N$_2$)(dppe)$_2$] (0.28 V) or *trans*-[ReCl(CNR)(dppe)$_2$] (*ca.* 0.1–0.4 V)[8] thus following the expected[33] order of the net electron σ-donor *minus* π-acceptor ability of these ligands: NCR > CNR > N$_2$. However, they are significantly higher (by *ca.* 0.20 V) than those exhibited by the corresponding *trans* complexes.[33]

The $^{I}E_{\frac{1}{2}}^{ox}$ values for complexes **1** are somewhat lower (by *ca.* 0.05–0.13 V) than those expected (*E*) on the basis of the general empirical expression (2) proposed by Lever,[34] assuming an

$$E = S_M(\Sigma E_L) + I_M \qquad (2)$$

additive contribution of all the ligands (as measured for each of them by the ligand parameter E_L), and in which S_M and I_M depend upon the metal and redox couple, the spin state and the

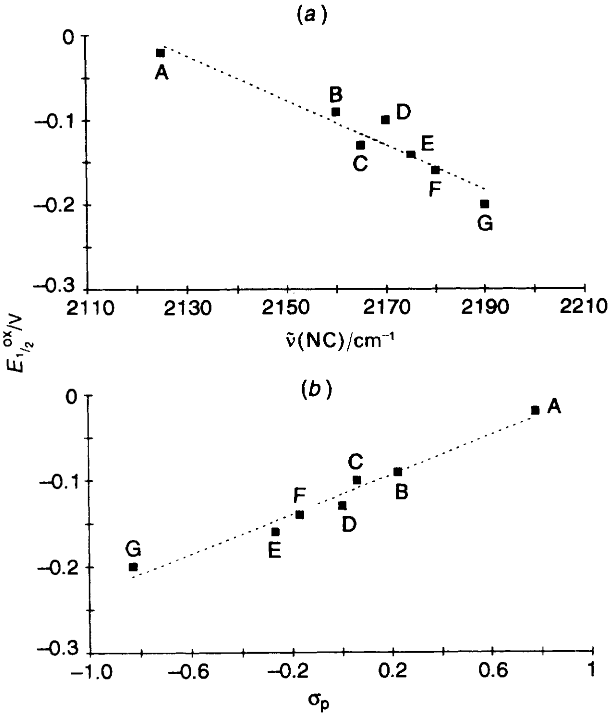

Fig. 3 Plot of ${}^{\mathrm{I}}E_{\frac{1}{2}}^{\mathrm{ox}}$ (V *vs.* SCE) for *cis*-[ReCl(NCR)(dppe)$_2$] **1** (R = aryl) *vs.* (*a*) ṽ(NC) of the nitrile ligand, and (*b*) Hammett's constant σ_p (for the phenyl substituent of the aromatic nitrile ligands); R = $C_6H_4NO_2$-4 (A), C_6H_4Cl-4 (B), C_6H_4F-4(C), Ph (D), C_6H_4OMe-4 (E), C_6H_4Me-4 (F), $C_6H_4NEt_2$-4 (G)

stereochemistry. Nevertheless, the differences between the observed and the estimated values* of the oxidation potential are within the scattering limits of the data used to establish this expression.

Within the aromatic nitrile complexes, the oxidation potential generally increases with the decreasing ν(NC) of the nitrile ligand and with the increasing electron-withdrawing influence of the substituent of the phenyl ring, as measured by Hammett's constant, σ_p. These trends are expressed by the (mainly) linear plots in Fig. 3(*a*) [${}^{\mathrm{I}}E_{\frac{1}{2}}^{\mathrm{ox}}$ *vs.* ν(NC)] and (*b*) (${}^{\mathrm{I}}E_{\frac{1}{2}}^{\mathrm{ox}}$ *vs.* σ_p[35]) with a correlation coefficient, *r*, of 0.917 and 0.968, respectively. This agrees with the expected stabilization of the highest occupied molecular orbital (HOMO) (as indicated by the increase of ${}^{\mathrm{I}}E_{\frac{1}{2}}^{\mathrm{ox}}$) as a result of the promotion of the π-electron-acceptor character of the aromatic nitrile ligand [as indicated by a decrease of ν(NC) and an increase in σ_p]. However, the alkyl nitrile complexes and the benzyl derivative **1** (R = $CH_2C_6H_4Cl$-4) do not follow the correlation between the oxidation potential and ν(NC).

Similar general trends have been observed for the related isocyanide complexes *trans*-[ReCl(CNR)(dppe)$_2$],[8] although in this case a better correlation is followed for σ_p^+, instead of σ_p, suggesting that the HOMO is conjugated to the aryl substituent of the isocyanide. This is in contrast with the nitrile complexes **1**, in which a better correlation is observed for σ_p than for σ_p^+, conceivably as a result of the weaker π acceptance of the nitrile compared with the isocyanide ligands, although the different geometry of the binding metal centre can also play a role.

Another difference between complexes **1** and *trans*-[ReCl(CNR)(dppe)$_2$] lies in the apparent lack of correlation between ${}^{\mathrm{I}}E_{\frac{1}{2}}^{\mathrm{ox}}$ and the energy bands observed in the electronic spectra for the former compounds, whereas in the latter an inverse gross linear variation has been detected for the lower energy band (see above) and interpreted[32] on the basis of the LUMO (lowest unoccupied molecular orbital) and HOMO compositions (mainly ligand or metal based, respectively).

Conclusion

A series of nitrile complexes with an electron-rich d^6 metal centre, *cis*-{ReCl(dppe)$_2$}, have been synthesized and spectroscopically and electrochemically characterized. Relative to the *trans* isomeric forms, the unusual *cis*-diphosphine complexes appear to be stabilized by the modest π-acceptor NCR ligand. In fact, the *trans* geometry for this metal centre is the only geometry previously reported for the analogous complexes with the stronger π-acceptor isocyanide, dinitrogen or carbon monoxide ligands. All of these complexes combine a π-acceptor with a π-donor (chloride) ligand, a situation which has not yet been theoretically investigated. As suggested by our study, the *cis* isomers appear to be thermodynamically more stable than the corresponding *trans* ones; however, the *cis* compounds are converted into *trans* isomers in sunlight, although not spontaneously. However, rapid *cis* ⟶ *trans* isomerisation occurs upon oxidation, as discussed separately.[26b]

In addition, the complexes obtained in this study provide rare examples of nitrile ligands binding an electron-rich metal centre without the stabilizing effect of an ancillary stronger π-acceptor.

Experimental

All the manipulations and rections were carried out in the absence of air using standard inert-gas flow and vacuum techniques. Solvents were purified by standard procedures, *trans*-[ReCl(N$_2$)(dppe)$_2$] was prepared by a published method[36] and the organonitriles were commercially available.

Infrared measurements were carried out on a Perkin-Elmer 683 spectrophotometer, and ^{1}H, ^{31}P and ^{13}C NMR spectra on a Varian Unity 300 spectrometer. The electrochemical experiments were performed either on an EG & G PARC 173 potentiostat and an EG & G PARC 175 universal programmer or on a HI-TEK DT 2101 potentiostat and an HI-TEK PP RI waveform generator. 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} [NBu$_4$][BF$_4$]–thf and are quoted relative to the saturated calomel electrode (SCE) by using the *trans*-[ReCl(N$_2$)(dppe)$_2$]$^{0/+}$ couple ($E_{\frac{1}{2}}^{\mathrm{ox}}$ = 0.28 V *vs.* SCE) as internal reference.

Synthesis of cis-[ReCl(NCR)(dppe)$_2$] (R = $C_6H_4NEt_2$-4, C_6H_4OMe-4, C_6H_4Me-4, Ph, C_6H_4F-4, C_6H_4Cl-4, $C_6H_4NO_2$-4, $CH_2C_6H_4Cl$-4, Et, Pr^i *or* Bu^t).—The complexes **1** were prepared by adding the appropriate nitrile, in a twofold molar ratio, to a toluene suspension of *trans*-[ReCl(N$_2$)(dppe)$_2$] and the mixture left stirring in sunlight for *ca.* 4 h. The solution was then concentrated and cooled, leading to the precipitation of the corresponding complex which was filtered off and dried *in vacuo* (*ca.* 50–25% yield). If tungsten filament or ambient light is used instead of sunlight, the reaction is much slower as indicated[26b] for **1** (R = C_6H_4Me-4).

As a typical example, *cis*-[ReCl(NCC$_6$H$_4$F-4)(dppe)$_2$] was prepared as follows: toluene (*ca.* 250 cm^3) was added to a mixture of *trans*-[ReCl(N$_2$)(dppe)$_2$] (0.30 g, 0.29 mmol) and NCC$_6$H$_4$F-4 (0.07 g, 0.58 mmol) and the system was stirred under dinitrogen and in sunlight for *ca.* 4 h. Concentration *in vacuo* of the final clear solution to a small volume (*ca.* 10 cm^3) and cooling to *ca.* −20 °C led to the precipitation of *cis*-

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* For the Re$^{\mathrm{I/II}}$ redox couple, S_M = 0.76 V and I_M = −0.95 V *vs.* normal hydrogen electrode (NHE), and $\Sigma E_L = 4 \times 0.36$ (2dppe) − 0.24 (Cl$^-$) + E_L(nitrile) *vs.* NHE;[34] hence, *e.g.*, for **1** (R = Ph), where E_L(NCPh) = 0.37 V *vs.* NHE,[34] the calculated redox potential is 0.24 V *vs.* NHE ≈ 0.00 V *vs.* SCE, whereas the observed value (Table 4) is −0.13 V *vs.* SCE.

$[ReCl(NCC_6H_4F\text{-}4)(dppe)_2]$ as a red solid which was filtered off and dried *in vacuo* (*ca.* 45% yield). Further crops could be obtained from the filtered solution by concentration and cooling but they were frequently contaminated with other products, such as the corresponding *trans* isomer.

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