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Solution-phase Disproportionation Equilibria for Monosubstituted *Pentakis*-(arylisocyanide)cobalt(I) Complexes by Proton-NMR Studies*

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Abstract

Equilibrium constants, K_{dis}, for the solvent-dependent, solution-phase disproportionation equilibria of monosubstituted *pentakis*(arylisocyanide)-cobalt(I) complexes:

$$2[\mathrm{Co(CNR)_4L}]^+ \rightleftharpoons [\mathrm{Co(CNR)_3L_2}]^+ + [\mathrm{Co(CNR)_5}]^+,$$

$$K_{\mathrm{dis}} = \frac{[\mathrm{Co(CNR)_3L_2}]\,[\mathrm{Co(CNR)_5}]}{[\mathrm{Co(CNR)_4L}]^2}$$

are measured by planimeter-integration of proton-NMR spectra at ambient temperature. The complexes, $[\mathrm{Co(CNR)_4L}]\mathrm{ClO_4}$, R = 2,6-$\mathrm{Me_2C_6H_3}$, L = $\mathrm{P(C_6H_5)_3}$, $\mathrm{P(C_6H_4Cl}$-$p)_3$, $\mathrm{P(OC_6H_5)_3}$, $\mathrm{P(OC_6H_4Cl}$-$p)_3$; R = o-$\mathrm{MeC_6H_4}$, L = $\mathrm{P(C_6H_4Cl}$-$p)_3$, $\mathrm{P(OC_6H_5)_3}$, $\mathrm{P(OC_6H_4Cl}$-$p)_3$; R = 2,4,6-$\mathrm{Me_3C_6H_2}$, L = $\mathrm{P(C_6H_5)_3}$; R = 2,6-$\mathrm{Et_2C_6H_3}$, L = $\mathrm{P(C_6H_5)_3}$; are investigated in the deuterated solvents, $\mathrm{CDCl_3}$, $\mathrm{CD_3CN}$, $\mathrm{(CD_3)_2CO}$, $\mathrm{C_5D_5N}$, $\mathrm{CD_3NO_2}$, and $\mathrm{(CD_3)_2SO}$. Disproportionation seems to occur in all $[\mathrm{Co(CNR)_4L}]^+$, but NMR study is facilitated by utilizing equivalent alkyl protons (*i.e.*, Me-groups) on the RNC ligands.

Correlation of K_{dis} values with steric-hindrance of the RNC in sets of complexes with the same P-ligand is evident in all solvents: K_{dis} decreases with increased steric-hindrance in RNC. The K_{dis} values for complexes with the same RNC and analogous triarylphosphine, triarylphosphite ligands (*i.e.*, $\mathrm{PR_3}$, $\mathrm{P(OR)_3}$, same R) are approximately equal. The K_{dis} values for complexes of P-ligands with Cl-substituent are significantly larger than K_{dis} values for complexes with the corresponding unsubstituted P-ligands (*e.g.*, $[\mathrm{Co(CNR)_4P(C_6H_4Cl}$-$p)_3]\mathrm{ClO_4}$ *vs.* $[\mathrm{Co(CNR)_4P(C_6H_5)_3}]\mathrm{ClO_4}$) in $\mathrm{(CD_3)_2CO}$ and $\mathrm{C_5D_5N}$ solution, but are smaller in $\mathrm{CDCl_3}$ and $\mathrm{CD_3CN}$, and approximately equal in $\mathrm{CD_3NO_2}$ and $\mathrm{(CD_3)_2SO}$. Properties of the solvents are also considered.

Introduction

Ligand substitution reactions in *pentakis*(arylisocyanide)cobalt(I) complexes with triarylphosphines and triarylphosphites produce monosubstituted, $[\mathrm{Co(CNR)_4L}]\mathrm{X}$, and disubstituted, $[\mathrm{Co(CNR)_3L_2}]\mathrm{X}$, L = $\mathrm{P(C_6H_5)_3}$, $\mathrm{P(C_6H_4Cl}$-$p)_3$, $\mathrm{P(OC_6H_5)_3}$, $\mathrm{P(OC_6H_4Cl}$-$p)_3$; X = $\mathrm{ClO_4}$, $\mathrm{BF_4}$; derivatives [1, 2]. These mixed-ligand Co(I) complexes are also prepared in a variety of reduction/ligand substitution reactions [3–5]. With Muetterties' NMR study [6] of the solution-phase formation reaction, $[\mathrm{Co(CNCMe_3)_5}]^+ + [\mathrm{Co(CNCMe_3)_3\{P(C_6H_4Me}$-$p)_3\}_2]^+ \rightleftharpoons 2[\mathrm{Co(CNCMe_3)_4P(C_6H_4Me}$-$p)_3]^+$ (K(40 °C) $\simeq$ 3) and solution stability/synthesis feasibility of $[\mathrm{Co(CNCMe_3)_4As(C_6H_5)_3}]^+$ [7], the chemical purity/integrity of the reported $[\mathrm{Co(CNR)_4L}]\mathrm{X}$ [1, 2] appeared challenged, so detailed NMR investigation was in order.

Triarylphosphine substitution in *pentakis*(arylisocyanide)cobalt(I) complexes produces ^{1}H-NMR spectra as pictured in Fig. 1. Aliphatic-proton signals (δ 2.16; 2.81, 1.75) for $[\mathrm{Co(CNC_6H_3Me_2}$-2,6$)_4\mathrm{P(C_6H_5)_3}]\mathrm{ClO_4}$ (Fig. 1B) demonstrate the disproportionation: $2[\mathrm{Co(CNC_6H_3Me_2}$-2,6$)_4\mathrm{P(C_6H_5)_3}]^+ \rightleftharpoons [\mathrm{Co(CNC_6H_3Me_2}$-2,6$)_5]^+ + [\mathrm{Co(CNC_6H_3Me_2}$-2,6$)_3\{\mathrm{P(C_6H_5)_3}\}_2]^+$. The strong signal ($\delta$ 2.16) is attributed to $[\mathrm{Co(CNC_6H_3Me_2}$-2,6$)_4\mathrm{P(C_6H_5)_3}]^+$, the upfield weak signal (δ 1.75) is recognized as coming from $[\mathrm{Co(CNC_6H_3Me_2}$-2,6$)_3\{\mathrm{P(C_6H_5)_3}\}_2]^+$ (*i.e.*, δ 1.74; Fig. 1A) and the downfield weak signal (δ 2.81), from $[\mathrm{Co(CNC_6H_3Me_2}$-2,6$)_5]^+$ (*i.e.*, δ 2.80; Fig. 1C). All three bands must be integrated for agreement with 4:1 ligand-composition (*i.e.*, 4.00:

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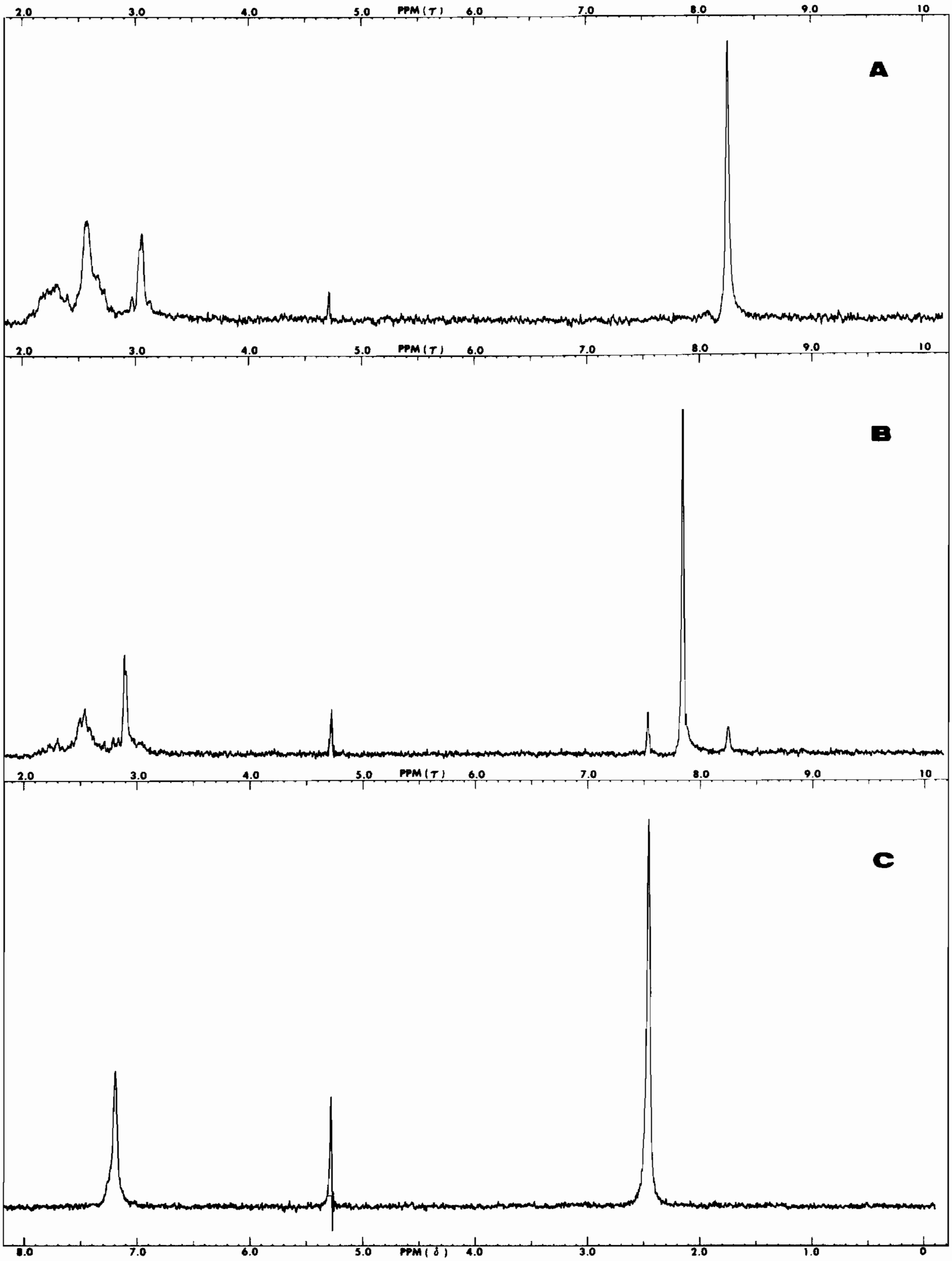

Fig. 1. The ^{1}H-NMR spectra (in 99.8% $CDCl_3$ with CH_2Cl_2 as secondary internal reference) for corresponding examples of a disubstituted, monosubstituted, and unsubstituted *pentakis*(arylisocyanide)cobalt(I) complex. A. $[Co(CNC_6H_3Me_2\text{-}2,6)_3\{P(C_6H_5)_3\}_2]ClO_4$; B. $[Co(CNC_6H_3Me_2\text{-}2,6)_4P(C_6H_5)_3]ClO_4$; C. $[Co(CNC_6H_3Me_2\text{-}2,6)_5]ClO_4$.

1.05) established by elemental analysis [1]. Suggestion that the monosubstituted complex contains a fortuitous mixture of disubstituted and unsubstituted compound can be disregarded from solubilities and solvent dependence of the disproportionation equilibrium constants. Solubility in general follows: $[Co(CNR)_5ClO_4 > [Co(CNR)_4L]ClO_4 > [Co(CNR)_3L_2]ClO_4$ [1], so equal amounts of the two extremes remaining after one or more re-crystallizations (80–90% recovery) is highly improbable. Furthermore, if amounts of the same sample are used for NMR spectra in different solvents, the K_{dis} calculated as $[Co(CNR)_3L_2][Co(CNR)_5][Co(CNR)_4L]^{-2}$ from the integrated areas are significantly solvent dependent [1]. This behavior is not that expected for a physical mixture of $[Co(CNR)_4L]ClO_4$ contaminated with small amounts of both $[Co(CNR)_3L_2]ClO_4$ and $[Co(CNR)_5]ClO_4$, but is that expected for pure $[Co(CNR)_4L]ClO_4$ establishing a solution-phase equilibrium.

Triarylphosphite substitution in *pentakis*(arylisocyanide)cobalt(I) complexes has produced only monosubstituted derivatives (except for $[Co(CNC_6H_5)_3\{P(OC_6H_5)_3\}_2]ClO_4$) [2], so NMR spectra of $[Co(CNR)_4P(OR)_3]^+$ can only be compared to $[Co(CNR)_5]^+$, as pictured in Fig. 2. The ^{1}H-NMR for $[Co(CNC_6H_4Me\text{-}o)_4P(OC_6H_5)_3]ClO_4$ (Fig. 2A) exhibits three aliphatic-proton signals: δ 2.30 flanked by δ 2.15 and δ 2.50. Again all three bands must be integrated for agreement with the 4:1 composition (*i.e.*, 4.00:1.00) established by elemental analysis [2]. The $[Co(CNC_6H_4Me\text{-}o)_5]ClO_4$ (Fig. 2C) has frequencies at δ 2.50 and δ 7.37. The minor band at δ 2.50 and one at δ 7.38 for $[Co(CNC_6H_4Me\text{-}o)_4P(OC_6H_5)_3]^+$ are attributed to a small amount of $[Co(CNC_6H_4Me\text{-}o)_5]^+$ present in solution, and the δ 2.15 spike is assigned to $[Co(CNC_6H_4Me\text{-}o)_3\{P(OC_6H_5)_3\}_2]^+$ that must be formed in solution. Analogous interpretation is possible for $[Co(CNC_6H_4Me\text{-}o)_4P(OC_6H_4Cl\text{-}p)_3]ClO_4$ (Fig. 2B); aliphatic-proton signals δ 2.36; 2.52; 2.22; ^{1}H-integration CNR:P(OR)$_3$ = 4.00:0.99 [2].

These solution-phase disproportionation constants, K_{dis}, should show normal equilibrium constant behavior; that is the subject of this investigation. Temperature is held constant (*i.e.*, 37 °C), so K_{dis} dependence may be expected for change in RNC, L, and solvent.

Experimental

The complexes, $[Co(CNR)_4L]ClO_4$, L = $P(C_6H_5)_3$, $P(C_6H_4Cl\text{-}p)_3$, $P(OC_6H_5)_3$, and $P(OC_6H_4Cl\text{-}p)_3$ were prepared as previously described [1, 2]. Commercial deuterated solvents 99.8% chloroform-d$_1$ (Merck), 99% acetonitrile-d$_3$ (Stohler), 99.8% acetone-d$_6$ (Merck), 99% pyridine-d$_5$ (BDH), 99% nitromethane-d$_3$ (Alfa), and 99.5% dimethyl sulfoxide-d$_6$ (Diaprep-Aldrich) were used without further purification. Proton-NMR spectra were recorded on a Varian T-60, the aliphatic portion expanded both horizontally and vertically for better integration. Whereas some spectra were sufficiently resolved for instrument integration, all integrations were performed by planimeter tracing to insure uniformity. Integration values for the main band were taken as the average of ten tracings, while values for the smaller bands were averaged from multiple tracings (five to ten each, depending on size).

Since K_{dis} is unitless; *i.e.*, $K_{dis} \equiv [Co(CNR)_3L_2][Co(CNR)_5][Co(CNR)_4L]^{-2}$; the proportionality factor relating concentration and integrated area cancels, and K_{dis} values are calculated directly from any set of relative integration areas. Planimeter parameters can thus be changed from one NMR spectrum to another. Experimental error could not be accurately determined, but is probably 10–15% in well-resolved spectra (estimated by K_{dis} reproducibility from independent spectra) and significantly higher in poorly-resolved spectra. Thus only major differences in K_{dis} should be considered significant.

Results and Discussion

The K_{dis} values for the nine monosubstituted complexes, $[Co(CNR)_4L]ClO_4$, R = 2,6-$Me_2C_6H_3$, L = $P(C_6H_5)_3$, $P(C_6H_4Cl\text{-}p)_3$, $P(OC_6H_5)_3$, $P(OC_6H_4Cl\text{-}p)_3$; R = o-MeC_6H_4, L = $P(C_6H_4Cl\text{-}p)_3$, $P(OC_6H_5)_3$, $P(OC_6H_4Cl\text{-}p)_3$; R = 2,4,6-$Me_3C_6H_2$, L = $P(C_6H_5)_3$; R = 2,6-$Et_2C_6H_3$, L = $P(C_6H_5)_3$; in the six deuterated solvents, $CDCl_3$, CD_3CN, $(CD_3)_2CO$, C_5D_5N, CD_3NO_2, $(CD_3)_2SO$; are listed in Table I. Three conditions prevented calculation of reliable K_{dis} values in some measurements. Some spectra were unresolved; *i.e.*, the signal for one but not both of $[Co(CNR)_3L_2]^+$ and $[Co(CNR)_5]^+$ was not resolved from that for $[Co(CNR)_4L]^+$ or was insufficiently resolved for accurate integration even by planimeter. Other spectra showed interference from the solvent; *i.e.*, the signal from the 0.2–1% non-deuterated solvent molecules interfered with some part of the aliphatic portion of the $[Co(CNR)_4L]^+$ spectrum so that accurate integration was not possible. In both of these cases there is evidence that disproportionation occurs, but accurate K_{dis} values cannot be obtained. For $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(C_6H_5)_3]ClO_4$ in all solvents, however, no evidence of disproportionation is observed. Here there is no solvent interference, and although the CH_3 and CH_2 multiplets are harder to resolve than singlets, some additional bands should be visible if disproportionation takes place. The probable

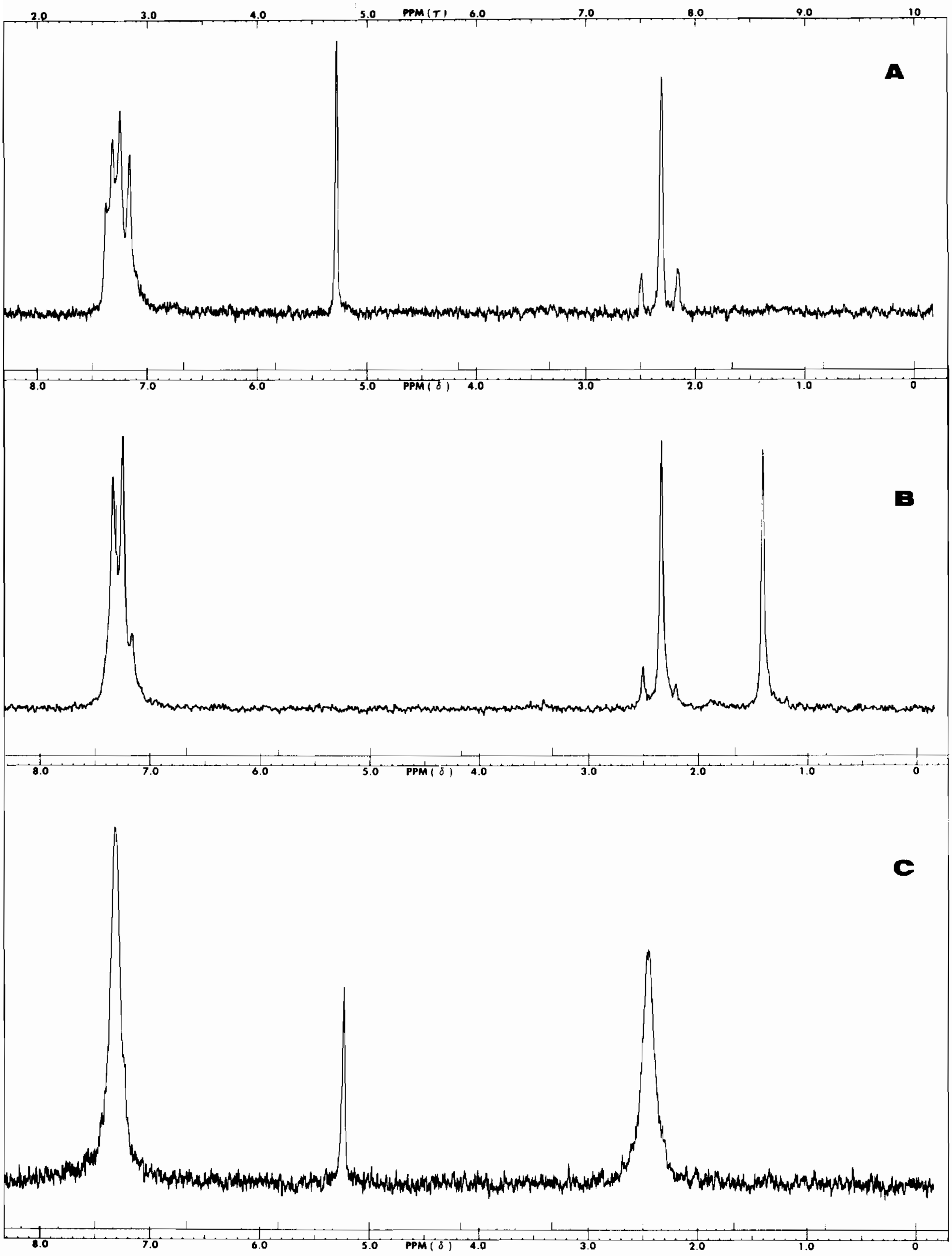

Fig. 2. The ^{1}H-NMR spectra (in 99.8% $CDCl_3$) for examples of triarylphosphitemonosubstituted *pentakis*(arylisocyanide)cobalt(I) complexes. A. $[Co(CNC_6H_4Me\text{-}o)_4P(OC_6H_5)_3]ClO_4$ (CH_2Cl_2 secondary internal reference); B. $[Co(CNC_6H_4Me\text{-}o)_4P(OC_6H_4Cl\text{-}p)_3]ClO_4$ (C_6H_{12} secondary internal reference); C. $[Co(CNC_6H_4Me\text{-}o)_5]ClO_4$ (CH_2Cl_2 secondary internal reference).

TABLE I. Disproportionation Equilibrium Constants for $[Co(CNR)_4L]X$ in Deuterated Solvents.[a]

Complex	$CDCl_3$	CD_3CN	$(CD_3)_2CO$	C_5D_5N	CD_3NO_2	$(CD_3)_2SO$
$L = P(C_6H_5)_3$						
$[Co(CNC_6H_3Me_2\text{-}2,6)_4L]ClO_4$	0.013	0.010	0.0035	0.0041	0.0032	0.0032
$[Co(CNC_6H_2Me_3\text{-}2,4,6)_4L]ClO_4$	0.0017	0.0015	0.0013	0.0015	0.00075	Interfer
$[Co(CNC_6H_3Et_2\text{-}2,6)_4L]ClO_4$	Not Obs	Not Obs	Not Obs	Not Obs	Not Obs	Not Obs
$L = P(C_6H_4Cl\text{-}p)_3$						
$[Co(CNC_6H_4Me\text{-}o)_4L]ClO_4$	0.038	0.046	0.092	0.060	0.032	0.030
$[Co(CNC_6H_3Me_2\text{-}2,6)_4L]ClO_4$	0.0035	0.0045	0.010	0.013	0.0047	0.0031
$L = P(OC_6H_5)_3$						
$[Co(CNC_6H_4Me\text{-}o)_4L]ClO_4$	0.029	0.012	0.0075	0.0060	0.0025	Interfer
$[Co(CNC_6H_3Me_2\text{-}2,6)_4L]ClO_4$	0.019	Interfer	0.0028	Unresolv	Interfer	0.0046
$L = P)OC_6H_4Cl\text{-}p)_3$						
$[Co(CNC_6H_4Me\text{-}o)_4L]ClO_4$	0.016	Unresolv	0.086	Unresolv	Unresolv	0.036
$[Co(CNC_6H_3Me_2\text{-}2,6)_4L]ClO_4$	0.0027	0.0021	0.0062	Unresolv	0.0014	Unresolv

[a] Abbreviations: Interfer = interference, the ^{1}H-NMR signal from non-deuterated solvent molecules interferes with the signal being measured; Unresolv = unresolved, the ^{1}H-NMR signal for one but not both of the $[Co(CNR)_3L_2]^+$ and $[Co(CNR)_5]^+$ species is not resolved from that for $[Co(CNR)_4L]^+$; Not Obs = not observed, no ^{1}H-NMR signal for the $[Co(CNR)_3L_2]^+$ or $[Co(CNR)_5]^+$ species is observed in the absence of solvent interference.

explanation, as developed later, is that the severe steric hindrance of the $CNC_6H_3Et_2$-2,6 causes the K_{dis} values to be immeasurably small.

The solution-phase disproportionation probably takes place in all monosubstituted complexes, but is easily measured for the complexes listed in Table I. An alkyl group (preferably methyl) on the RNC is practically a necessity for NMR resolution. In $[Co(CNC_6H_4X\text{-}p)_4P(OC_6H_5)_3]ClO_4$, X = H, F, Cl, Br, I; the triphenylphosphite so dominates the aromatic region that evidence for disproportionation was not observed [2]. For $[Co(CNC_6H_4I\text{-}p)_4P(C_6H_5)_3]ClO_4$ and $[Co(CNC_6H_4Cl\text{-}p)_4P(C_6H_5)_3]ClO_4$ (impure) disproportionation was observed, but the weak AB patterns from $[Co(CNR)_3L_2]^+$ and/or $[Co(CNR)_5]^+$ suffered interference from coordinated $P(C_6H_5)_3$ [1]. The $[Co(CNC_6H_4Me\text{-}p)_4P(C_6H_4Cl\text{-}p)_3]ClO_4$ spectra are unresolved [1], and pure samples of $[Co(CNR)_4P(C_6H_5)_3]ClO_4$, R = C_6H_4Me-*o*, C_6H_4Me-*p*; could not be obtained.

The K_{dis} values in $CDCl_3$and CD_3CN are smaller than reciprocal formation-constants reported for $[Co(CNCMe_3)_4P(C_6H_4Me\text{-}p)_3]^+$ (*i.e.*, $K^{-1} = K_{dis} \simeq 0.33$ [6]) and $[Co(CNC_6H_4Me\text{-}p)_4P(C_6H_5)_3]^+$ ($K^{-1} \approx 0.05$ [3]), compounds whose purity was questioned [6, 1]. Dichloromethane principally, but chloroform and acetonitrile occasionally, were solvents of re-crystallization for these complexes [1, 2]. From the K_{dis} values, re-crystallization of some of these complexes from other solvents (*e.g.*, $[Co(CNC_6H_4Me\text{-}o)_4L]ClO_4$, L = $P(C_6H_4Cl\text{-}p)_3$, $P(OC_6H_4Cl\text{-}p)_3$; from acetone) may lead to decomposition in the sense of producing free $[Co(CNR)_3L_2]ClO_4$ in the solid. This was the difficulty in preparing monosubstituted complexes with triphenylphosphine; the monosubstituted derivative could always be observed, but often the less-soluble disubstituted complex could not be completely removed [1].

Correlation of K_{dis} with RNC Steric Hindrance

Of several possible interdependencies, the most expected numerically obvious from Table I is correlation of K_{dis} values with steric hindrance of the arylisocyanide. Ease of preparation of monosubstituted triphenylphosphine complexes parallels RNC steric hindrance [1]: *p*-MeC_6H_4NC < *o*-$MeC_6H_4NC \ll$ 2,6-$Me_2C_6H_3NC \approx$ 2,4,6-$Me_3C_6H_2NC \ll$ 2,6-$Et_2C_6H_3NC$; so K_{dis} should behave analogously. In all instances for each solvent where comparison is possible for $[Co(CNR)_4L]ClO_4$ same L, $K(R = C_6H_4Me\text{-}o) > K(R = C_6H_3Me_2\text{-}2,6) > K(R = C_6H_2Me_3\text{-}2,4,6) > K(R = C_6H_3Et_2\text{-}2,6)$. The K_{dis} values reflect substantially greater apparent steric hindrance in 2,4,6-$Me_3C_6H_2NC$ over 2,6-$Me_2C_6H_3NC$ than observed in reactivity [1], however, and RNC steric hindrance appears less important for triarylphosphite complexes than triarylphosphine.

Since $[Co(CNC_6H_3Et_2\text{-}2,6)_3\{P(C_6H_5)_3\}_2]ClO_4$ can be made in Co(II) reduction/substitution reaction [9], the equilibrium, $2[Co(CNC_6H_3Et_2\text{-}2,6)_4P(C_6H_5)_3]^+ \rightleftharpoons [Co(CNC_6H_3Et_2\text{-}2,6)_3\{P(C_6H_5)_3\}_2]^+ + [Co(CNC_6H_3Et_2\text{-}2,6)_5]^+$ should not be totally absent, but K_{dis} should be very small due to the severe steric hindrance of 2,6-$Et_2C_6H_3NC$. The K_{dis} is possibly too small to measure or even observe

TABLE II. Some Physical Properties of the Solvents.[a, b]

Solvent	ϵ	μ	κ	K
$CHCl_3$	4.806	1.15	$<1 \times 10^{-10}$	
CH_3CN	37.5	3.44	6×10^{-10}	$K_s = 3.2 \times 10^{-27}$
C_5H_5N	12.4	2.37	4.0×10^{-8}	K_b(aq HCl) = 1.8×10^{-9}
$(CH_3)_2CO$	20.70	2.69	4.9×10^{-9}	K_b(aq H_2SO_4) = 6.3×10^{-22}
CH_3NO_2	35.87	3.56	5×10^{-9}	K_a(aq NaOH) = 6.15×10^{-11}
$(CH_3)_2SO$	46.68	3.9	2×10^{-9}	$K_s = 5.0 \times 10^{-18}$

[a] Symbols: ϵ, dielectric constant; μ, dipole moment in Debye units; κ, electrical conductivity in ohm^{-1}; K_s, autoprotolysis constant, $2HR \rightleftharpoons H_2R^+ + R^-$, $K_s = \gamma[H_2R^+]\gamma[R^-] \simeq [H_2R^+][R^-]$; K_i, ionization constant, usually K_a(acid) or K_b(base) dissociation constants, for ionization in another solvent (often water). [b] Values obtained from ref. 10.

by this method. Unlike reactions with other arylisocyanides, disubstituted triarylphosphine complexes with $2,6\text{-}Et_2C_6H_3NC$ have never been observed as minor products in $[Co(CNR)_5]X$ substitution reaction [1, 8], so there may be little tendency for $[Co(CNC_6H_3Et_2\text{-}2,6)_3\{PR_3\}_2]^+$ formation.

Correlation of K_{dis} with Triarylphosphine vs. Triarylphosphite Ligand

Since monosubstitution is the almost-exclusive reaction in triarylphosphite substitution [2], while $P(C_6H_5)_3$, if not the less reactive $P(C_6H_4Cl\text{-}p)_3$, favors disubstitution except with sterically-hindered RNC [1], K_{dis} for complexes of the same RNC and analogous triarylphosphine, triarylphosphite ligand are expected: $K([Co(CNR)_4P(C_6H_5)_3]ClO_4)$ > $K([Co(CNR)_4P(OC_6H_5)_3]ClO_4)$ and $K([Co(CNR)_4P(C_6H_4Cl\text{-}p)_3]ClO_4)$ > $K([Co(CNR)_4P(OC_6H_4Cl\text{-}p)_3]ClO_4)$. This behavior is not apparent from Table I. The K_{dis} values for the ten pairs of complexes where comparion is possible are almost remarkably similar; no correlation between K_{dis} and substitution preference in triarylphosphine *vs.* triarylphosphite reactions is observed.

Why there is no correlation is not immediately evident, other than possible intrinsic difficulty of comparing complexes with tertiary phosphine and phosphite ligands; these are dissimilar types of ligands. Similar problem was encountered in comparison/interpretation of the first $d_\pi \to \pi^*(eq)$ charge transfer band in the $[Co(CNR)_3L_2]^+$ electronic spectra [9].

Correlation of K_{dis} with Cl-Substituted vs. Unsubstituted P-Ligand

Triphenylphosphine favors disubstitution while $P(C_6H_4Cl\text{-}p)_3$ favors monosubstitution in $[Co(CNR)_5]^+$ [1, 8], so for the same RNC, $K([Co(CNR)_4P(C_6H_5)_3]ClO_4)$ > $K([Co(CNR)_4P(C_6H_4Cl\text{-}p)_3]ClO_4)$, if not also $K([Co(CNR)_4P(OC_6H_5)_3]ClO_4)$ > $K([Co(CNR)_4P(OC_6H_4Cl\text{-}p)_3]ClO_4)$, would be expected. Table 1 gives different results. Comparison is incomplete because of numerous instances of solvent interference or partial resolution, but a trend seems to emerge. The K_{dis} values for Cl-substituted P-ligands are larger than K_{dis} for analogous complexes with unsubstituted P-ligands in $(CD_3)_2CO$ and C_5D_5N solution, are smaller in $CDCl_3$ and CD_3CN, and are approximately equal in CD_3NO_2 and $(CD_3)_2SO$. The $[Co(CNC_6H_3Me_2\text{-}2,6)_4P(C_6H_5)_3]ClO_4$, $[Co(CNC_6H_3Me_2\text{-}2,6)_4P(C_6H_4Cl\text{-}p)_3]ClO_4$ pair is best for comparison, with values 0.013, 0.0035; 0.010, 0.0045; 0.0035, 0.010; 0.0041, 0.013; 0.0032, 0.0047; 0.0032, 0.0031; in $CDCl_3$, CD_3CN, $(CD_3)_2CO$, C_5D_5N, CD_3NO_2, $(CD_3)_2SO$, respectively. Not only do these pairs of solvents show the same trend, but also show similar K_{dis} absolute values. This behavior is apparently a function of the solvent, not the RNC or P-ligand.

Physical properties of deuterated solvents are not readily available, so possibly-relevant properties of the non-deuterated solvents are listed in Table II [10]. From these data C_5H_5N and $(CH_3)_2CO$, and CH_3NO_2 and $(CH_3)_2SO$, could be analogous solvents, but similarity of $CHCl_3$ and CH_3CN is not obvious. The electrical conductivities (κ) are somewhat similar, but dielectric constant (ϵ) and dipole moment (μ), the quantitative aspects from which the more useful but qualitative solvent property, polarity, is usually assessed, place CH_3CN with CH_3NO_2 and $(CH_3)_2SO$, very polar solvents, and far from the semi-polar $CHCl_3$. At present there is really no satisfactory explanation for this solvent behavior.

References

1 C. A. L. Becker, *J. Inorg. Nucl. Chem., 42*, 27 (1980).
2 C. A. L. Becker and B. L. Davis, *J. Inorg. Nucl. Chem., 39*, 781 (1977).
3 S. Otsuka and M. Rossi, *Bull. Chem. Soc. Jpn., 46*, 3411 (1973).
4 J. W. Dart, M. K. Lloyd, R. Mason, J. A. McCleverty and J. Williams, *J. Chem. Soc., Dalton Trans.*, 1747 (1973).

5 C. A. L. Becker, *Synth. React. Inorg. Met.-Org. Chem., 9,* 445 (1979).
6 E. L. Muetterties, *Chem. Commun.*, 221 (1973).
7 R. B. King and M. S. Saran, *Inorg. Chem., 11,* 2112 (1972).
8 C. A. L. Becker, *Inorg. Chim. Acta, 77,* L223 (1983).
9 C. A. L. Becker and N. K. Homsy, *Inorg. Chim. Acta, 89,* 95 (1984).
10 J. A. Riddick and W. B. Bunger, in A. Weissberger (ed.), 'Techniques of Chemistry, Vol. II Organic Solvents, 3rd edn.', Wiley-Interscience, New York, 1970, and references therein.