Properties of Isocyanide Ligands in Metal Complexes. Characterisation and Voltammetric Properties of Bis(tertiary phosphine)Tris(isonitrile)Cobalt(I) Complexes

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The cobalt complexes $[Co(PPh_3)_2(CNR)_3][PF_6]$ (R = Me, Pr^i, Bu^t, *p*-MeC_6H_4, or *p*-ClC_6H_4), $[Co(PMePh_2)_2(CNR)_3][PF_6]$, $[Co(Ph_2PCH_2CH_2PPh_2)(CNR)_3][PF_6]$ (R = *p*-Me_6CH_4 or *p*-ClC_6H_4) and $[Co(Ph_2PCH_2CH_2PPh_2)(CNBu^t)_4][PF_6]_3$, have been prepared and characterised. The half-wave potential for the general reaction $[Co(PR'_3)_2(CNR)_3]^+ \rightleftharpoons [Co(PR'_3)_2(CNR)_3]^{2+} + e^-$ depended on the nature of R and R′. Chemical oxidation of the appropriate cobalt(I) complex afforded $[Co(PPh_3)_2(CNBu^t)_3][PF_6]_2$. Assuming that the σ-donor characteristics of RNC remain constant, it is shown that as a π-acceptor Bu^{t}NC is better than MeNC, and that aryl isocyanides are better than their alkyl analogues.

VOLTAMMETRY is one of the most effective methods of studying the redox behaviour of co-ordination and organometallic compounds, and it can afford information about the electronic behaviour of ligands in such compounds.[1] Voltammetric studies have already provided some insight into the behaviour of isocyanides in $[M(CO)_{6-n}(CNR)_n]^0$ (M = Cr, Mo, or W; $0 \leqslant n \leqslant 3$) [2] where the contribution of RNC to $(d \longrightarrow \pi^*)$ π-bonding was found to be negligible and that variations in the σ-donor strength of the isonitriles were principally responsible for changes in the oxidation potentials observed. For the general reaction however, the $E_{\frac{1}{2}}$-value was

$$[M(CO)_{6-n}(CNR)_n]^0 \rightleftharpoons [M(CO)_{6-n}(CNR)_n]^+ + e^-$$

insensitive to the nature of R when R = Me, Et, Pr^i, cyclohexyl, or Bu^t.

With a view to obtaining further information about the σ-donor/π-acceptor behaviour of co-ordinated RNC, we have investigated voltammetrically the oxidation of cobalt(I) isocyanide complexes. This system was chosen for its inherent stability and for the general accessibility of the Co^I/Co^{II} couple. However, chemical oxidation of the diamagnetic $[Co(CNR)_5]^+$ has afforded either the paramagnetic ($S = 1/2$), monomeric $[Co(CNR)_5]^{2+}$ (R = Ph) [3] or the diamagnetic, binuclear $[Co(CNR)_5]_2^{4+}$ (R = Me), which is isosteric with $Mn_2(CO)_{10}$.[4] Consequently, voltammetric studies of $[Co(CNR)_5]^+$ proved to be complicated [5] and, in an attempt to avoid systems which

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[1] J. A. McCleverty, ' Redox Reactions and Electron Transfer Chains of Inert Transition Metal Compelxes,' ch. 9 of ' Reactions of Molecules at Electrodes,' ed. N. S. Hush, Wiley–Interscience, London, 1971.

[2] J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd, and J. A. McCleverty, *J.C.S. Dalton*, 1972, 1246.

[3] L. Malatesta and A. Sacco, *Gazzetta*, 1953, **83**, 499; J. M. Pratt and P. R. Silverman, *J. Chem. Soc. (A)*, 1967, 1286.

[4] F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 1494; A. Sacco, *Gazzetta*, 1954, **84**, 370.

[5] M. E. Kimball and W. C. Kaska, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 10.

might dimerise on oxidation, we prepared a series of mixed tertiary phosphine–isocyanide complexes. Brief mention had been made of phosphine *p*-tolyl isocyanide complexes of cobalt(I),[6] and during the conclusion of an electrochemical work, the syntheses of $[Co(PPh_3)_2(CNBu^t)_3][PF_6]$ and $[Co(Ph_2PCH_2CH_2PPh_2)(CNBu^t)_3][PF_6]$ were reported.[7]

RESULTS

Synthetic Studies.—The complexes prepared were of the type $[Co(PPh_3)_2(CNR)_3][PF_6]$ (R = Me, Pr^i, Bu^t, *p*-MeC_6H_4, or *p*-ClC_6H_4), $[Co(PMePh_2)_2(CNR)_3][PF_6]$, $[Co(Ph_2PCH_2CH_2PPh_2)(CNR)_3][PF_6]$ (R = *p*-MeC_6H_4 or *p*-ClC_6H_4), and $[Co(Ph_2PCH_2CH_2PPh_2)(CNBu^t)_4][PF_6]_3$. They were obtained by addition of an excess of isocyanide to an ethanol solution containing $Co(PPh_3)_2Cl_2$, $Co(PMePh_2)_2Cl_2$, or $Co(Ph_2PCH_2CH_2PPh_2)Cl_2$. Reduction of Co^{II} to Co^{I} was achieved using an excess of RNC when R = alkyl, but hydrazine was also necessary when R = aryl. Attempts to obtain pure $[Co(Ph_2PCH_2CH_2PPh_2)(CNBu^t)_3]^+$ by this method proved impossible and, indeed, the major product of the reaction between $Co(Ph_2PCH_2CH_2PPh_2)Cl_2$, Bu^tNC, and an excess of N_2H_4 was the cobalt(III) complex, $[Co(Ph_2PCH_2CH_2PPh_2)(CNBu^t)_4][PF_6]_3$. However, $[Co(Ph_2PCH_2CH_2PPh_2)(CNBu^t)_3][PF_6]$ could be prepared [7] by reaction of the diphosphine with $[Co(CNBu^t)_5][PF_6]$. We were unable to isolate alkyl isocyanide complexes of cobalt(I) containing $PMePh_2$.

Oxidation of $[Co(PPh_3)_2(CNBu^t)_3][PF_6]$ with $AgPF_6$ in dichloromethane afforded $[Co(PPh_3)_2(CNBu^t)_3][PF_6]_2$. This complex, formally described as containing Co^{II}, was moderately stable in air in the solid, but reverted in solution, in the absence of an oxidising agent, to its Co^{I} precursor. This experiment established unequivocally that the cobalt(II) species could be obtained synthetically and that therefore they could probably be detected voltammetrically.

The complexes were obtained as yellow or orange crystals which were insoluble in, and did not react with ethanol or methanol, but dissolved in dichloromethane or chloroform. The compounds were satisfactorily characterised by elemental analyses and conductivity measurements (Table 1).

Spectral Studies.—The CN stretching frequencies of the co-ordinated isocyanides in the new complexes occurred in the range 2000—2300 cm^{-1} (Table 1). In solution, the species $[Co(PR_3)_2(CNR)_3]^+$ exhibited one weak and one strong absorption in this range which were assigned as the A_1' and E' modes, respectively, in D_{3h} symmetry (axial PR_3). Since only the E' mode should be i.r. active in idealised D_{3h} symmetry, the observation of the 'forbidden' A_1 mode could be due to interactions between the cation and anion, or to the axial phosphine ligands adopting a staggered configuration. Similar spectra have been obtained from the isoelectronic $FeL_2(CO)_3$ (L = Lewis base) and $[Co(PPh_3)_2(CO)_3]^+$, which have D_{3h} symmetry.[8] The complexes containing $Ph_2PCH_2CH_2PPh_2$ exhibited three CN stretching frequencies but definite conclusions about structure cannot be made; the species may have axial–equatorial or di-equatorial phosphorus donor atoms in a trigonal bipyramidal configuration, or the molecules may be square pyramidal.

Comparison of ν_{CN} (E'-mode) obtained from the cobalt complexes with that of the free isonitriles revealed a drop of 50—60 cm^{-1} on co-ordination, which suggests that RNC functions as a π-acceptor in these complexes. The value of ν(CN) in the compounds depended on the nature of the isocyanide and phosphine substituents: ν(CN) for the co-ordinated aryl isocyanides was lower than that for the co-ordinated alkyl ligands, implying that the former ligands are probably better π-acceptors than the latter. Complexes containing $PMePh_2$ exhibited lower CN stretching frequencies than those containing PPh_3, probably because PPh_3 is a better π-acceptor/poorer σ-donor than $PMePh_2$. A comparison of ν(CN) obtained from the various species $[Co(PPh_3)_2(CNR)_3]^+$ showed that the frequency increased in the order R = Pr^i, Bu^t, Me, suggesting that MeNC is a poorer π-acceptor than Bu^tNC.

The rather complicated spectrum obtained from $[Co(PMePh_2)_2\{CN(p\text{-}MeC_6H_4)\}_3][PF_6]$ suggested that more than one species was present in solution. This could arise by virtue of partial oxidation, giving the dication which would have higher ν(CN), or because of the presence of several isomers.

The ^1H n.m.r. spectra were obtained at room temperature and confirmed the stoicheiometries of the complexes (Table 3). The ^1H resonances of the isocyanide substituents in $[Co(PPh_3)_2(CNR)_3]^+$, R = Me or Bu^t, occurred as singlets consistent with D_{3h} symmetry, assuming that the compounds are stereochemically rigid. However, studies of the ^1H n.m.r. spectrum of $[Co(CNBu^t)_5]^+$ over a temperature range revealed that it was stereochemically non-rigid and this is probably a general property of these five-co-ordinate Co^{I} complexes. The Bu^t ^1H resonances in the spectrum of $[Co(Ph_2PCH_2CH_2PPh_2)(CNBu^t)_4]^{3+}$ also occurred as a singlet indicating either that the resonances of the Bu^tNC groups *cis*- and *trans*- to the diphosphine were degenerate, or that, more likely, the compound is fluxional. The methyl group resonances of $[Co(PMePh_2)_2\{CN(p\text{-}ClC_6H_4)\}_3]^+$ appeared as a 1 : 2 : 1 triplet because of 'virtual coupling' of the protons with ^{31}P.

The oxidised species $[Co(PPh_3)_2(CNBu^t)_3]^{2+}$ exhibited a broad e.s.r. signal ($g = 2{\cdot}12$) at 298 K in dichloromethane. This datum is similar to that obtained [3] from $[Co(CNPh)_5][ClO_4]$, confirming that the phosphine complex is monomeric and low-spin ($S = \frac{1}{2}$).

The mixed phosphine–alkyl isocyanide complexes exhibited two electronic transitions in the range 20 000—45 000 cm^{-1} (Table 2). By analogy with assignments made for $[Co(CNR)_5]^+$, which was assumed to have trigonal bipyramidal symmetry,[9] the lower band was designated as a *d–d* transition and the higher as a metal $\longrightarrow$ ligand ($d \longrightarrow \pi^*$) charge transfer. The observed decrease in energy of the metal $\longrightarrow$ ligand charge transfer band when alkyl isocyanides were replaced by their aryl analogues was consistent with the greater π-acceptor properties of the latter. An additional absorption detected in the spectra of the aryl isocyanide species is presumably associated [10] with intra-aromatic ring transitions.

Voltammetric Studies.—All the complexes $[Co(PPh_3)_2(CNR)_3]^+$, $[Co(PMePh_2)_2(CNR)_3]^+$, and $[Co(Ph_2PCH_2CH_2PPh_2)(CNR)_3]^+$ underwent a one-electron voltammetric

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[6] M. Rossi, personal communication referred to in 'Isocyanide Complexes of Metals,' L. Malatesta and F. Bonati, Wiley–Interscience, 1969, p. 185.

[7] R. B. King and M. S. Saran, *Inorg. Chem.*, 1972, **11**, 2112.

[8] F. A. Cotton and R. W. Parrish, *J. Chem. Soc.*, 1960, 1440; A. Vohler, *Chem. Ber.*, 1958, **91**, 1235.

[9] Y. Dartiguenave, M. Dartiguenave, and H. B. Gray, *Bull. Soc. chim. France*, 1969, 4227.

[10] J. A. Connor and E. M. Jones, *J. Chem. Soc. (A)*, 1971, 1974, 3368.

oxidation process in dichloromethane at a rotating platinum electrode. In most cases this wave was reversible, but in a few instances the electron transfer was accompanied by a coupled chemical reaction (cyclic voltammetry), the nature of which is unknown.

TABLE 1

Analytical, conductivity, melting point, and spectral data obtained from cobalt isocyanide complexes

Complex	Elemental analyses (%)								I.r.[b] ν(NC)	^{1}H N.m.r. data[c]				Electronic spectra[d]
	Found			Calc.										
	C	H	N	C	H	N	Λ[a]	M.p. (°C)						
$[Co(PPh_3)_2(CNMe)_3][PF_6]$	58·9	5·0	5·3	59·2	4·6	5·1	102	225	2110mbr 2210w	A	2·49 7·58	10 3	(m) $P(C_6\mathit{H}_5)_3$ (s) broad ($w\frac{1}{2}$ 6 Hz); $CNC\mathit{H}_3$	37 400 (4·17)[e] 44 000 (4·67)
$[Co(PPh_3)_2(CNPr^i)_3][PF_6]$	60·8	5·6	4·7	61·5	5·1	4·4	86	204	2034w 2090sbr	B	2·52 6·83 9·45	10 1 6	(m) $P(C_6\mathit{H}_5)_3$ (m) $CNC\mathit{H}Me_2$ (d) $CNCH(C\mathit{H}_3)_2$ (J 7 Hz)	36 580 (4·53) 43 190 (4·70)[f]
$[Co(PPh_3)_2(CNBu^t)_3][PF_6]$	62·5	5·7	4·3	62·5	5·8	4·3	84	196	2060w 2089sbr	A	2·38 9·24	10 9	(s) broad $P(C_6\mathit{H}_5)_3$ (s) $CNC(C\mathit{H}_3)_3$	36 800 (4·59) 43 050 (4·71)[f]
$[Co(PPh_3)_2\{CN(p\text{-}Cl\text{-}C_6H_4)\}_3][PF_6]$[g]	60·5	3·7	3·7	60·0	3·4	3·6	84	257	2068sbr 2120w	A	2·40 3·41	5 2	(m) $P(C_6\mathit{H}_5)_3$ (dd) A_2B_2 system (J(AB) 7 Hz); $p\text{-}ClC_6\mathit{H}_4NC$	27 680 (4·58) 35 050 (4·66) 42 210 (4·88)[f]
$[Co(PPh_3)_2\{CN(p\text{-}MeC_6H_4)\}_3][PF_6]$	66·5	5·2	2·7	66·7	4·7	2·9	82	206	2088s 2124m 2140w	A	2·41 3·57 7·81	10 4 3	(m) $P(C_6\mathit{H}_5)_3$ (dd) A_2B_2 system (J(AB) 8·2 Hz); $p\text{-}MeC_6\mathit{H}_4NC$ (s) $C\mathit{H}_3C_6H_4NC$	28 800 (4·51) 35 500 (4·55) 42 300 (4·86)[f]
$[Co(PMePh_2)_2\{CN(p\text{-}ClC_6H_4)\}_3][PF_6]$[h]	50·8	3·5	5·0	50·8	3·7	4·1	81	74	2055sbr 2005sh	A	2·40 3·06 7·70	10 6 3	(m) $PMe(C_6\mathit{H}_5)_2$ (dd) A_2B_2 system (J(AB) 8·5 Hz) $p\text{-}ClC_6\mathit{H}_4NC$ (asymm t) [$\lvert J(PH)\rvert$ 3·8 Hz] $PC\mathit{H}_3Ph_2$	27 950 (4·39) 36 500 (4·71) 42 900 (4·75)[f]
$[Co(PMePh_2)_2\{CN(p\text{-}MeC_6H_4)\}_3][PF_6]$	62·7	5·0	4·6	62·9	4·9	4·4	79	78 (dec.)	2168w 2150w 2112mbr 2087sbr 2060sh 2036w	B	2·75 7·70	32 15	(m) broad, ($w\frac{1}{2}$ 50 Hz); overlapping signals due to aromatic protons (m) broad; overlapping signals due to Me protons	30 100 (4·38) 38 500 (4·75) 43 000 (4·80)
$[Co(Ph_2PCH_2CH_2PPh_2)\text{-}\{CN(p\text{-}ClC_6H_4)\}_3][PF_6]$[i]	55·8	3·9	4·1	55·6	3·6	4·1	82	100 (dec.)	2140mbr 2088sbr 2068sbr 2020sh	B	2·57 3·04 7·25	5 3 1	(m) $\{(C_5\mathit{H}_5)_2PCH_2\}_2$ (dd) A_2B_2 system (J(AB) 8·0 Hz); $p\text{-}ClC_6\mathit{H}_4NC$ (m) broad ($w\frac{1}{2}$ 32 Hz); $\{Ph_2PC\mathit{H}_2\}_2$	28 300 (4·29) 37 800(2·77sh) 43 500 (4·83)
$[Co(Ph_2PCH_2CH_2PPh_2)\text{-}\{CN(p\text{-}MeC_6H_4)\}_3][PF_6]$	62·8	5·1	4·3	62·9	4·7	4·4	84	109	2143m 2078sbr 2095sh 2039w	B	2·58 3·18 7·28 7·72	20 12 4 9	(m) $\{(C_6\mathit{H}_5)_2PCH_2\}_2$ (dd) A_2B_2 system [J(AB) 8·0 Hz] $p\text{-}MeC_6\mathit{H}_4NC$ (m) $\{Ph_2PC\mathit{H}_2\}_2$ (s) $C\mathit{H}_3C_6H_4NC$	29 300 (4·33) 38 200 (4·14sh) 43 800 (4·84)
$[Co(PPh_3)_2(CNBu^t)_3][PF_6]_2$	54·6	4·8	3·6	54·5	5·1	3·7	172		2150w 2184sbr					21 410 (3·75) 28 000 (3·96) 30 050 (3·99) 36 800 (4·14)
$[Co(Ph_2PCH_2CH_2PPh_2)(CNBu^t)_4][PF_6]_3$	45·5	5·1	4·6	45·1	4·9	4·6	261	170—175	2230s 2200sh					

[a] In 10^{-3}M-MeNO$_2$ solution, in Ω^{-1} cm^{-2} mol^{-1}; for a 1 : 1, 1 : 2, and 1 : 3 electrolyte, Λ = 80—100, 150—200, and *ca.* 260, respectively. [b] In cm^{-1}, for solutions in CH$_2$Cl$_2$. [c] Quoted as solvent, τ-value, relative area, multiplicity, and assignment; solvent A, $(CD_3)_2SO$; B, $CDCl_3$. [d] In cm^{-1}, log ϵ in parentheses, for solutions in methanol unless otherwise stated. [e] In CH$_2$Cl$_2$ solution: 36 700 (4·38). [f] In CH$_2$Cl$_2$ solution. [g] Cl Analysis: found 9·3, calc. 9·3%. [h] Cl Analysis: found 10·5, calc. 10·5%. [i] Cl Analysis found 10·6, calc. 10·5%.

TABLE 2

Voltammetric data obtained from cobalt isocyanide complexes

Complex	Voltammetry			Cyclic voltammetry[d]		Comments[e]
	$E_{\frac{1}{2}}$[a]	R[b]	D[c]	E_{pa}	E_{pc}	
$[Co(PPh_3)_2(CNMe)_3]^+$	+0·12	61	5·2	0·240	0·015	R
$[Co(PPh_3)_2(CNPr^i)_3]^+$	+0·20	69	6·5	0·265	0·070	R
$[Co(PPh_3)_2(CNBu^t)_3]^+$	+0·29	80	7·0	0·410	0·210	R
$[Co(PPh_3)_2\{CN(p\text{-}MeC_6H_4)\}_3]^+$	+0·47	65	4·7	0·590	*f*	CCR
$[Co(PPh_3)_2\{CN(p\text{-}ClC_6H_4)\}_3]^+$	+0·54	58	4·3	0·650	0·440	R
$[Co(PMePh_2)_2\{CN(p\text{-}MeC_6H_4)\}_3]^+$	+0·39	61	5·2	0·160	*f*	CCR
$[Co(PMePh_2)_2\{CN(p\text{-}ClC_6H_4)\}_3]^+$	+0·49	80	4·6	0·600	0·400	R
$[Co(Ph_2PCH_2CH_2PPh_2)\{CN(p\text{-}MeC_6H_4)\}_3]^+$	+0·24	60	5·6	0·335	0·150	R
$[Co(Ph_2PCH_2CH_2PPh_2)\{CN(p\text{-}ClC_6H_4)\}_3]^+$	+0·29	56	4·8	0·370	0·215	R

[a] In V *vs* S.C.E. using rotating Pt electrode. [b] Reversibility criterion, $E_{\frac{3}{4}} - E_{\frac{1}{4}}$; for reversible process R = 56 mV for one-electron wave. [c] i_d/c, in μA/mmol^{-1}; for couple $[Ni\{S_2C_2(CN)_2\}_2]^{-1,-2}$, D = 4·9—5·3. [d] Anodic and cathodic peaks in mV, for reversible couple $[Ni\{S_2C_2(CN)_2\}_2]^{-1,-2}$, peak separation = 200 mV. [e] R = reversible; CCR = coupled chemical reactions.

The half-wave potential for the general process is dependent on the nature of the phosphine and the isocyanide

$$[Co(PR'_3)_2(CNR)_3]^+ \rightleftharpoons [Co(PR'_3)_2(CNR)_3]^{2+} + e^-$$

substituent, R. Thus, there was a significant decrease in $E_{\frac{1}{2}}$ when PPh$_3$ was replaced by PMe$_2$Ph, indicating that oxidation of the Co^I complex became easier when the axial ligands became more basic (or less good π-acceptors). The compounds containing Ph$_2$PCH$_2$CH$_2$PPh$_2$ had $E_{\frac{1}{2}}$-values lower than that of their PMe$_2$Ph analogues. We might reasonably have expected the effective basicity (or π-acceptor ability) of the diphosphine to be similar to that of two PMe$_2$Ph ligands, such that the oxidation potentials in the two complexes would be similar. However, the observed differences could be attributed to geometrical differences between the diphosphine and the bis-phosphine complexes. Such structural differences may, of course, be sufficient to modify the nature of the redox orbital in the former with respect to the latter.

The half-wave potentials obtained from the aryl isocyanide complexes were more anodic than those obtained from their alkyl analogues.[*] This is consistent with the greater stabilisation of the Co^I species by a better π-acceptor ligand. Within the aryl isocyanide series, $E_{\frac{1}{2}}(p\text{-}ClC_6H_4) > E_{\frac{1}{2}}(p\text{-}MeC_6H_4)$, which may readily be understood in terms of the inductive and/or mesomeric effects of the *para*-substituents on the acceptor properties of the aryl group.

In contrast to our previous studies [2] of substituent effects on the redox behaviour of alkyl isocyanide complexes we found that there is a significant variation of $E_{\frac{1}{2}}$ in relation to the alkyl group. Thus, $E_{\frac{1}{2}}$ increased, and the stability of the Co^I species also increases, in the order $R = Me < Pr^i < Bu^t$. Initially, this result was surprising, since we expected the reverse order, which would reflect the increase in basicity of RNC in going from MeNC to Bu^tNC. Previous studies in dithiolene chemistry [1] had led us to expect a direct correlation between $E_{\frac{1}{2}}$ and basicity of a Lewis base ligand. However, the inverse order here is similar to that found in our studies of $[Cr(NO)(CNR)_5]^+$.[11]

The $E_{\frac{1}{2}}$-values for the oxidation of the cobalt(I) alkyl isocyanide complexes were such that formation of $[Co^I(PR'_3)_2(CNR)_3]^{2+}$ should be accomplished easily using Ag^+, and this was confirmed.

DISCUSSION

Correlations have been made between $E_{\frac{1}{2}}$ (oxidation) and electronic spectral (metal $\longrightarrow$ ligand) charge transfer transitions in the system $[Fe(o\text{-}phen)_2(CNBX_3)_2]$ (X = Me, H, F, Cl, or Br).[12] Unless there are unusual variations in the free energies of solvation, the oxidation potentials should provide a measure of the energy of the highest occupied molecular orbital (HOMO) in the complex, assuming that it is also the redox orbital.[†] Within the series $[Co(PPh_3)_2(CNR)_3]^+$, R = Me, Pr^i, Bu^t, $p\text{-}MeC_6H_4$, or $p\text{-}ClC_6H_4$, a linear relationship exists between $E_{\frac{1}{2}}$ and the frequency of the (Co $\longrightarrow$ CNR) charge transfer transitions.

These data, together with the i.r. spectral results, indicate that it is harder to oxidise aryl isocyanide complexes than their alkyl analogues, and, also, that it is harder to oxidise species containing Bu^tNC than those containing MeNC. The first comment may reasonably be justified in terms of the superior π-acceptor properties of aryl isocyanides: aryl substituents are more effective electron withdrawing (π) substituents than alkyl groups and this would lead to a stabilisation of the redox orbital and therefore cause an increase in the $E_{\frac{1}{2}}$-values of the aryl isocyanide species relative to those of their alkyl analogues. While we might expect to interpret the effect of alkyl substituents on the $E_{\frac{1}{2}}$-values in terms of inductive (σ-donor) effects, implying that Bu^tNC should be a better σ-donor (lower $E_{\frac{1}{2}}$) than MeNC, we found that this was not consistent with the experimental facts. However, it has been suggested [14] that, in the Pt^{II} complexes, $[PtL_2(CNR)Me]^+$ (L = $PMePh_2$ or PMe_2Ph), the σ-donor strength of CNR is essentially independent of the inductive properties of R. If this is also true in our cobalt complexes, then the relative energy of the redox orbital, and hence $E_{\frac{1}{2}}$, also must depend on the π-acceptor properties of CNR (R = alkyl).

The control exerted by the basicity and/or π-acceptor abilities of the axial phosphine ligands can be rationalised either in terms of a general increase in the energies of all molecular orbitals in $[Co(PR'_3)_2(CNR)_3]^+$ occasioned by an increase in the basicity of PR'_3, or by destabilisation of the redox orbital brought about by a decrease in the π-acceptor ability of the phosphine ligand, when PPh_3 is replaced by $PMePh_2$.

It is tempting to accept these conclusions, particularly when they are generally consistent with data obtained from $[Cr(NO)(CNR)_5]$.[11] We recognise, however, that they rest on two major assumptions: (a) that the σ-donor properties of CNR do not vary significantly with R, and (b) that some purely physical phenomenon (*e.g.* an insulation effect caused by the Bu^t group, which is sterically more protective than the Me group, which might make diffusion of an electron away from the Bu^tNC complexes in the electron transfer process energetically more difficult than that in the MeNC-containing species) does not invert the 'normal' order of potential values. We can only observe that the $E_{\frac{1}{2}}$ data have inverse linear relationships with ν(NC) [‡] and with the frequency of the first observed charge-transfer transition in the electronic spectra of the complexes, and that these last two properties are unlikely to be influenced by diffusion effects. Molecular models show that there is no serious steric hindrance in $[Co(PPh_3)_2(CNBu^t)_3]^+$.

EXPERIMENTAL

Elemental analyses were obtained by the Microanalytical Laboratory of this Department. Conductivity measurements were made with a Phillips conductivity meter. I.r. and electronic spectra were obtained using Infracord 457, Perkin-Elmer 180, and Unicam SP 700 spectrophotometers. ^1H N.m.r. and e.s.r. spectra were measured using Varian HA 100 and E3 spectrometers, respectively.

Voltammetric data were obtained using a Beckman Electroscan 30 polarograph. The solvent was dichloromethane (complex 10^{-3}M) and the base electrolyte was $[Et_4N][ClO_4]$ (0·05M). Results are quoted relative to the SCE (1M in LiCl), and are corrected, where appropriate, for *iR* drop; the estimated error in data is ±10 mV. Voltammograms were recorded (at 20 ± 2 °C). Using a rotating Pt electrode (620 rev. min^{-1}) and cyclic voltammograms were obtained with a stationary Pt electrode (sweep scans 0·05 V s^{-1}).

Bis(triphenylphosphine)tris(methyl isocyanide)cobalt Hexafluorophosphate.—To the orange solution obtained by dis-

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[*] *Note added in proof:* Similar, but more limited data have been obtained from manganese(I) isocyanides.

[†] Studies of the properties of $Cr(CO)_5L$ suggest that this is not necessarily so (ref. 13).

[‡] ν(NC) for the complexes $[Co(PPh_3)_2(CNR)_3]^+$ increases in the order $R = Bu^t < Pr^i < Me$.

[11] M. K. Lloyd and J. A. McCleverty, *J. Organometallic Chem.*, in the press.

[12] D. F. Shriver and J. Posner, *J. Amer. Chem. Soc.*, 1966, **88**, 1672.

[13] M. K. Lloyd, J. A. McCleverty, D. G. Orchard, J. A. Connor, M. B. Hall, I. H. Hillier, E. M. Jones, and G. K. McEwen, preceding paper.

[14] H. C. Clark, W. J. Cherwinski, and L. E. Manzer, *Inorg. Chem.*, 1972, **11**, 1511.

solving $Co(PPh_3)_2Cl_2$ (0·5 g) in $MeOH–CH_2Cl_2$ (20 ml; 1 : 1 v/v) in the presence of MeNC (1·0 g) was added NH_4PF_6 (0·15 g). A brick-red powder precipitated, was filtered off, washed with ethanol and ether, and dried *in vacuo*. Ethanol was added to the orange filtrate and the solvent was removed slowly *in vacuo* affording orange plates which were filtered off, washed with ethanol, and dried *in vacuo*. The brick red powder was $[Co(CNMe)_5]_2[PF_6]_4$ (0·19 g, 22%) and the orange plates $[Co(PPh_3)_2(CNMe)_3][PF_6]$ (0·4 g, 61%).

Bis(triphenylphosphine)tris(isopropyl isocyanide)cobalt Hexafluorophosphate.—$Co(PPh_3)_2Cl_2$ (0·2 g) was dissolved in $MeOH–CH_2Cl_2$ (20 ml, 1 : 1 v/v) and treated with hydrazine hydrate (2 drops) and Me_2CHNC (0·06 g). To the resulting orange solution was added NH_4PF_6 (0·2 g), the mixture was cooled and the light-yellow crystalline material which precipitated was filtered off, and washed with water, ethanol, and ether. The *complex* was recrystallised from dichloromethane–ethanol (yield 0·24 g, 82%).

The complexes $[Co(PPh_3)_2(CNBu^t)_3][PF_6]$ (0·95 g, 64%), $[Co(PPh_3)_2\{CN(p\text{-}ClC_6H_4)\}_3][PF_6]$ (0·2 g, 55%), $[Co(PPh_3)_2\{CN(p\text{-}MeC_6H_4)\}_3][PF_6]$ [0·6 g, 73%), $[Co(PMePh_2)_2\{CN(p\text{-}ClC_6H_4)_3\{][PF_6]$ [0·51 g, 64% based on 0·5 g $Co(PMePh_2)_2Cl_2]$, $[Co(PMePh_2)_2\{CN(p\text{-}MeC_6H_4)\}_3][PF_6]$ (0·55 g, 62%), $[Co(Ph_2PCH_2CH_2PPh_2)\{CN(p\text{-}ClC_6H_4)\}_3][PF_6]$ [0·51 g, 59% based on 0·5 g $Co(Ph_2PCH_2CH_2PPh_2)Cl_2]$, $[Co(Ph_2PCH_2CH_2PPh_2)\{CN(p\text{-}MeC_6H_4)\}_3][PF_6]$ (0·6 g, 79%), and $[Co(Ph_2PCH_2CH_2PPh_2)(CNBu^t)_4][PF_6]_3$ [0·23 g, 69% based on 0·19 g $Co(Ph_2PCH_2CH_2PPh_2)Cl_2]$ were obtained in the same way as $[Co(PPh_3)_2(CNPr^i)_3][PF_6]$.

Bis(triphenylphosphine)tris(t-butyl isocyanide)cobalt Bis(hexafluorophosphate).—To a dichloromethane solution (15 ml) of $[Co(PPh_3)_2(CNBu^t)_3][PF_6]$ (0·3 g) was added $AgPF_6$ (0·08 g, 1 : 1 mole ratio) and the mixture was stirred for several minutes at room temperature. The mixture was then filtered, and n-hexane (*ca.* 20 ml) was added to the filtrate which was then evaporated to low volume (water pump) and cooled. The microcrystalline precipitate which formed was filtered off and dried in air giving the *complex* (0·25 g, 74%).

We are grateful to the S.R.C. for studentships (J. W. D. and M. K. L.) and to Mrs. J. Bray and Mr. G. A. Wright for technical assistance. We thank Drs. D. W. Smith and R. W. Jotham for useful and stimulating discussions.

[2/2843 *Received, 18th December*, 1972]