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Cyclic Voltammetric Studies of Arylisocyanidecobalt(I) Complexes with Tertiary Phosphine Ligands

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50 Arylisocyanide-Co(I) complexes with tertiary phosphine ligands, both monosubstituted $[Co(CNR)_4PR'_3]X$ and disubstituted $[Co(CNR)_3(PR'_3)_2]X$, $X = ClO_4$, BF_4, have been investigated by cyclic voltammetry in acetonitrile solution. Behaviour ranges from reversible to irreversible. Several distinct trends emerge. The E_{ox} values systematically increase as substituents in the arylisocyanide ligand progress from electron-donating to electron-withdrawing. Sometimes this trend is reversed, possibly attributable to steric hindrance. The E_{ox} values also systematically increase as the tertiary phosphine ligand becomes weaker σ-donating/stronger π*-accepting due to substituents. Trialkylphosphines show weaker π-acidity than triarylphosphines, except with electron-withdrawing substituents, like $P(CH_2Ph)_3$ and $P(CH_2CH_2CN)_3$. Cobalt(I) complexes of 4:1 arylisocyanide: tertiary phosphine ligand composition tend to have substantially higher E_{ox} values than 3:2 complexes with identical arylisocyanide and tertiary phosphine ligands.

Key Words: Cyclic voltammetry, Arylisocyanides, Cobalt(I), Triarylphosphines, Trialkylphosphines.

INTRODUCTION

Cyclic voltammetric studies of a number of alkylisocyanide-Co(I) complexes disubstituted with tertiary phosphine ligands, $[Co(CNR)_3(PR'_3)_2]ClO_4$, $R = CMe_3$, $CHMe_2$, C_6H_{11}, CH_2Ph, C_4H_9-n, with PR'_3 being a selection of triarylphosphines and trialkylphosphines, were reported in acetonitrile solution[1]. Complexes of the triarylphosphine ligands PPh_3, $P(C_6H_4Me\text{-}p)_3$ and $P(C_6H_4OMe\text{-}p)_3$ tended to show reversible oxidation[1,2] and their corresponding Co(II) complexes, $[Co(CNR)_3(PR'_3)_2]X_2$, $X = ClO_4$, BF_4, have been subsequently synthesized[3,4]. These Co(II) complexes also exhibiting reversible cyclic voltammograms, under initial reduction[2,4]. Voltammetric studies have also been reported for alkylisocyanide-Co(I) complexes $[Co(CNR)_3(PR'_3)_2]PF_6$, $R = Me$, $CHMe_2$, CMe_3; $PR'_3 = PPh_3$, $PMePh_2$, $PPh_2CH_2CH_2PPh_2$; in dichloromethane solution[5].

Less extensive data for cyclic voltammetric studies of arylisocyanide-Co(I) complexes with tertiary phosphine ligands seems to be available. Measurements for $[Co(CNR)_3(PR'_3)_2]PF_6$, R = C_6H_4Me-*p*, C_6H_4Cl-*p*, $PR'_3 = PPh_3$, $PMePh_2$ and for $[Co(CNR)_3Ph_2PCH_2CH_2PPh_2]PF_6$, R = C_6H_4Me-*p*, C_6H_4Cl-*p*; are reported in dichloromethane solution[5]. Measurements in CH_2Cl_2 have also been reported for monometallic complexes $[Co(CNR)_4L\text{-}L]ClO_4$ and bimetallic complexes $[\{Co(CNR)_4\}_2(\mu\text{-}L\text{-}L)](ClO_4)_2$, R = $C_6H_3Et_2$-2,6, $C_6H_3iPr_2$-2,6, with a variety of potentially chelating and non-chelating tertiary diphosphine ligands L-L[6] and for chelated monometallic complexes $[Co(CNC_6H_3iPr_2\text{-}2,6)_3L\text{-}L]BF_4$, L-L = (*p*-$MeC_6H_4)_2PCH_2CH_2P$ $(C_6H_4Me$-*p*$)_2$, $PPh_2CH{=}CHPPh_2$-*cis*, $PPh_2C_5H_4PPh_2$-*o*, (*p*-$CF_3C_6H_4)_2PCH_2CH_2P(C_6H_2CF_3$-*p*$)_2$[7]. Cyclic voltammetric data have also been reported for some arylisocyanide-Co(I) complexes with trialkylphosphite ligands in dichloromethane solution[8].

In view of the substantial number of currently available arylisocyanide-Co(I) complexes, both mono- and disubstituted, with tertiary phosphine ligands and the possibility of reversible oxidative behaviour of at least some of these complexes, a systematic study of the oxidation by cyclic voltammetry seems merited. Such a study should provide bonding information about these complexes and give insight into the viability of synthesis of the corresponding Co(II) complexes.

EXPERIMENTAL

For cyclic voltammetry, 1 mM solutions of the compounds were freshly prepared in chromatrographic-grade acetonitrile containing 0.05 M tetramethylammonium hexaflurophosphate (TMAH) as the supporting electrolyte. Cyclic voltammetry measurements were performed using a Metrohm 757 VA Computerace system with a three-electrode compartment cell. The working and auxiliary electrodes were both made of glassy carbon. The reference electrode was a double junction Ag/AgCl system. The voltammograms were recorded in the potential range -0.5 to +1.0 V *vs.* Ag-AgCl, at a scan rate of 0.1 V s^{-1}. Nitrogen gas was bubbled through each solution for 500 s prior to the run. IR spectra, used to confirm literature data, were recorded on a Perkin Elmer 2000 FT-IR spectrophotometer.

Arylisocyanide ligands were synthesized from the commercially available anilines, which were first converted to the N-formamide by standard procedure[9], using Becker's modification[10] of a synthesis by Hertler and Corey[11] or the method of Appel *et al.*[12]. $CNC_6H_3Me_2$-2,6 was available from Fluka. All of the tertiary phosphine ligands were commercially available and could be used without further purification. The various Co(I) complexes were all prepared by known procedures[13-17] and routinely re-crystallized from CH_2Cl_2/diethyl ether.

RESULTS AND DISCUSSION

Cyclic voltammetry data for 50 arylisocyanide-Co(I) complexes containing tertiary phosphine ligands are summarized in Tables 1 and 2. Complexes with triarylphosphines are listed in Table-1, complexes with other tertiary phosphines, primarily trialkylphosphines, are listed in Table-2. In both the tables the disubstituted complexes have been listed before the monosubstituted complexes.

TABLE-1
CYCLIC VOLTAMMETRIC DATA FOR Co(I)-ARYLISOCYANIDE COMPLEXES WITH TRIARYLPHOSPHINE LIGANDS

	Compound	E_{ox}	E_{red}	$E_{1/2}$	ΔE
1	$[\mathrm{Co(CNC_6H_4Me}\text{-}p)_3(\mathrm{PPh_3})_2]\mathrm{ClO_4}$	547	452	500	95
2	$[\mathrm{Co(CNC_6H_3Me_2}\text{-}2,6)_3(\mathrm{PPh_3})_2]\mathrm{ClO_4}$	553	466	510	87
3	$[\mathrm{Co(CNC_6H_2Me_3}\text{-}2,4,6)_3(\mathrm{PPh_3})_2]\mathrm{ClO_4}$	577	315	446	262
4	$[\mathrm{Co(CNC_6H_3Et_2}\text{-}2,6)_3(\mathrm{PPh_3})_2]\mathrm{ClO_4}$	613	428	521	185
5	$[\mathrm{Co(CNC_6H_4Cl}\text{-}p)_3(\mathrm{PPh_3})_2]\mathrm{ClO_4}$	643	476	560	167
6	$[\mathrm{Co(CNC_6H_4I}\text{-}p)_3(\mathrm{PPh_3})_2]\mathrm{ClO_4}$	643	494	569	149
7	$[\mathrm{Co(CNC_6H_4Br}\text{-}p)_3(\mathrm{PPh_3})_2]\mathrm{ClO_4}$	666	524	595	142
8	$[\mathrm{Co(CNC_6H_2Me_3}\text{-}2,4,6)_3\{\mathrm{P(C_6H_4OMe}\text{-}p)_3\}_2\}\mathrm{ClO_4}$	416	315	366	101
9	$[\mathrm{Co(CNC_6H_2Me_3}\text{-}2,4,6)_3\{\mathrm{P(C_6H_4Me}\text{-}p)_3\}_2\}\mathrm{ClO_4}$	458	339	399	119
10	$[\mathrm{Co(CNC_6H_3Me_2}\text{-}2,6)_3\{\mathrm{P(C_6H_4OMe}\text{-}p)_3\}_2]\mathrm{ClO_4}$	470	357	414	113
11	$[\mathrm{Co(CNC_6H_3Me_2}\text{-}2,6)_3\{\mathrm{P(C_6H_4Me}\text{-}p)_3\}_2]\mathrm{BF_4}$	488	410	449	78
12	$[\mathrm{Co(CNPh)_3}\{\mathrm{P(C_6H_4OMe}\text{-}p)_3\}_2]\mathrm{BF_4}$	488	375	432	113
13	$[\mathrm{Co(CNC_6H_4Cl}\text{-}p)_3\{\mathrm{P(C_6H_4OMe}\text{-}p)_3\}_2]\mathrm{BF_4}$	559	464	512	95
14	$[\mathrm{Co(CNC_6H_3Et_2}\text{-}2,6)_4\mathrm{P(C_6H_4Me}\text{-}p)_3]\mathrm{ClO_4}$	541	410	476	131
15	$[\mathrm{Co(CNC_6H_3Et_2}\text{-}2,6)_4\mathrm{P(C_6H_4OMe}\text{-}p)_3]\mathrm{ClO_4}$	553	398	476	155
16	$[\mathrm{Co(CNC_6H_3Me_2}\text{-}2,6)_4\mathrm{PPh_3}]\mathrm{ClO_4}$	619	470	545	149
17	$[\mathrm{Co(CNC_6H_3}i\mathrm{Pr_2}\text{-}2,6)_4\mathrm{PPh_3}]\mathrm{ClO_4}$	648	–	–	–
18	$[\mathrm{Co(CNC_6H_3Et_2}\text{-}2,6)_4\mathrm{PPh_3}]\mathrm{ClO_4}$	690	–	–	–
19	$[\mathrm{Co(CNC_6H_3}i\mathrm{Pr_2}\text{-}2,6)_4\mathrm{P(C_6H_4OMe}\text{-}p)_3]\mathrm{ClO_4}$	696	–	–	–
20	$[\mathrm{Co(CNC_6H_3Me_2}\text{-}2,6)_3\{\mathrm{P(C_6H_4Cl}\text{-}p)_3\}_2]\mathrm{BF_4}$	797	–	–	–
21	$[\mathrm{Co(CNC_6H_3Et_2}\text{-}2,6)_3\{\mathrm{P(C_6H_4Cl}\text{-}p)_3\}_2]\mathrm{ClO_4}$	922	–	–	–
22	$[\mathrm{Co(CNC_6H_4Me}\text{-}p)_3\{\mathrm{P(C_6H_4Cl}\text{-}p)_3\}_2]\mathrm{ClO_4}$	988	–	–	–
23	$[\mathrm{Co(CNC_6H_3Et_2}\text{-}2,6)_4\mathrm{P(C_6H_4Cl}\text{-}p)_3]\mathrm{ClO_4}$	637	–	–	–
24	$[\mathrm{Co(CNC_6H_3Et_2}\text{-}2,6)_4\mathrm{P(C_6H_4F}\text{-}p)_3]\mathrm{ClO_4}$	696	–	–	–
25	$[\mathrm{Co(CNC_6H_3Et_2}\text{-}2,6)_4\mathrm{P(C_6H_4CF_3}\text{-}p)_3]\mathrm{ClO_4}$	994	–	–	–

Behaviour of the cyclic voltammograms: Behaviour of the cyclic voltammograms ranges from reversible to clearly irreversible, as for complexes **17-25** (Table-1) and **48-50** (Table-2). Using the non-variance of peak

TABLE-2
CYCLIC VOLTAMMETRIC DATA FOR Co(I)-ARYLISOCYANIDE COMPLEXES WITH TRIALKYLPHOSPHINE AND OTHER TERTIARY PHOSPHINE LIGANDS

	Compound	E_{ox}	E_{red}	$E_{1/2}$	ΔE
26	$[Co(CNC_6H_2Me_3\text{-}2,4,6)_3\{P(NMe_2)_2\}_2]BF_4$	286	214	250	72
27	$[Co(CNC_6H_3Me_2\text{-}2,6)_3\{P(NMe_2)_3\}_2]BF_4$	345	256	301	89
28	$[Co(CNC_6H_2Me_3\text{-}2,4,6)_3\{P(C_3H_7\text{-}n)_3\}_2]ClO_4$	396	280	338	116
29	$[Co(CNC_6H_3Me_2\text{-}2,6)_4P(NMe_2)_3]BF_4$	399	327	363	72
30	$[Co(CNC_6H_3Et_2\text{-}2,6)_3\{P(C_6H_{13}\text{-}n)_3\}_2]ClO_4$	410	297	354	113
31	$[Co(CNC_6H_3Et_2\text{-}2,6)_3\{P(C_3H_7\text{-}n)_3\}_2]ClO_4$	440	274	357	166
32	$[Co(CNC_6H_3Et_2\text{-}2,6)_4P(NMe_2)_3]BF_4$	452	381	417	71
33	$[Co(CNC_6H_3iPr_2\text{-}2,6)_3\{P(C_3H_7\text{-}n)_3\}_2]ClO_4$	470	363	417	107
34	$[Co(CNC_6H_3iPr_2\text{-}2,6)_3\{P(C_4H_9\text{-}n)_3\}_2]ClO_4$	518	268	393	250
35	$[Co(CNC_6H_2Me_3\text{-}2,4,6)_4P(NMe_2)_3]ClO_4$	375	286	331	89
36	$[Co(CNC_6H_2Me_3\text{-}2,4,6)_4P(C_6H_{11})_3]ClO_4$	416	333	375	83
37	$[Co(CNC_6H_3Me_2\text{-}2,6)_4P(C_4H_9\text{-}n)_3]BF_4$	428	321	375	107
38	$[Co(CNC_6H_3Me_2\text{-}2,6)_4P(C_6H_{11})_3]BF_4$	440	351	396	89
39	$[Co(CNC_6H_3Et_2\text{-}2,6)_4P(NEt_2)_3]ClO_4$	464	375	420	89
40	$[Co(CNC_6H_3Et_2\text{-}2,6)_4P(C_4H_9\text{-}n)_3]ClO_4$	482	339	411	143
41	$[Co(CNC_6H_3iPr_2)_4P(C_6H_{11})_3]ClO_4$	500	405	453	95
42	$[Co(CNC_6H_3iPr_2\text{-}2,6)_4P(C_3H_7\text{-}n)_3]ClO_4$	518	387	453	131
43	$[Co(CNC_6H_3Et_2\text{-}2,6)_4P(C_6H_{11})_3]ClO_4$	518	393	456	125
44	$[Co(CNC_6H_3Et_2\text{-}2,6)_4P(C_3H_7\text{-}n)_3]BF_4$	530	268	399	262
45	$[Co(CNC_6H_3Me_2\text{-}2,6)_4P(CH_2Ph)_3]ClO_4$	547	440	494	107
46	$[Co(CNC_6H_3Et_2\text{-}2,6)_4P(CH_2Ph)_3]ClO_4$	571	452	512	119
47	$[Co(CNC_6H_3Et_2\text{-}2,6)_4(2\text{-}Ph_2PC_5H_4N)]ClO_4$	619	309	464	310
48	$[Co(CNC_6H_3Et_2\text{-}2,6)_4P(CH_2CH_2CN)_3]ClO_4$	684	–	–	–
49	$[Co(CNPh)_3\{P(CH_2CH_2CN)_3\}_2]ClO_4$	732	–	–	–
50	$[Co(CNC_6H_4Me\text{-}2)_3\{P(CH_2CH_2CN)_3\}_2]ClO_4$	815	–	–	–

potentials with change in the scan rate as the criterion for reversibility[18-20], many of these cycles are reversible. The non-aqueous nature of the solvent and the relatively low concentration of the background electrolyte cause the solutions to have high solution resistance between the working and reference electrodes. This ohmic (iR) drop[19], combined with the higher junction potential created across the ion bridge between the reference electrode and sample solution[2,21], contribute to the apparent non-conformity of non-aqueous systems to the criterion for reversibility in aqueous systems, ΔE < 57 mV.

A characteristic set of cyclic voltammograms for $[Co(CNC_6H_3Me_2\text{-}2,6)_3\{P(C_6H_4Me\text{-}p)_3\}_2]BF_4$ at various scan rates is pictured in Fig. 1. The peak potentials are seen to be essentially non-variant with change in scan rate. This behaviour is analogous to that observed with the *tris*(alkylisocyanide)*bis*(triarylphosphine)cobalt(I) complexes[2]. In identifying trends attention has been focused primarily on the E_{ox} values measured.

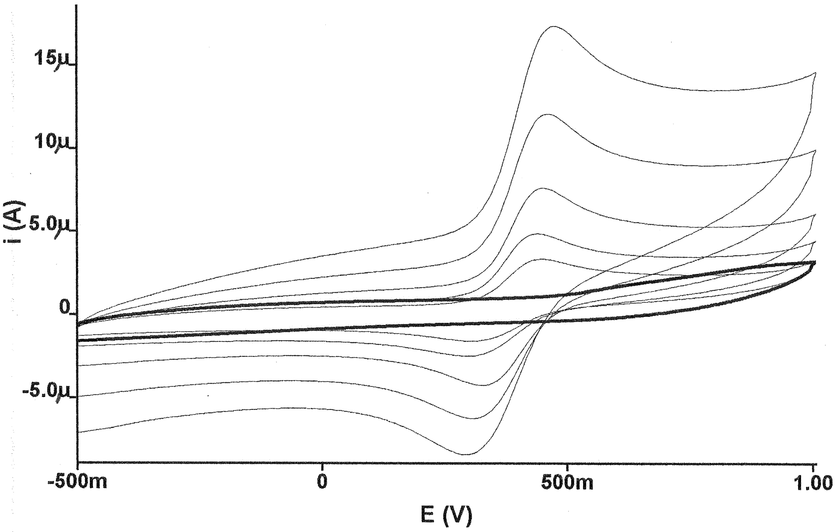

Fig. 1. Cyclic voltammograms of $[Co(CNC_6H_3Me_2\text{-}2,6)_3\{P(C_6H_4Me\text{-}p)_3\}_2]BF_4$ in CH_3CN at various scan rates. The bold trace is for the background electrolyte at 0.1 V s^{-1}. The scan rates for the solutions of the complex are, starting from the inner most trace outwards, 0.05, 0.10, 0.20, 0.50 and 1.00 V s^{-1}

Variation of E_{ox} with arylisocyanide ligand: With *para*-substituted phenylisocyanide ligands $p\text{-}XC_6H_4NC$, the E_{ox} increases with increasing π*-accepting ability (π-acidity) of the RNC, X = Me < Cl ~ I < Br (*e.g.*, **1** < **5** ≈ **6** < **7**). This is expected behaviour as stronger π-acidity (due to electron-withdrawing substituents on the phenyl ring) will further stabilize the Co(I) oxidation state, making oxidation to Co(II) more difficult. Pattern for the *ortho*-substituted phenylisocyanide ligands $2,6\text{-}Me_2C_6H_3NC$, $2,4,6\text{-}Me_3C_6H_2NC$, $2,6\text{-}Et_2C_6H_3NC$, $2,6\text{-}iPr_2C_6H_3NC$, sometimes appears inconsistent. This may be due to the two opposing trends, induction effects where electron-donating ability iPr > Et > Me should favour oxidation to Co(II) and steric effects that may retard a reaction in general. Comparing $2,4,6\text{-}Me_3C_6H_2NC$ with $2,6\text{-}Me_2C_6H_3NC$, one would expect in the former increased inductive but a comparable steric effect, so lower E_{ox} values are anticipated. This is observed for pairs of complexes with identical tertiary phosphine ligands; *e.g.*, **8** < **10**, **9** < **11**, **26** << **27**, **34** < **36**, **33** << **38**. The one exception to this trend is **3** > **2** and **3** is also unexpectedly irreversible in behaviour. In view of this exception, the series **1** → **4** shows increasing E_{ox} values following only increasing steric hindrance in the arylisocyanide.

In comparing E_{ox} values for complexes containing the 2,6-$Et_2C_6H_3NC$ and 2,6-$Me_2C_6H_3NC$ ligands with the same numbers of identical tertiary phosphine ligands, steric hindrance in the R substituent of RNC appears to be more significant than the inductive effect. The E_{ox} values are consistently higher; *e.g.*, **4** > **2**, **18** > **16**, **21** > **20**, **42** > **36**, **44** > **38**, **46** > **45**. In comparing E_{ox} values for the Co(I) complexes containing 2,6-$iPr_2C_6H_3NC$ and 2,6-$Et_2C_6H_3NC$ ligands and the same numbers of identical tertiary phosphine ligands, however, results are inconsistent. The E_{ox} values can be higher (*e.g.*, **31** > **30**, **19** >> **15**) or lower (*e.g.*, **17** < **18**, **40** < **42**, **41** < **43**). This irregular pattern may be due to the conflicting inductive and steric trends.

As seen from both Tables 1 and 2, the E_{ox} values can span a range well over 100 mV for change in the arylisocyanide ligand with the same tertiary phosphine. This is much stronger dependence on the organoisocyanide ligands than previously seen for Co(I) complexes with alkylisocyanide ligands where changes in E_{ox} were either relatively small[2,5] or negligible[1]. Stronger dependence on aryl RNC ligands is expected since both inductive effect and the stronger resonance effects can make the R group strongly electron-withdrawing or donating while alkyl RNC ligands have only inductive effects.

Variation of E_{ox} with tertiary phosphine ligand: The E_{ox} values show strong dependence on the triarylphosphine ligands, increasing sometimes dramatically as the *p*-substituent changes from electron-donating to electron-withdrawing, $P(C_6H_4X\text{-}p)_3$, X = OMe < Me < H << Cl ~ F << CF_3, at least for the disubstituted Co(I) complexes $[Co(CNR)_3(PR'_3)_2]X$. This is expected behaviour since *para*-substituents with decreasing electron-donating ability will make the phosphines stronger π^*-accepting and less σ-donating, favouring stabilization of Co(I) and making oxidation to Co(II) more difficult. With strong electron-withdrawing substituents (*e.g.*, $P(C_6H_4Cl\text{-}p)_3$, $P(C_6H_4F\text{-}p)_3$, $P(C_6H_4CF_3\text{-}p)_3$) stabilization of Co(I) is so great that oxidation to Co(II) is marginally possible and the voltammograms become irreversible. For some of the monosubstituted complexes $[Co(CNR)_4PR'_3]X$ this trend is not so apparent, possibly because E_{ox} values are more difficult to measure for irreversible waves.

The E_{ox} values also show strong dependency on the other tertiary phosphine ligands (Table-2), spanning an even wider range (*e.g.*, 300-800 mV). For disubstituted complexes with the same arylisocyanide ligands, the E_{ox} increase as $P(NMe_2)_3$ << $P(C_6H_{13}\text{-}n)_3$ = $P(C_3H_7\text{-}n)_3$ = $P(C_4H_9\text{-}n)_3$ << $P(CH_2CH_2CN)_3$, with little differentiation seen between the three tri-*n*-alkylphosphines. This behaviour follows strong electron-donation in $P(NMe_2)_3$

to increasing electron-withdrawal in $P(CH_2CH_2CN)_3$, resulting in the increased stabilization of the Co(I) oxidation state through effective Co → P back-bonding. For monosubstituted complexes, an expected order of increasing E_{ox} for Co(I) complexes with identical arylisocyanide ligands of $P(NMe_2)_3 = P(NEt_2)_3 < P(C_4H_9\text{-n})_3 = P(C_6H_{11})_3 = P(C_3H_7\text{-n})_3 < P(CH_2Ph)_3 < 2\text{-}Ph_2PC_5H_4N < P(CH_2CH_2CN)_3$, is seen with all complexes.

Comparison of E_{ox} values for triarylphosphine and trialkylphosphine Co(I) complexes with the same arylisocyanide ligands is less useful as many of the trialkylphosphine complexes are monosubstituted while monosubstituted triarylphosphine complexes tend to give irreversible voltammograms. Since trialkylphosphines are, in general, better σ-donating and weaker π*-accepting ligands than triarylphosphines, an increase in E_{ox} would be expected for substituting trialkylphosphine ligands with triarylphosphines. The trialkylphosphines with electron-withdrawing substituents, $P(CH_2Ph)_3$ and $P(CH_2CH_2CN)_3$ and the essentially triarylphosphine, $2\text{-}Ph_2PC_6H_4N$, overlap with E_{ox} values for Co(I) complexes with triarylphosphines. Otherwise the trialkylphosphine-arylisocyanide complexes systematically show lower E_{ox} values than the triarylphosphine complexes. This was also the trend seen with alkyliso-cyanide-tertiary phosphine Co(I) complexes[1].

Variation of E_{ox} with 3:2 and 4:1 arylisocyanide:tertiary phosphine ligand composition: Changing from 3:2 to 4:1 arylisocyanide:tertiary phosphine ligand composition involves exchanging the phosphine ligand in a trigonal bipyramidal axial position with an arylisocyanide ligand. This is because the best σ-donating ligands for d^8 metal complexes always bond in axial positions in trigonal bipyramidal coordination[22] and tertiary phosphines are stronger σ-donors than organoisocyanides. This change in ligand type, therefore, results in net loss of σ-donation to the Co(I) center and should make oxidation to Co(II) more difficult. In the examples for pairs of complexes having 3:2 and 4:1 composition with the same arylisocyanide and tertiary phosphine ligands, the 4:1 complexes show substantially higher E_{ox} values in all instances (*e.g.*, **18** > **4**, **16** > **2**, **35** > **26**, **29** > **27**, **42** > **33**, **44** > **31**) except for **23** < **21**, both giving irreversible voltammograms. Complexes with two $P(C_6H_4Cl\text{-}p)_3$ ligands (*e.g.*, **20-22**) show very high E_{ox} values, so maybe a phenylisocyanide ligand *ortho*-substituted with electron-donating Et groups is providing more σ-donation/less π*-acceptance than this particular triarylphosphine, although steric complication cannot be excluded.

Conclusion

This work shows that arylisocyanide-Co(I) complexes with tertiary phosphine ligands, both mono- and disubstituted, are readily oxidized to Co(II) in CH_3CN solution, with many of the cyclic voltammograms being reversible. Increase in E_{ox} values follows progressive change from electron-donating to electron-withdrawing nature of substituents in both arylisocyanide and tertiary phosphine ligands, with few exceptions. Steric hindrance in the arylisocyanide ligand may account for any irregularities in this pattern. There is, therefore, viable possibility that the corresponding five-coordinate Co(II) complexes can be synthesized by chemical oxidation of many of these Co(I) complexes.

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