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THE ELECTRONIC PROPERTIES OF ISOCYANIDES AT RHENIUM—DINITROGEN BINDING SITES. PREPARATION AND REDOX PROPERTIES OF THE ISOCYANIDE COMPLEXES *trans*-[ReCl(CNR)($Ph_2PCH_2CH_2PPh_2$)$_2$]

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Summary

The isocyanide complexes *trans*-[ReCl(CNR)(dppe)$_2$] (R = Me, Bu^t, $C_6H_4CH_3$-4, $C_6H_4CH_3$-2, C_6H_4Cl-4, $C_6H_4OCH_3$-4 and $C_6H_3Cl_2$-2,6; dppe = $Ph_2PCH_2CH_2PPh_2$) have been prepared by isocyanide displacement of dinitrogen from the parent complex *trans*-[ReCl(N_2)(dppe)$_2$]. Their redox properties have been studied by cyclic voltammetry and are interpreted on the basis of the electronic properties and the geometry of the ligating isocyanides which are believed to be bent in these complexes, appearing to exhibit ligand parameter (P_L) values ca. +0.3 V higher than those which would be expected for linear geometry. A very high polarisability ($B \simeq 3.4$) is observed for the {ReCl(dppe)$_2$} site.

Introduction

Isocyanides, CNR (R = alkyl or aryl), show two extreme modes of coordination to transition metal complex sites, linear (I) and bent (II), and, in addition, two modes of activation at such sites towards nucleophilic and towards electrophilic attack, giving carbene- (III) and carbyne-type (IV) species, respectively. This ambivalence in behaviour is determined by the electronic interactions between site and ligand and makes coordinated isocyanide an interesting probe of the character of transition metal complex sites.

A priori it is difficult to assess whether a particular site will induce linear or bent CNR coordination and whether or not the ligand will be activated towards

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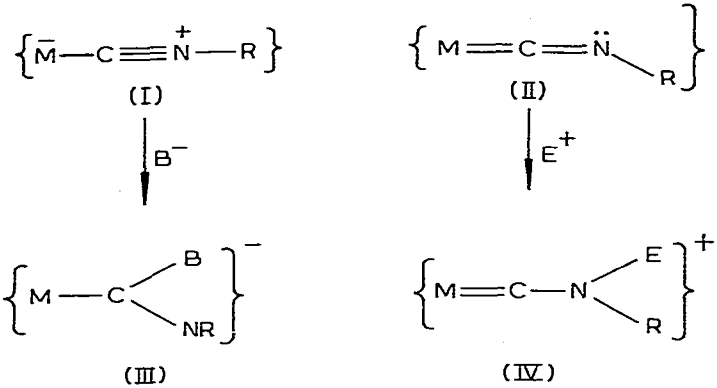
nucleophilic or electrophilic attack. Certain generalisations are possible, how-



ever: if the site is electron-rich then a bent coordination mode, a low infrared ν(CN) value and tendency towards electrophilic attack should be favoured [1—9]; if electron poor, a linear coordination, a high ν(CN) value and tendency to undergo nucleophilic attack [10,11] should be evident. A rather more precise indication of the electron-richness or -poorness of a site and of the influence of various ligands at that site, can be derived by measuring the energy of the highest occupied molecular orbital (HOMO) since, in a closely related series of complexes, this is a sensitive function of the distribution of electron density in the frontier orbitals. A convenient method of monitoring such changes in the HOMO is to measure, where possible, reversible one-electron oxidation potentials. In this paper we describe the preparation and properties of a series of isocyanide complexes of rhenium(I) and an attempt to relate changes in the energy of the HOMO to the nature of the interaction between the site $\{ReCl(dppe)_2\}$ and the isocyanide ligand.

Results and discussion

Preparation and characterization of complexes trans-[ReCl(CNR)(dppe)₂] (A, R = alkyl or aryl)

Displacement by isocyanides of the labile dinitrogen ligands in the complexes *trans*-$[M(N_2)_2(dppe)_2]$ (where M = Mo or W) proved to be a convenient route to prepare species with isocyanides ligating an electron-rich metal site [2]. Analogous reactions (1) were carried out with the *trans*-$[ReCl(N_2)(dppe)_2]$ complex, leading to the isocyanide species *trans*-$[ReCl(CNR)(dppe)_2]$ (A; R = $C_6H_4CH_3$-4, $C_6H_4CH_3$-2, $C_6H_4OCH_3$-4, C_6H_4Cl-4 and $C_6H_3Cl_2$-2,6; for R = Me or Bu^t, complexes A have previously been reported [8,9]).

The greater stability of *trans*-$[ReCl(N_2)(dppe)_2]$, compared to that of *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W), required the use of more drastic conditions (longer reflux time or irradiation) for complete displacement of dinitrogen to occur in the rhenium case (eq. 1).

$$trans\text{-}[ReCl(N_2)(dppe)_2] + CNR \rightarrow \underset{(A)}{trans\text{-}[ReCl(CNR)(dppe)_2]} + N_2 \qquad (1)$$

(R = Me, Bu^t, $C_6H_4CH_3$-4, $C_6H_4CH_3$-2, $C_6H_4OCH_3$-4, C_6H_4Cl-4 or $C_6H_3Cl_2$-2,6)

The reactions were carried out under argon, in refluxing THF, and in the presence of an excess of isocyanide. Typical conditions were a six molar excess of isocyanide and reaction times of ca. 2—5 days, but irradiation of the solution by tungsten filament light resulted in a considerable shortening of the time required for completion. The reaction with CNC_6H_4OMe-4 appeared to be considerably slower than with the other isocyanides, and longer refluxing under irradiation was required.

The reactions were monitored by following, by solution infrared spectra, the N_2 stretching bands of the parent dinitrogen complex and NC stretching bands of free and ligating isocyanide. All the isocyanide complexes A exhibit, in the infrared spectra, low ν(CN) values (Table 1), well below the corresponding values for free isocyanide, e.g., for (A, R = C_6H_4Cl-4), ν(CN) 1760 cm^{-1}, whereas in free CNC_6H_4Cl-4 ν(CN) 2110 cm^{-1}. The large shift of ν(CN) to lower values which occurs upon coordination of the isocyanide agrees with its expected strong electronic π-acceptance from an electron-rich metal site as was previously observed [2] for *trans*-[M(CNR)$_2$(dppe)$_2$]. Two ν(CN) bands were observed in each of the solid complexes (A, R = $C_6H_4CH_3$-2 and $C_6H_4OCH_3$-4), whereas in THF or dichloromethane solution only one broad band was seen for each species, which suggests that the splitting is due to a solid state effect, although the bands in each pair display an unusually high separation (ca. 150 and 90 cm^{-1}, respectively).

All the complexes A exhibit singlet resonances in their $^{31}P\{^1H\}$ NMR spectra (Table 2) in agreement with a *trans*-geometry.

In the ^1H NMR spectra (Table 2) the four phenyl protons of the *para*-substituted ligating isocyanides exhibit an AB type resonance pattern consisting of two doublets, each integrating for 2 protons, at a higher field than the aromatic phosphine protons. The higher field doublet may be assigned to the 2 phenyl

TABLE 1

PHYSICAL DATA FOR COMPLEXES *trans*-[ReCl(CNR)(dppe)$_2$] (A: R = $C_6H_4CH_3$-4, $C_6H_4CH_3$-2, $C_6H_4OCH_3$-4, C_6H_4Cl-4, $C_6H_3Cl_2$-2,6)

R	Colour	ν(C≡N) [a]	Elemental analysis (Found (calcd.) (%))		
			C	H	N
$C_6H_4CH_3$-4 [b]	Orangish-yellow	1880s(br)	64.0	5.2	1.3
			(63.7)	(5.4)	(1.1)
$C_6H_4CH_3$-2 [c]	Yellow	1900s(br) [d]	63.8	5.0	1.3
		1750s(br)	(63.6)	(5.1)	(1.2)
$C_6H_4OCH_3$-4	Brownish-yellow	1930s(br) [e]	62.1	4.8	1.4
		1840s(br)	(62.6)	(4.8)	(1.2)
C_6H_4Cl-4 [c]	Yellow	1760s(br)	61.3	5.0	1.6
			(61.5)	(4.7)	(1.2)
$C_6H_3Cl_2$-2,6	Yellow	1770s(br)	59.3	4.5	1.3
			(59.5)	(4.3)	(1.2)

[a] In Nujol mull (cm^{-1}). [b] With 1.5 THF of crystallisation as indicated by the ^1H NMR spectrum. [c] With 0.5 THF of crystallisation as indicated by the ^1H NMR spectrum. [d] Only one broad band is observed in CH_2Cl_2 or THF solution at ca. 1780 cm^{-1}. [e] Only one very broad band is observed in THF solution at ca. 1880 cm^{-1}.

TABLE 2

^{1}H NMR AND ^{31}P$\{{}^1$H$\}$ NMR DATA [a] FOR COMPLEXES *trans*-[ReCl(CNR)(dppe)$_2$] (A; R = $C_6H_4CH_3$-4, $C_6H_4CH_3$-2, $C_6H_4OCH_3$-4, C_6H_4Cl-4 AND $C_6H_3Cl_2$-2,6)

R	^{1}H NMR			^{31}P$\{{}^1$H$\}$ NMR
	δ (ppm) [b]	Intensity	Assignment	δ (ppm) [c]
$C_6H_4CH_3$-4	7.5—6.7m	40(40)	C_6H_5(dppe)	111.4
	6.55d [d]	2(2)	Isocyanide aromatic *ortho* to Me	
	5.60d [d]	2(2)	Isocyanide aromatic *ortho* to N	
	3.65m	6(6)	CH_2(THF) [e]	
	2.85—2.3m(br)	8(8)	CH_2(dppe)	
	2.15s	3(3)	$CNC_6H_4CH_3$-4	
	1.80m	6(6)	CH_2(THF) [e]	
$C_6H_4CH_3$-2	7.5—6.7m	41(41)	C_6H_5(dppe) + isocyanide aromatic H(3) *ortho* to CH_3(2)	108.8
	6.48t [f]	1(1)	Isocyanide aromatic H(4) and H(5)	
	6.18t [f]	1(1)		
	5.18d [f]	1(1)	Isocyanide aromatic H(6) *ortho* to N(1)	
	3.65m	2	CH_2(THF) [e]	
	3.1—2.3m(br)	8(8)	CH_2(dppe)	
	1.92s	3(3)	$CNC_6H_4CH_3$-2	
	1.83m	2	CH_2(THF) [e]	
$C_6H_4OCH_3$-4	7.6—6.7m	40(40)	C_6H_5(dppe)	104.4
	6.31d [g]	2(2)	Isocyanide aromatic *ortho* to OCH_3	
	5.63d [g]	2(2)	Isocyanide aromatic *ortho* to N	
	3.72s	3(3)	$CNC_6H_4OCH_3$-4	
	3.1—2.3m(br)	8(8)	CH_2(dppe)	
C_6H_4Cl-4	7.5—6.7m	40(40)	C_6H_5(dppe)	111.7
	6.60d [h]	2(2)	Isocyanide aromatic *ortho* to Cl	
	5.48d [h]	2(2)	Isocyanide aromatic *ortho* to N	
	3.68m	2	CH_2(THF) [e]	
	2.9—2.5m(br)	8(8)	CH_2(dppe)	
	1.85m	2	CH_2(THF) [e]	
$C_6H_3Cl_2$-2,6	7.5—6.2m	43(43)	C_6H_5(dppe) + isocyanide aromatic	115.9
	3.74m	2	CH_2(THF) [e]	
	3.2—2.7m	8(8)	CH_2(dppe)	
	1.94m	2	CH_2(THF) [e]	

[a] In CD_2Cl_2 at ca. 303 K. [b] Values (ppm) relative to internal TMS. [c] Values (ppm) upfield from external TMP. [d] ${}^3J$(H—H) 8.0 ± 0.5 Hz. [e] Solvent of crystallisation. [f] ${}^3J$(H—H) 7.5 ± 1.0 Hz. [g] ${}^3J$(H—H) 8.9 ± 0.5 Hz. [h] ${}^3J$(H—H) 8.3 ± 0.2 Hz. Coupling evidenced by decoupling experiments.

ring protons of the isocyanide *ortho* to the N atom, by analogy with assignments for [Co($CNC_6H_4NO_2$-4)$\{PPh(OEt)_2\}_2$]ClO_4 [12] and [MoX($CNC_6H_4CH_3$-4)$_2$(dppe)$_2$]Y (X = Cl, Y = BPh_4; X = Br, Y = Br) [13], whereas the lower field doublet may be due to the 2 phenyl protons *ortho* to the substituent. The observed coupling constant (${}^3J \simeq 8.0$—8.9 Hz) agrees with the values reported for the Mo and Co isocyanide complexes mentioned above.

In agreement with the assignment of the described AB-type resonance pattern to the *ortho* and *meta* phenyl protons of ligating *para* substituted isocyanide, such a pattern is not observed in complex (A, R = $C_6H_3Cl_2$-2,6) and is replaced, in complex (A, R = $C_6H_4CH_3$-2), by a pair of triplets and a higher field doublet (with a coupling constant value of ca. 7.5 Hz), each integrating for one proton.

This doublet may be assigned to the phenyl proton in position 6, *ortho* to the N atom, whereas the two triplets may be due to the phenyl protons in positions 4 and 5. Each of these triplets may result from the partial overlap of two doublets with analogous coupling constants. The expected doublet for the phenyl proton in position 3 is not observed, being buried under the aromatic dppe proton resonances.

Electrochemical behaviour of complexes A at a platinum electrode

Each of the complexes A shows two successive reversible one-electron oxidations at a Pt electrode, in tetrahydrofuran — 0.2 *M* $[NBu_4][BF_4]$ by cyclic voltammetry. The reversibility of the redox processes demonstrates that no gross structural change results from removal of one or of two-electrons, [equation (2)]. $E^{ox}_{1/2}$ data are given in Table 3.

$$\begin{array}{lcl} \textit{trans}\text{-}[\mathrm{ReCl(CNR)(dppe)_2}] & \underset{+e}{\overset{-e}{\rightleftharpoons}} & \textit{trans}\text{-}[\mathrm{ReCl(CNR)(dppe)_2}]^{+} \\ \text{18-electron} & {}^{I}E^{ox}_{1/2} & \text{17-electron} \\ & \underset{+e}{\overset{-e}{\rightleftharpoons}} & \textit{trans}\text{-}[\mathrm{ReCl(CNR)(dppe)_2}]^{2+} \qquad (2) \\ & {}^{II}E^{ox}_{1/2} & \text{16-electron} \end{array}$$

The variation of ${}^{I}E^{ox}_{1/2}$ *with R in complexes A*

The oxidation potentials of the complexes A become more positive in the order of R = $Bu^t \gtrsim CH_3 < C_6H_4OCH_3\text{-}4 < C_6H_4CH_3\text{-}4 \gtrsim C_6H_4CH_3\text{-}2 < C_6H_4Cl\text{-}4 < C_6H_3Cl_2\text{-}2,6$. This order is not unexpected since it broadly reflects the increasing electron-withdrawing influence of the R group. A plot of ${}^{I}E^{ox}_{1/2}$ versus Hammett's σ constant [14] is shown in Fig. 1 (for the *ortho* substituents, values of the Taft polar σ^* parameter [15] were taken and they were considered to be additive).

The gross linear correlation shows the essential trend but for the limited range of *para* substituted complexes a substantially better linear correlation of ${}^{I}E^{ox}_{1/2}$ with Hammett's σ^+_p constant [16] (Fig. 2) appears to be valid and this tends to suggest that the HOMO is conjugated to the aryl substituent.

TABLE 3

CYCLIC VOLTAMMETRIC DATA [a] FOR COMPLEXES *trans*-$[ReCl(CNR)(dppe)_2]$ (A; R = Me, Bu^t, $C_6H_4CH_3$-4, $C_6H_4CH_3$-2, $C_6H_4OCH_3$-4, C_6H_4Cl-4 AND $C_6H_3Cl_2$-2,6)

R	${}^{I}E^{ox}_{1/2}$	${}^{II}E^{ox}_{1/2}$
Me	+0.08	+0.99
Bu^t	+0.06	+0.98
$C_6H_4CH_3$-4	+0.24	+1.10
$C_6H_4CH_3$-2	+0.26	+1.09
$C_6H_4OCH_3$-4	+0.19	+1.04
C_6H_4Cl-4	+0.30	
$C_6H_3Cl_2$-2,6	+0.43	+1.22

[a] Values in Volt (±0.02) relative to SCE, measured by using as internal reference the $[Mo(N_2)_2(dppe)_2]^{0/+}$ couple (with $E^{ox}_{1/2} = -0.16$ V vs. SCE in 0.2 *M* $[NBu_4][BF_4]$, THF). Experiments carried out in 0.2 *M* $[NBu_4][BF_4]$, THF at a platinum electrode.

Fig. 1.

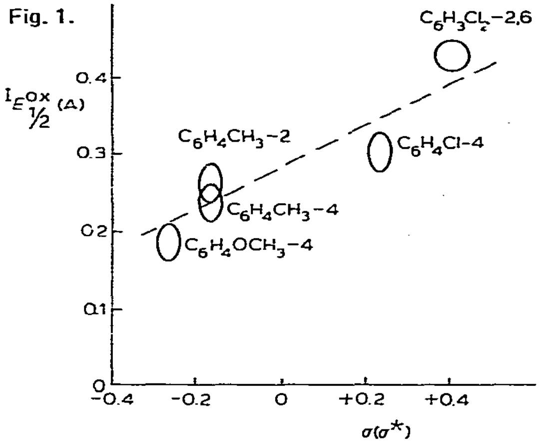


Fig. 2.

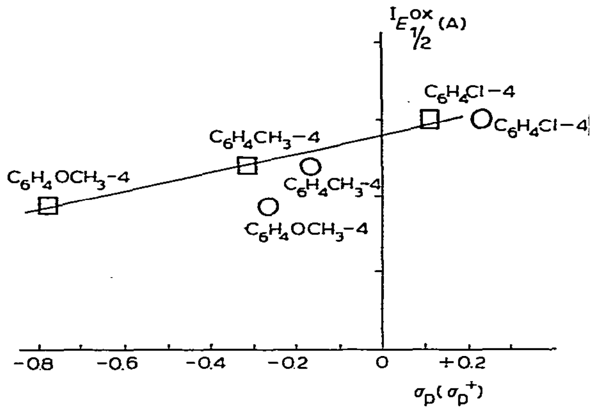


Fig. 1. Plot of ${}^{I}E^{ox}_{1/2}$ for substituted arylisocyanide complexes *trans*-[ReCl(CNR)(dppe)$_2$], A, versus the Hammett's σ_p constant (or the Taft polar σ^* constant for the *ortho* substituents).

Fig. 2. Plots of ${}^{I}E^{ox}_{1/2}$ for *para*-substituted arylisocyanide complexes *trans*-[ReCl(CNR)(dppe)$_2$], A, versus the Hammett's σ_p or σ_p^+ constants (○ refers to the former and □ to the latter).

Correlation of ${}^{I}E^{ox}_{1/2}$ with the ligand parameter P_L

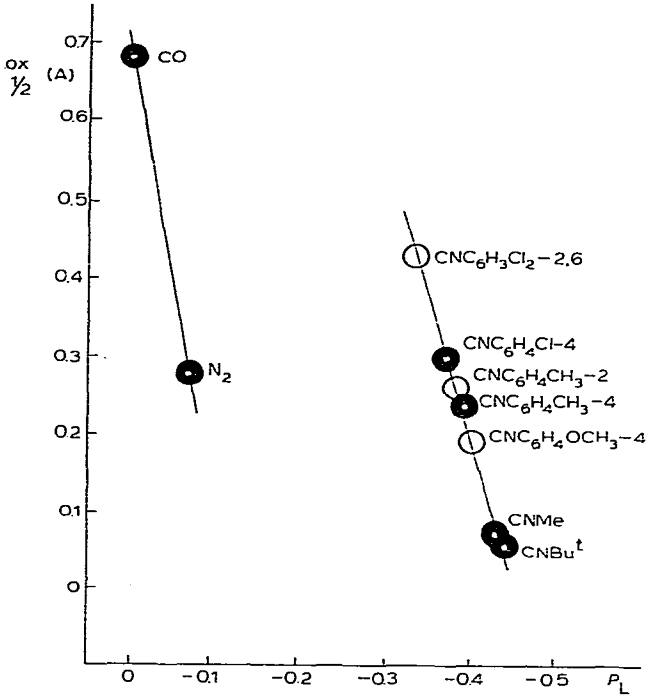
The ligand parameter P_L has been used as a measure of the net σ and π acceptor/donor properties of a particular ligand.

Using eq. 3 [17] and data in the literature [18], we have estimated P_L for various isocyanide ligands: -0.43 V (CNMe) [17], -0.44 V (CNBu^t), -0.39 V ($C_6H_4CH_3$-4) and -0.37 V (C_6H_4Cl-4) (Table 4).

$$P_L = {}^{I}E^{ox}_{1/2}[\mathrm{Cr(CO)_5(CNR)}] - {}^{I}E^{ox}_{1/2}[\mathrm{Cr(CO)_6}] \qquad (3)$$

Figure 3 shows a plot of ${}^{I}E^{ox}_{1/2}$ for the rhenium(I) isocyanide complexes versus P_L and also corresponding data for N_2 and CO coordinated to the same site. A linear correlation appears to be followed by the isocyanide complexes and from the plot it is possible to estimate P_L values for other isocyanide ligands: $CNC_6H_4CH_3$-2 (-0.38 V), $CNC_6H_4OCH_3$-4 (-0.40 V) and $CNC_6H_3Cl_2$-2,6 (-0.33 V) (Table 4). However, the CO and N_2 complexes lie substantially off the isocyanide line, possibly corresponding to a separate line to that of the isocyanide series. This discontinuity in the ${}^{I}E^{ox}_{1/2}$ versus P_L plot is particularly interesting since it may bear upon the mode of coordination of the isocyanide, linear or bent. We now consider this in more detail.

Isocyanides coordinated to the {Cr(CO)$_5$} site are linear; the mode of coordination of CNR to the {ReCl(dppe)$_2$} site has not yet been determined by X-rays but may well deviate from linearity on account of the high electron-richness of this site, as discussed below. Linear CNR should be a better net donor of electron density than bent CNR. Electronically, linear and bent isocyanides can be considered to behave as distinct ligands since different bonding orbitals are available on each. P_L values for linear CNR as determined from eq. 3 would therefore be expected to be more negative than those for P_L (bent). The correlation of P_L with ${}^{I}E^{ox}_{1/2}$ for the N_2 and CO complexes, would suggest ${}^{I}E^{ox}_{1/2}$ for *trans*-[ReCl(CNMe)(dppe)$_2$] should be ca. -1.8 V whereas we have



ig. 3. Plots of $^{I}E^{ox}_{1/2}$ versus the P_L (V) ligand constant for the isocyanide *trans*-[ReCl(CNR)(dppe)$_2$], A, omplexes, and for the analogous carbonyl and dinitrogen species. Open circles correspond to inter- or ktrapolated P_L values.

ıeasured it as +0.08 V versus SCE. That the isocyanide complexes are substanially more difficult to oxidise than the extrapolation would predict is consisent with a different coordination of CNR on the rhenium(I) site to that on he {Cr(CO)$_5$} site and a reasonable suggestion is that CNR is bent when coorinated to {ReCl(dppe)$_2$}. From Fig. 3 we can estimate eq. 4 for P_L values xpressed in volts, if the interpretation is correct.

$$ {}_{L}(\text{CNR linear}) \simeq P_{L}(\text{CNR bent}) - 0.3 \qquad (4) $$

Data which support the conclusion that isocyanide is bent at the Re site are

ABLE 4

IGAND PARAMETER P_L FOR LINEAR ISOCYANIDE LIGANDS

ocyanide	P_L (V)	Ref. [a]
NMe	–0.43	a
NBu^t	–0.44	b
NC$_6$H$_4$CH$_3$-4	–0.39	b
NC$_6$H$_4$CH$_3$-2	–0.38	c
NC$_6$H$_4$OCH$_3$-4	–0.40	c
NC$_6$H$_4$Cl-4	–0.37	b
NC$_6$H$_3$Cl$_2$-2,6	–0.33	c

a, previously reported (ref. 17); b, calculated from data of ref. 18; c, estimated from data of the present ork.

as follows. The complexes *trans*-[M(CNR)$_2$(dppe)$_2$] (M = Mo, W) show low ν(CN) values in the range 1790—1920 cm^{-1} [2], they oxidise at relatively negative potentials [2] and they protonate [4] and alkylate [5] at the nitrogen atom. In the *trans*-[Mo(CNMe)$_2$(dppe)$_2$] complex, both CNR ligands show a bent CNC angle of 156(1)° [3]. The Re complexes similarly show low ν(CN) values, are relatively easy to oxidise and they also protonate at nitrogen [8,9].

There are nevertheless other interpretations of the $^{\text{I}}E^{\text{ox}}_{1/2}$ versus P_{L} plot of Fig. 3 which may be equally valid. For example, if the HOMO in the Re(CNR) series is substantially conjugated to the isocyanide substituent then it may be stabilised, resulting in $^{\text{I}}E^{\text{ox}}_{1/2}$ at a higher value than that expected on the basis of the trend followed by the N$_2$ and CO complexes where such a conjugation is obviously absent.

The sensitivity of the {ReCl(dppe)$_2$} site to ligand coordination

If we consider Fig. 3 for the isocyanide series it is apparent that the slope, β (polarisability), of ca. 3.4 represents a dramatic change in oxidation potential as R is changed, compared to the change observed for the standard {Cr(CO)$_5$} site with coordinated isocyanide ligands. Similarly, the slope for the carbonyl- and dinitrogen-rhenium complexes is large. Previously we have observed [16] β values for series of complexes in the range 0.5 to 1.0 (eq. 5).

$$E^{\text{ox}}_{1/2} = \text{constant} + \beta P_{\text{L}} \qquad (5)$$

The marked sensitivity of the HOMO in the Re series to a change in ligand is entirely consistent with the inability of the *trans*-Cl ligand to buffer changes in electron density at the metal.

Conclusions

We have attempted to interpret changes in $^{\text{I}}E^{\text{ox}}_{1/2}$ for the complexes *trans*-[ReCl(CNR)(dppe)$_2$] in terms of the site and electronic influence of the CNR ligand. We suggest that $^{\text{I}}E^{\text{ox}}_{1/2}$ versus P_{L} plots may be used to discriminate between linear and bent coordination of isocyanide, and that in this rhenium(I) series the CNR ligand is bent. Further work is clearly necessary to substantiate this suggestion, indeed P_{L}(linear) and P_{L}(bent) parameters may range over more than 0.3 V and reflect the degree of CNR bending (180 to 120°). Other ligands, such as NO and RN$_2$, which can show an ambivalent geometry when coordinated to a metal site, may similarly show a range of P_{L} values.

Experimental

All the reactions were carried out under dinitrogen using solvents purified by standard techniques.

The preparations of complexes (A, R = Me or Bu^t) were described in an earlier paper [9], and the preparation of *trans*-[ReCl(N$_2$)(dppe)$_2$] was by a published method [19].

The redox potentials were measured by cyclic voltammetry in 0.2 *M* [NBu$_4$]-[BF$_4$], THF at a platinum electrode. Usually the complexes displayed diffusion controlled one-electron reversible oxidations at scan rates 0.02—0.2 V s^{-1} as evidenced by the peak current separation, $[E_p^{ox} - E_p^{red}]$, and by the ratio of the peak currents. The $E_{1/2}^{ox}$ values are quoted relative to SCE by using as internal reference the $[Mo(N_2)_2(dppe)_2]^{0/+}$ couple (which has $E_{1/2}^{ox} = -0.16$ V vs. SCE in 0.2 *M* $[NBu_4][BF_4]$, THF).

The electrochemical experiments were performed on an EG&G PAR 174A Polarographic Analyser or an EG&G PARC 175 Universal Programmer.

Infrared measurements were carried out on a Perkin—Elmer 577 or 457 spectrometer, ^1H and ^{31}P NMR spectra were recorded on a Jeol PS 100, Jeol PFT 100 Fourier-transform or Jeol FX90Q spectrometer.

Preparation of complexes trans-[ReCl(CNR)(dppe)₂] (A, R = $C_6H_4CH_3$*-4,* $C_6H_4CH_3$*-2,* $C_6H_4OCH_3$*-4,* C_6H_4Cl*-4,* $C_6H_3Cl_2$*-2,6)*

trans-Bis[1,2-bis(diphenylphosphino)ethane](chloro)(4-methylphenylisocyanide)rhenium(I), trans-[ReCl($CNC_6H_4CH_3$*-4)(dppe)*$_2$*] (A, R =* $C_6H_4CH_3$*-4).* $CNC_6H_4CH_3$-4 (0.35 cm^3, 3.3 mmol) was added to a suspension of *trans*-[ReCl(N_2)(dppe)$_2$] (0.62 g, 0.59 mmol) in THF (130 cm^3) and the stirred mixture was refluxed under argon for two days. The solution was concentrated under vacuum and pentane was added with heating until a yellow solid started to separate. The mixture was left to cool, the solid was filtered off (it was a mixture of the product with the unchanged starting material) and the solution was concentrated and cooled to ca. —10° C. The resulting orangish-yellow crystalline solid of *trans*-[ReCl($CNC_6H_4CH_3$-4)(dppe)$_2$] was filtered off, washed with a mixture of THF/pentane, and dried under vacuum (0.13 g, 19% yield).

trans-Bis[1,2-bis(diphenylphosphino)ethane](chloro)(2-methylphenylisocyanide)rhenium(I), trans-[ReCl($CNC_6H_4CH_3$*-2)(dppe)*$_2$*] (A, R =* $C_6H_4CH_3$*-2).* $CNC_6H_4CH_3$-2 (0.5 cm^2) was added to a suspension of *trans*-[ReCl(N_2)(dppe)$_2$] (0.58 g, 0.55 mmol) in THF (110 cm^3) and the mixture was refluxed under argon for two days. It was then filtered and concentrated and, pentane was added with heating. The solution was filtered again and left to cool to ca. —10°C. The resulting yellow solid of complex *trans*-[ReCl($CNC_6H_4CH_3$-2)(dppe)$_2$] was filtered off, washed with a mixture of THF/pentane and dried under vacuum. Further crops were obtained by addition of pentane to the mother liquour (0.20 g, 32% yield).

trans-Bis[1,2-bis(diphenylphosphino)ethane](chloro)(4-methoxyphenylisocyanide)rhenium(I), trans-[ReCl($CNC_6H_4OCH_3$*-4)(dppe)*$_2$*] (A, R =* $C_6H_4OCH_3$*-4).* $CNC_6H_4OCH_3$-4 (0.155 g, 1.16 mmol) was added to a suspension of *trans*-[ReCl(N_2)(dppe)$_2$] (0.212 g, 0.202 mmol) in THF (35 cm^3) and the mixture was refluxed under argon, irradiated by a 150 Watt tungsten filament bulb for a day, and then refluxed for 10 days. The infrared spectrum of the light brownish solution showed still a substantial amount of unchanged dinitrogen complex and free isocyanide, and so the irradiation was started again and maintained for three days. The solution was filtered and pentane was added until a brown solid separated. The solution was filtered again and pentane was added slowly until the appearance of the complex *trans*-[ReCl($CNC_6H_4OCH_3$-4)(dppe)$_2$] as a brownish yellow solid. This was filtered off, washed with pentane and dried under vacuum; a further crop was obtained from the mother liquour by concentration and addition of pentane (ca. 60 mg, 25% yield).

trans-Bis[1,2-bis(diphenylphosphino)ethane](chloro)(4-chlorophenyliso-

cyanide)rhenium(I), trans-[ReCl(CNC$_6$H$_4$Cl-4)(dppe)$_2$] (A, R = C$_6$H$_4$Cl-4). A suspension of *trans*-[ReCl(N$_2$)(dppe)$_2$] (0.30 g, 0.29 mmol) in THF (60 cm^3) with CNC$_6$H$_4$Cl-4 (0.25 g, 1.8 mmol) was refluxed under argon for three days. The solution was filtered and concentrated under vacuum and pentane was added with heating until a solid started to separate. The solution was filtered and cooling gave the complex *trans*-[ReCl(CNC$_6$H$_4$Cl-4)(dppe)$_2$] as a yellow crystalline solid, which was filtered off, washed with a mixture of THF/pentane, and dried under vacuum. A further crop was obtained from the mother liquour by concentration and addition of pentane (0.15 g, 44% yield).

trans-Bis[1,2-bis(diphenylphosphino)ethane](chloro)(2,6-dichlorophenylisocyanide)rhenium(I), trans-[ReCl(CNC$_6$H$_3$Cl$_2$-2,6)(dppe)$_2$] (A, R = C$_6$H$_3$Cl$_2$-2,6). A suspension of *trans*-[ReCl(N$_2$)(dppe)$_2$] (0.50 g, 0.48 mmol) in THF (100 cm^3) with CNC$_6$H$_3$Cl$_2$-2,6 (0.50 g, 2.9 mmol) was refluxed under argon for five days. The solution was then concentrated and pentane was added with heating until a yellow solid started to separate. This solid was filtered off (it was mainly the unchanged parent N$_2$ complex), and the complex *trans*-[ReCl(CNC$_6$H$_3$Cl$_2$-2,6)(dppe)$_2$] (mixed with some unreacted N$_2$ complex) precipitated from the solution as a yellow solid on cooling. It was filtered off, washed with a mixture of THF/pentane, and dried under vacuum. A further crop was obtained from the mother liquour by concentration and addition of pentane. The yellow solid was then recrystallized from THF/pentane to give *trans*-[ReCl(CNC$_6$H$_3$Cl$_2$-2,6)(dppe)$_2$] still slightly contaminated by the parent N$_2$ complex (0.060 g, ca. 10% yield).

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