Alkylation of cyanide at [NBu₄]trans-[Re(CN)₂(Ph₂PCH₂CH₂PPh₂)₂]. Syntheses and properties of derived isocyanide complexes and X-ray structure of trans-[Re(CNEt)₂(Ph₂PCH₂CH₂PPh₂)₂][PF₆]

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Abstract

The reaction of RI (R = Me, Et or Pr) or [Et₃O][PF₆] with [NBu₄]trans-[Re(CN)₂(dppe)₂] (dppe = Ph₂PCH₂CH₂PPh₂) affords the diisocyanide complexes trans-[Re(CNR)₂(dppe)₂]A (R = Me, A = I; R = Pr, A = I₃; R = Et, A = PF₆), whereas trans-[Re(CNH)(CNSiMe₃)(dppe)₂]CF₃SO₃ is obtained from the reaction with Me₃SiO₃SCF₃. The X-ray crystal structure of trans-[Re(CNEt)₂(dppe)₂][PF₆] was determined. The redox properties of the compounds were studied by cyclic voltammetry and controlled potential electrolysis, and are discussed in terms of the electronic properties of the metal centres and ligands.

Keywords: Rhenium; Isocyanide complexes; Bis(isocyanide complexes); Electrochemistry; Reactivity; X-ray structure; Alkylation

1. Introduction

Cyanide alkylation is a naturally occuring process [1], involved in the synthesis of natural products, e.g. isocyanides [2] and nitriles [3]. However, although the laboratory preparation of isocyanides was initially undertaken by direct alkylation of cyanide, nowadays this is not the most common way to synthesize either free or coordinated isocyanides. In fact only a few examples of the preparation of isocyanide complexes by direct cyanide alkylation are known [4].

Nevertheless, the previously reported [5] compound [NBu₄]trans-[Re(CN)₂(dppe)₂] (dppe = Ph₂PCH₂CH₂-PPh₂), with an electron-rich cyano-metal centre, should have a high reactivity towards electrophiles and consequently be a convenient precursor for the formation of isocyanide complexes through the alkylation or protonation of the cyanide ligand.
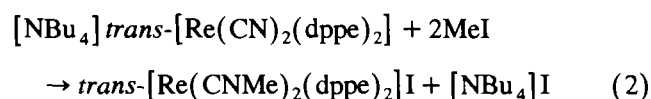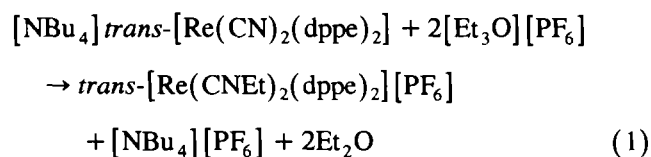
At the related rhenium(I) {ReCl(dppe)₂} centre, ligated cyanide is known [6] to undergo readily reversible stepwise protonation to give trans-[ReCl(CNH)(dppe)₂] and trans-[ReCl(CNH₂)(dppe)₂]⁺. Moreover, the activation of isocyanides [7,8], nitriles [8,9], alkynes [7,8] and other small unsaturated molecules [9] at electron-rich metal centres has concerned us for a considerable time, and the present study extends this work to cyanide.

2. Results and discussion

2.1. Syntheses and properties

Treatment of a dichoromethane solution of [NBu₄]trans-[Re(CN)₂(dppe)₂] (1) with [Et₃O][PF₆] or RI (R = Me or Pr) (in ca. five-fold molar ratio) affords the dialkylated products trans-[Re(CNEt)₂(dppe)₂][PF₆] (2a) or trans-[Re(CNR)₂(dppe)₂]A (2b, R = Me, A = I; 2c, R = Pr, A = I₃) (e.g. Eqs. (1) and (2)).

$$[NBu_4]trans\text{-}[Re(CN)_2(dppe)_2] + 2[Et_3O][PF_6]$$

$$\rightarrow trans\text{-}[Re(CNEt)_2(dppe)_2][PF_6]$$

$$+ [NBu_4][PF_6] + 2Et_2O \qquad (1)$$

$$[NBu_4]trans\text{-}[Re(CN)_2(dppe)_2] + 2MeI$$

$$\rightarrow trans\text{-}[Re(CNMe)_2(dppe)_2]I + [NBu_4]I \qquad (2)$$

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Table 1

Analytical data for complexes $trans$-[Re(CNR)$_2$(dppe)$_2$]A (2a, R = Et, A = PF$_6$; 2b, R = Me, A = I; 2c, R = Pr, A = I$_3$), $trans$-[Re(CNH)(CNSiMe$_3$)(dppe)$_2$]CF$_3$SO$_3$ (3) and $trans$-[ReI(CNPr)(dppe)$_2$] (4)

Complex	Colour	Microanalysis: Found (Calc.) (%)			IR (cm^{-1}), ν(CN)	Yield (%)
		C	N	H		
2a	Pale yellow	55.2 (55.5)	2.2 (2.2)	4.9 (4.6)	2050 s, 2030 sh	50
2b [a]	Pale pink	57.7 (57.7)	1.6 (2.2)	5.0 (5.2)	2075 s	50
2c [b]	Pale yellow	49.8 (48.2)	2.2 (1.9)	6.5 (4.4)	2060	30
3	Pale green	54.1 (53.8)	2.1 (2.2)	4.5 (4.6)	1985 s [c], 1950 s [c]	70
4	Yellow	57.7 (57.0)	1.7 (1.2)	4.7 (4.8)	1970 s	< 10

[a] With 4/5 n-pentane of crystallization. [b] Not analytically pure due to the presence of [NBu$_4$]CN. [c] Partially overlapping.

They have been isolated as pale yellow (2a or 2c) or pink (2b) solids in ca. 50% (2a or 2b) or 30% (2c) yields.

The related compounds $trans$-[Re(CNR)$_2$(dppe)$_2$]-[BF$_4$] (R = Me, ^{t}Bu or aryl) have been prepared previously [10] by direct reaction (in THF for a few days) of $trans$-[ReCl(N$_2$)(dppe)$_2$] with the appropriate isocyanide in the presence of Tl[BF$_4$] (Eq. (3)).

$$trans\text{-}[ReCl(N_2)(dppe)_2] + 2CNR + Tl[BF_4]$$

$$\rightarrow trans\text{-}[Re(CNR)_2(dppe)_2][BF_4] + TlCl + N_2 \tag{3}$$
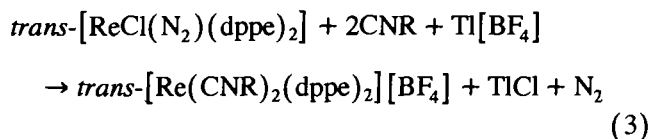
Although the same dinitrogen complex is the starting material for the preparation of [NBu$_4$]$trans$-[Re(CN)$_2$-(dppe)$_2$] (obtained from the reaction of the former complex with [NBu$_4$]CN [15]), the route for the diisocyanide complexes described in the present work has considerable advantages over that of reaction (3) because (i) it does not require the previous and cumbersome syntheses of the noxious isocyanides (which, apart from very limited exceptions, are not commercially available) since they are generated in situ at the metal, and (ii) the alkylation of the cyanide ligands in complex 1 (which appears to be complete in just a few seconds) is much faster than reaction (3) (which seems to require a few days for completion [10]).

Moreover, the reactions with alkyl iodides can lead to other products, for example $trans$-[ReI(CNPr)(dppe)$_2$] (4) was also isolated as a minor product (yield lower than 10%) in the reaction of 1 with PrI (Eq. (4)),

Table 2

^{1}H and ^{31}P-{^{1}H} NMR data [a] for complexes $trans$-[Re(CNR)$_2$(dppe)$_2$]A (2a, R = Et, A = PF$_6$; 2b, R = Me, A = I; 2c, R = Pr, A = I$_3$), $trans$-[Re(CNH)(CNSiMe$_3$)(dppe)$_2$]CF$_3$SO$_3$ (3) and $trans$-[ReI(CNPr)(dppe)$_2$] (4)

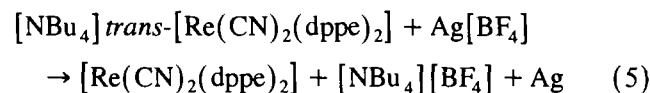| Complex	^{1}H			^{31}P
	δ (ppm) [b]	Integration	Assignment	δ (ppm) [c]
2a [d]	7.3–7.0 m	40	C$_6$H$_5$ (dppe)	
	3.04 q [e]	4	CH$_2$ (CNEt)	−108.5
	2.38 t [f]	8	CH$_2$ (dppe)	
	0.81 t [e]	6	CH$_3$ (CNEt)	
2b	7.5–6.8 m	40	C$_6$H$_5$ (dppe)	
	2.90 s	6	CH$_3$ (CNMe)	−111.7
	2.38 t [g]	8	CH$_2$ (dppe)	
2c	7.3–6.9 m	40	C$_6$H$_5$ (dppe)	
	2.95 t [h]	4	CH$_2$ (CNPr)	−109.6
	2.42 t [i]	8	CH$_2$ (dppe)	
	1.15 sx [j]	4	CH$_2$ (CNPr)	
	0.61 t [l]	6	CH$_3$ (CNPr)	
3 [d]	7.2–7.0 m	40	C$_6$H$_5$ (dppe)	
	2.5–2.3 m	4	CH$_2$ (dppe)	−110.3
	1.7–1.4 m	4	CH$_2$ (dppe)	
	1.08 br	1	NH (CNH)	
	0.15 s	9	CH$_3$ (CNSiMe$_3$)	
4	7.5–6.5 m	40	C$_6$H$_5$ (dppe)	−116.5 [d]
	3.5–3.4 m	2	CH$_2$ (CNPr)	
	1.59 s, br	10	CH$_2$ (CNPr + dppe)	
	1.22 t [h]	3	CH$_3$ (CNPr)	

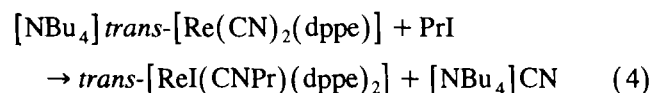[a] In CDCl$_3$ unless otherwise: q, quartet; m, multiplet; s, singlet; sx, sextet; t, triplet; br, broad. [b] Relative to SiMe$_4$. [c] Relative to P(OMe)$_3$. [d] In CD$_2$Cl$_2$. [e] $^3J_{HH}$ = 7.0 Hz. [f] 1/2 | ^2J(HP) + ^3J(HP)| = 9.0 Hz. [g] 1/2 | ^2J(HP) + ^3J(HP)| = 8.0 Hz. [h] $^3J_{HH}$ = 6.8 Hz. [i] 1/2 | ^2J(HP) + ^3J(HP)| = 8.4 Hz. [j] $^3J_{HH}$ = 7.3 Hz. [l] $^3J_{HH}$ = 6.4 Hz.

Table 3
Bond lengths (Å) for trans-[Re(CNEt)₂(dppe)₂][PF₆] (2a)

C(3)–Re(1)	2.005(5)	P(1)–Re(1)	2.401(3)
P(2)–Re(1)	2.406(3)	N(1)–C(3)	1.165(5)
C(4)–N(1)	1.436(6)	C(5)–C(4)	1.423(8)
C(1)–P(1)	1.856(5)	C(111)–P(1)	1.846(6)
C(121)–P(1)	1.840(6)	C(2)–C(1)	1.535(7)
P(2)–C(2)	1.848(5)	C(112)–C(111)	1.383(6)
C(116)–C(111)	1.405(6)	C(113)–C(112)	1.389(6)
C(114)–C(113)	1.376(7)	C(115)–C(114)	1.379(7)
C(116)–C(115)	1.380(6)	C(122)–C(121)	1.392(6)
C(126)–C(121)	1.384(6)	C(123)–C(122)	1.380(7)
C(124)–C(123)	1.369(7)	C(125)–C(124)	1.382(7)
C(126)–C(125)	1.397(7)	C(211)–P(2)	1.842(6)
C(221)–P(2)	1.844(5)	C(212)–C(211)	1.377(6)
C(216)–C(211)	1.390(6)	C(213)–C(212)	1.382(6)
C(214)–C(213)	1.375(7)	C(215)–C(214)	1.363(7)
C(216)–C(215)	1.384(6)	C(222)–C(221)	1.395(6)
C(226)–C(221)	1.392(6)	C(223)–C(222)	1.387(7)
C(224)–C(223)	1.368(7)	C(225)–C(224)	1.383(7)
C(226)–C(225)	1.390(6)	F(1)–P	1.588(5)
F(2)–P	1.565(5)	F(3)–P	1.579(5)

whereas the known [5] oxidized Re^{II} complex [Re-(CN)₂(dppe)₂] is formed in reactions with bulkier alkyl iodides such as sec-butyl iodide. The same product is also obtained upon oxidation of 1 in THF, by Ag[BF₄] (Eq. (5)), consistent with electrochemical studies [5] (which indicate that this complex is readily oxidizable) and with the known [11] oxidizing ability of the silver

salt towards related rhenium(I) complexes such as trans-[ReCl(CNR)(dppe)₂]. An intermediate species in the oxidation process was isolated as a yellow solid, with a strong IR $\nu(CN)$ band at 1985 cm⁻¹ and with elemental analysis suggestive of an Ag^+ adduct such as [Re(CN)(CNAg)(dppe)₂], but its ready conversion in solution into the final oxidized product [Re(CN)₂-(dppe)₂] precluded its full characterization.

$$[NBu_4] \, trans\text{-}[Re(CN)_2(dppe)] + PrI$$

$$\rightarrow trans\text{-}[ReI(CNPr)(dppe)_2] + [NBu_4]CN \quad (4)$$

$$[NBu_4] \, trans\text{-}[Re(CN)_2(dppe)_2] + Ag[BF_4]$$

$$\rightarrow [Re(CN)_2(dppe)_2] + [NBu_4][BF_4] + Ag \quad (5)$$

The cyanide in complex 1 is prone to protonation and its reaction with $Me_3SiO_3SCF_3$ affords the mixed isocyanide complex trans-[Re(CNH)(CNSiMe₃)(dppe)₂]-CF₃SO₃ (3), instead of the dialkylated product. Traces of water in the reaction medium conceivably constitute the proton source, whereas the sterically demanding nature of the large $SiMe_3$ group should favour protic over organosilyl attack.

The above-mentioned complexes 2–4 have been characterized by IR (Table 1), and ¹H and ³¹P-{¹H} NMR spectroscopies (Table 2), as well as by elemental analysis (Table 1), and, in the case of 2a, by X-ray diffraction analysis. All the complexes show strong IR

Table 4
Bond angles (°) for trans-[Re(CNEt)₂(dppe)₂][PF₆] (2a)

P(1)–Re(1)–C(3)	83.1(2)	P(2)–Re(1)–C(3)	84.9(2)
P(2)–Re(1)–P(1)	82.0	N(1)–C(3)–Re(1)	176.1(3)
C(4)–N(1)–C(3)	168.2(4)	C(5)–C(4)–N(1)	114.9(6)
C(1)–P(1)–Re(1)	107.2(2)	C(111)–P(1)–Re(1)	122.5(2)
C(111)–P(1)–C(1)	99.2(3)	C(121)–P(1)–Re(1)	118.2(2)
C(121)–P(1)–C(1)	103.8(3)	C(121)–P(1)–C(111)	102.9(3)
C(2)–C(1)–P(1)	107.3(3)	P(2)–C(2)–C(1)	108.6(3)
C(112)–C(111)–P(1)	118.9(4)	C(116)–C(111)–P(1)	122.4(4)
C(116)–C(111)–C(112)	118.5(4)	C(113)–C(112)–C(111)	120.9(5)
C(114)–C(113)–C(112)	120.1(5)	C(115)–C(114)–C(113)	119.6(5)
C(116)–C(115)–C(114)	121.0(5)	C(115)–C(116)–C(111)	119.8(5)
C(122)–C(121)–P(1)	120.7(4)	C(126)–C(121)–P(1)	120.9(4)
C(126)–C(121)–C(122)	118.3(5)	C(123)–C(122)–C(121)	121.3(5)
C(124)–C(123)–C(122)	120.2(5)	C(125)–C(124)–C(123)	119.7(5)
C(126)–C(125)–C(124)	120.2(5)	C(125)–C(126)–C(121)	120.3(5)
C(2)–P(2)–Re(1)	108.1(2)	C(211)–P(2)–Re(1)	124.2(2)
C(211)–P(2)–C(2)	100.4(3)	C(221)–P(2)–Re(1)	115.9(2)
C(221)–P(2)–C(2)	103.1(3)	C(221)–P(2)–C(211)	102.3(3)
C(212)–C(211)–P(2)	119.4(4)	C(216)–C(211)–P(2)	122.1(4)
C(216)–C(211)–C(212)	118.5(5)	C(213)–C(212)–C(211)	121.1(5)
C(214)–C(213)–C(212)	119.7(5)	C(215)–C(214)–C(213)	120.0(5)
C(216)–C(215)–C(214)	120.5(5)	C(215)–C(216)–C(211)	120.2(5)
C(222)–C(221)–P(2)	123.4(4)	C(226)–C(221)–P(2)	118.1(4)
C(226)–C(221)–C(222)	118.5(5)	C(223)–C(222)–C(221)	119.9(5)
C(224)–C(223)–C(222)	121.4(5)	C(225)–C(224)–C(223)	119.3(5)
C(226)–C(225)–C(224)	120.1(5)	C(225)–C(226)–C(221)	120.8(5)
F(2)–P–F(1)	89.1(3)	F(3)–P–F(1)	90.4(3)
F(3)–P–F(2)	89.5(3)	F(1)–P–F(1)	180.0
F(2)–P–F(2)	180.0	F(3)–P–F(3)	180.0

bands in the range 1950–2075 cm^{-1}, which are assigned to ν(CN) of the isocyanide ligand in accordance with those reported [10,12] for the related diisocyanide complexes trans-[Re(CNMe)(CNR)(dppe)$_2$]$^+$ (R = alkyl or aryl). Moreover, they are to lower frequency than the values observed for the free isocyanides (ca. 2150 cm^{-1}), indicating a significant π-electron release from the metal to a π^*-CN orbital of the isocyanide. The ^{1}H NMR spectrum of 2b is also consistent with that reported [10] for trans-[Re(CNMe)$_2$(dppe)$_2$][BF$_4$] (singlet methyl resonance at 2.9 ppm and dppe–methylene resonance as a broad triplet, $J = 8$ Hz, due to virtual coupling to phosphorus nuclei). However, in contrast to the latter complex which is white [10], compound 2b is pink, possibly as a result of a slight contamination by triiodide as the counter ion. This might be formed by oxidation of iodide by adventitious air during its synthesis.

In the ^{31}P-{^{1}H} NMR spectra of the complexes (Table 2), the observed singlet resonance is indicative of the trans geometry which has been clearly established by X-ray crystallography for 2a.

2.2. X-ray molecular structure of trans-[Re(CNEt)$_2$-(dppe)$_2$][PF$_6$] (2a)

The single-crystal X-ray diffraction analysis of this compound showed it crystallizes in the monoclinic space group $P2_1/n$ and displays a pseudo octahedral geometry, Fig. 1. Selected bond lengths and angles are displayed in Tables 3 and 4 respectively, and the fractional atomic coordinates are available as supplementary material from the Cambridge Crystallographic Data Centre.
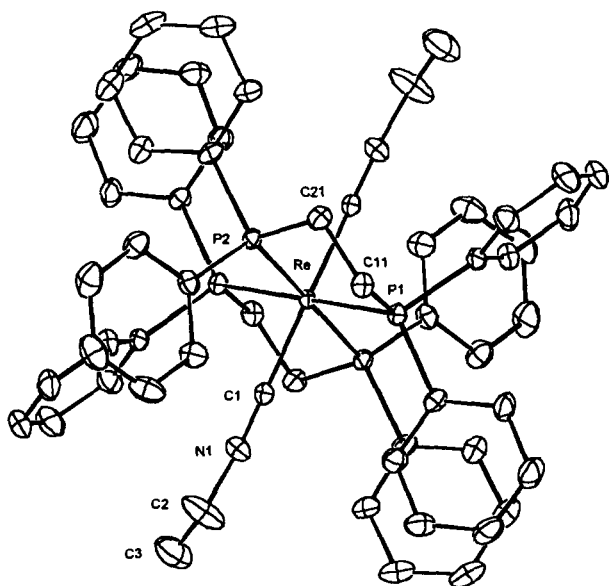

Fig. 1. ORTEP drawing of the cation. The atoms are represented by 50% probability level ellipsoids. Hydrogen atoms are ommited for clarity.

Table 5
Cyclic voltammetric data ^{a} for complexes trans-[Re(CNR)$_2$(dppe)$_2$]A (2a, R = Et, A = PF$_6$; 2b, R = Me, A = I; 2c, R = Pr, A = I$_3$), trans-[Re(CNH)(CNSiMe$_3$)(dppe)$_2$]CF$_3$SO$_3$ (3) and trans-[ReI(CNPr)(dppe)$_2$] (4)

Complex		$E_{1/2}^{ox}$ (V)
trans-[Re(CNEt)$_2$(dppe)$_2$][PF$_6$]	(2a)	0.81
trans-[Re(CNMe)$_2$(dppe)$_2$]I	(2b)	0.74 ^{b,c}
trans-[Re(CNPr)$_2$(dppe)$_2$]I$_3$	(2c)	0.79
trans-[Re(CNH)(CNSiMe$_3$)(dppe)$_2$]CF$_3$SO$_3$ ^{d}	(3)	0.73 ^{e,f}
trans-[ReI(CNPr)(dppe)$_2$]	(4)	0.22

^{a} Values in V ±0.02 V vs. SCE, measured at 200 mV s^{-1}, in 0.2 M [NBu$_4$][BF$_4$]/THF electrolyte solution, unless stated otherwise, using [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ ($E_{1/2}^{ox}$ = 0.545 V vs. SCE) as internal standard. ^{b} In CH$_2$Cl$_2$; an irreversible wave is observed at E_p^{ox} = 0.49 V, being attributed to the oxidation of iodide. ^{c} 0.79 V in THF. ^{d} A partially reversible cathodic wave is observed at $E_{1/2}^{red}$ = −2.0 V and on the reverse scan a new wave is detected at $E_{1/2}^{ox}$ = −0.44 V. ^{e} Irreversible wave (E_p^{ox}); upon scan reversal, a new reversible cathodic wave is detected at $E_{1/2}^{red}$ = 0.43 V. ^{f} A second irreversible oxidation wave is detected at a higher potential, E_p^{ox} = 0.96 V.

The isocyanide ligands are trans to each other and are slightly bent ($\angle$CNEt = 168.2(4)°). Bending of coordinated isocyanides at electron-rich metal centres is commonly attributed [5,7,8,10,13] to electronic effects. Hence, at the {ReY(dppe)$_2$} (Y = Cl or H) centres, a strong bending is observed for methyl isocyanide [5] ($\angle$CNMe = 139.4(10)° or 147.7(7)° respectively). Considerable though less pronounced bending ($\angle$CNMe = 156(1)°) [13] occurs for trans-[Mo(CNMe)$_2$(dppe)$_2$]. However, for compound 2a a much lower deviation from linearity is observed, and may result from weaker electronic effects and/or steric influences. A significantly longer Re–C bond length is displayed by 2a (2.005(5) Å) compared with trans-[ReX(CNMe)(dppe)$_2$] (1.861(12) or 1.947(8) Å for X = Cl or H respectively) [5], in which there is an extensive π-backbonding. However, the former distance is still considerably shorter than that expected (2.30 Å) [14] for an Re–C(sp^3) single bond.

The unsaturated carbon–nitrogen bond length in 2a, 1.165(5) Å, is shorter than that quoted for trans-[ReX(CNMe)(dppe)$_2$] (1.210(15) and 1.207(9) Å for X = Cl or H respectively) [5], which has a significant double bond character and is consistent with a triple bond approaching that of HCN (1.158 Å) [15]. All these observations are in accord with the expected weaker π-electron releasing ability of the cationic rhenium centre in 2a compared with those in the neutral hydride or chloride complexes.

2.3. Electrochemical studies

The redox behaviour of all the complexes has been studied by cyclic voltammetry in an aprotic medium

(commonly in 0.2 M [NBu$_4$][BF$_4$]/THF), at a Pt electrode.

The cationic diisocyanide complexes *trans*-[Re-(CNR)$_2$(dppe)$_2$]$^+$ (R = Et, Me or Pr) (2) and *trans*-[Re-(CNH)(CNSiMe$_3$)(dppe)$_2$]CF$_3$SO$_3$ (3) show a single-electron reversible (2) or irreversible (3) anodic wave at $E_{1/2}^{ox}$ or E_p^{ox} in the range 0.73–0.81 V vs. SCE (Table 5), which is assigned to the Re^I → Re^{II} oxidation as reported [10,12] for the related species *trans*-[Re(CNR)-(CNR')(dppe)$_2$]$^+$ (R,R' = alkyl or aryl) ($E_{1/2}^{ox}$ in the range 0.79–1.05 V). These oxidation potential values are substantially more anodic than that observed (0.22 V) (Table 5) for the single-electron reversible Re^I oxidation of the neutral isocyanide complex *trans*-[Re-I(CNPr)(dppe)$_2$] (4), due to the positive charge of the former complexes and the expected electron-poorer character of their cationic metal centres. The oxidation potential of 4 (0.22 V) is only marginally larger than those reported (0.06–0.08 V) [16] for the analogous chlorocomplexes *trans*-[ReCl(CNR)(dppe)$_2$] (R = Me or ^{t}Bu), in accordance with the expected slightly weaker electron-donor ability of the iodide compared with the chloride. In fact, the former ligand gives a value (− 1.15 V) [17] of the electrochemical ligand parameter (P_L) (a measure of the net electron-donor character of a ligand, the more negative values corresponding to more effective electron-releasing abilities from the ligand) which is slightly higher than that quoted (− 1.19 V) [17] for chloride.

Moreover, the oxidation of I$^-$, the counter-ion of complex 2b, is detected as an irreversible anodic wave at E_p^{ox} = 0.49 V (Table 5), as observed for NaI (E_p^{ox} = 0.46 V) under similar experimental conditions.

In contrast with the complexes (2) with two alkyliso-cyanides and for which the anodic wave associated with the metal oxidation is reversible, *trans*-[Re(CNH)(CN-SiMe$_3$)(dppe)$_2$]CF$_3$SO$_3$ displays an irreversible anodic wave at E_p^{ox} = 0.73 V. The irreversibility conceivably results from proton loss from the CNH induced by oxidation to give [Re(CN)(CNSiMe$_3$)(dppe)$_2$]$^+$, as is known [6] to occur for the related species *trans*-[ReCl-(CNH)(dppe)$_2$]$^+$ which, upon single-electron anodic oxidation (at ca. 1.5 V), forms the cyanide product *trans*-[ReCl(CN)(dppe)$_2$]$^+$. The number of electrons (one per metal atom) involved in the irreversible anodic process of 3 was confirmed by controlled potential electrolysis in NCMe, at the peak potential of the anodic wave, using a platinum gauze working electrode.

A partially reversible cathodic wave was observed for complex 3 at $E_{1/2}^{red}$ = − 2.0 V. Upon scan reversal, a new reversible anodic wave is observed at $E_{1/2}^{ox}$ = − 0.44 V, a value similar to that reported (− 0.49 V) [5] for the oxidation of *trans*-[Re(CN)$_2$(dppe)$_2$]$^-$. Exhaustive controlled potential electrolysis at the cathodic process involves two electrons per rhenium atom, and generates the above-mentioned anodic wave. These ob-

servations suggest that the cathodic process of 3 involves desilylation and dehydrogenation of the isocyanide ligands according to reaction (6).

$$\text{*trans*-}[Re(CNH)(CNSiMe_3)(dppe)_2]^+ + 2e$$

$$\rightarrow \text{*trans*-}[Re(CN)_2(dppe)_2]^- + SiMe_3 \qquad (6)$$
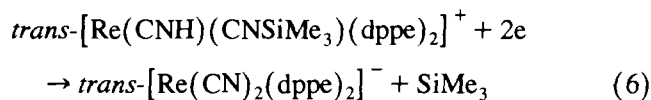
3. Final comments

Both cyanide ligands in the negatively charged complex *trans*-[Re(CN)$_2$(dppe)$_2$]$^-$, with an electron-rich metal centre, undergo electrophilic attack by alkylating agents (such as organic iodides) to form the corresponding diisocyanide products according to the following overall process in which M = *trans*-{Re(dppe)$_2$}:

$$[NC\text{-}M\text{-}CN]^- + 2R^+ \rightarrow [RNC\text{-}M\text{-}CNR]^+$$
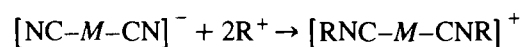
The reaction is fast and no cyano-monoalkylated product of the type [M(CN)(CNR)], a conceivable intermediate in the process, was isolated. However, replacement of one cyanide by iodide can also occur and the mono-isocyanide complex [MI(CNR)] (R = propyl) was also isolated. Since neutral complexes of this type, such as *trans*-[ReCl(CNR)(dppe)$_2$], are known [12] to undergo ready protonation at the isocyanide to give the corresponding aminocarbyne species *trans*-[ReCl-(CNHR)(dppe)$_2$]$^+$, we have thus demonstrated the conversion of cyanide to aminocarbyne by activation, atom electron-rich phosphine Re^I centre via an isocyanide intermediate.

$$M\text{-}CN^- \xrightarrow{R^+} M\text{-}CNR \xrightarrow{H^+} M \equiv CN(H)R^+$$

We have previously achieved [6] this in the case of protonation (R$^+$ = H$^+$) of coordinated cyanide (reversible conversion into the aminocarbyne CNH$_2$ ligand) and now we have extended it to the alkylation reaction (R = alkyl) of cyanide.

4. Experimental

All manipulations and reactions were performed under dinitrogen using standard inert-gas flow and vacuum techniques. Solvents were purified before use by standard procedures. [NBu$_4$]*trans*-[Re(CN)$_2$(dppe)$_2$] was prepared as previously reported [5]. Alkyl halides and [Et$_3$O][PF$_6$] were purchased from Aldrich and used without further purification. IR measurements were carried out with a Perkin-Elmer 683 spectrophotometer. NMR spectra were obtained on a Varian 300 spectrometer. The electrochemical experiments were performed on an EG & G PAR 173 potentiostat/galvanostat and an EG & G PARC 175 universal programmer. The electrochemical behaviour of the complexes was studied

by cyclic voltammetry and controlled potential electrolysis in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]-dichloromethane or tetrahydrofuran (THF) at platinum electrodes. The values of the oxidation or reduction potentials are quoted relative to SCE, and were measured using as internal reference the redox couple [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ ($E^{ox}_{1/2}$ = 0.545 V vs. SCE).

4.1. Structure solution and refinement for trans-[Re(CNEt)$_2$(dppe)$_2$][PF$_6$] (2a)

The complex trans-[Re(CNEt)$_2$(dppe)$_2$][PF$_6$], Mr = 1238.18, crystallizes in the monoclinic space group $P2_1/n$ with a = 12.192(5) Å, b = 16.299(4) Å, c = 13.462(5) Å, β = 102.01(2)°, V = 2616.6(16) Å^3, Z = 2, Dc = 1.57 g cm^{-3}, μ(Mo Kα) = 24.1 cm^{-1}. The unit cell and orientation matrix were obtained by least-squares refinement of 25 centred reflections with 15 < θ < 18.5536 reflections with 1.5 < θ < 25 were collected by the ω–2θ scan mode, in an Enraf-Nonius TURBO CAD4 diffractometer equipped with a rotating anode (50 KV, 70 mA), using graphite monochromated radiation. Three standard reflections were monitored during data collection but no decay or instrumental instability was detected (the loss of intensity is less then 0.02% h^{-1}). Using the CAD4 software, data were corrected for Lorentz and polarization effects and empirically for absorption (minimum transmission factor 83.5%, average transmission factor 94.9%). 4525 unique reflections with $F \geq 0$ were used in structure solution and refinement of 357 parameters. The position of the Re atom was obtained by a three-dimensional Patterson synthesis and was found to be located at the special position. All the other non-hydrogen atoms were located in subsequent difference Fourier maps and refined with anisotropic thermal motion parameters. The hydrogen atoms were inserted in calculated positions and refined isotropically with fixed distances (1.08Å) from the parent carbon atom. The weighting scheme w = 0.497/[σ2(F_o) + 0.0001 F_o^2] was found to give an acceptable agreement analysis. Final refinement converged at R = 0.04 and Rw = 0.025. The largest peak in the final difference Fourier synthesis was 0.66 eÅ^{-3} and was located at 1.06 Å of the Re atom. The molecular structure is shown in Fig. 1, and the final atomic coordinates for all the non-hydrogen atoms, lists of observed and calculated structure factors, tables of anisotropic thermal parameters, hydrogen atomic coordinates, bond lengths and angles and inter- and intramolecular contact distances are available as supplementary material. The structure solution and refinement were carried out with SHELX76 [18] and the illustrations were drawn with ORTEP-II [19]. The atomic scattering factors and anomalous scattering terms were taken from *International Tables in X-Ray Crystallography* [20].

4.2. Syntheses of the complexes

trans-[Re(CNEt)$_2$(dppe)$_2$][PF$_6$] (2a). 0.14 g (0.74 mmol) of [Et$_3$O][PF$_6$] were added to a solution of 0.20 g (0.16 mmol) of [NBu$_4$]trans[Re(CN)$_2$(dppe)$_2$] (1) in 10 cm^3 of CH$_2$Cl$_2$ and the mixture stirred for 1 h. Separation of the cloudy suspension by filtration and addition to the filtrate of 3 cm^3 of pentane afforded pale yellow crystals of 2a which were separated from the solution by filtration, washed with Et$_2$O and dried in vacuo (0.080 g, 50% yield).

trans-[Re(CNR)$_2$(dppe)$_2$]X {R = Me, X = I (2b); R = Pr, X = I$_3$ (2c)} and trans-[ReI(CNPr)(dppe)$_2$] (4). As a general procedure, a five-old molar excess of the appropriate alkyl iodide was added to a solution of complex 1 (0.20 g) in CH$_2$Cl$_2$ (10 cm^3) and the mixture stirred for 1 h. Upon addition of pentane (6 cm^3), filtration and addition of Et$_2$O (2 cm^3) to the filtrate, yellow crystals of 2b or 2c were obtained. They were filtered-off and dried in vacuo (30–50% yield). From the mother-liquor other minor products could be isolated, such as trans-[ReI(CNPr)(dppe)$_2$] (4) (< 10% yield) after concentration in vacuo, addition of Et$_2$O and cooling at ca. 0°C for five days.

trans-[Re(CNH)(CNSiMe$_3$)(dppe)$_2$]CF$_3$SO$_3$ (3). 0.10 cm^3 (0.52 mmol) of Me$_3$SiCF$_3$SO$_3$ were added to the suspension of 0.10 g (0.08 mmol) of 1 in 15 cm^3 of THF and the system was stirred for 20 min. The white precipitate was removed by filtration and Et$_2$O (4 cm^3) was added to the filtrate until light green crystals of 3 started to precipitate. They were filtered off, washed with Et$_2$O (2 × 2 cm^3) and dried in vacuo (0.070 g, 70% yield).

[Re(CN)$_2$(dppe)$_2$]. A suspension of [NBu$_4$]trans[Re(CN)$_2$(dppe)$_2$] (0.16 g, 0.125 mmol) and Ag[BF$_4$] (0.034 g, 0.17 mmol) in THF (10 cm^3) was stirred for 1 h. The dark solid was filtered off and dissolved in CH$_2$Cl$_2$ (2 cm^3). The insoluble material was removed by filtration. Addition of Et$_2$O (10 cm^3) to the orange–red filtered solution led to the precipitation of [Re(CN)$_2$(dppe)$_2$] as a red solid which was filtered off and dried in vacuo (0.065 g, 50% yield).

Acknowledgments

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