Inductive and Steric Effects for Triarylphosphine Substitution in Pentakis(arylisocyanide)cobalt(I)

C. A. L. BECKER

Department of Chemistry, Washburn University of Topeka, Topeka, Kans. 66621, U.S.A.

Received June 27, 1983

In a previous investigation [1] of triarylphosphine substitution in pentakis(arylisocyanide)cobalt(I), PPh_3 was observed to favor disubstitution of all but the sterically-hindered arylisocyanides (*e.g.*, 2,6-$Et_2C_6H_3$-, 2,6-$Me_2C_6H_3$-, 2,4,6-$Me_3C_6H_2NC$), while the less reactive $P(C_6H_4Cl\text{-}p)_3$ clearly favored monosubstitution with even the most reactive $[Co(CNR)_5]X$ (*e.g.*, R = *p*-MeC_6H_4). Steric hindrance of the less-reactive arylisocyanides and electron-withdrawing effect of the chlorosubstituent in $P(C_6H_4Cl\text{-}p)_3$ were cited as probable causes for these substitution patterns, but inductive effects in the arylisocyanides and steric hindrance in $P(C_6H_4Cl\text{-}p)_3$ have hitherto not been excluded. Current investigation using PPh_3, $P(C_6H_4Cl\text{-}p)_3$, and $P(C_6H_4OMe\text{-}p)_3$ extended to the arylisocyanides R = C_6H_4Cl-*p*, C_6H_4Me-*o*, $C_6H_3Et_2$-2,6 seems to confirm the original hypothesis, although the behavior of $P(C_6H_4OMe\text{-}p)_3$, the triarylphosphine with electron-donating substituent, relative to PPh_3 is somewhat unexpected.

Experimental

The $[Co(CNC_6H_4Cl\text{-}p)_5]BF_4$, $[Co(CNC_6H_4Me\text{-}o)_5]ClO_4$, $[Co(CNC_6H_3Et_2\text{-}2,6)_5]ClO_4$, and PPh_3-substituted complexes listed in Table I were prepared as previously described [1–3]. Commercial $P(C_6H_4Cl\text{-}p)_3$ and $P(C_6H_4OMe\text{-}p)_3$ (Strem Chemicals) were used without further purification. Anhydrous diethyl ether was filtered through alumina immediately before use. IR spectra were recorded on a Perkin-Elmer 398 spectrophotometer. Electronic spectra were recorded on a Cary 219 spectrophotometer. Elemental analyses were performed commercially.

Results and Discussion

Arylisocyanide–triarylphosphine complexes of Co(I) containing *p*-ClC_6H_4NC, *o*-MeC_6H_4NC, or 2,6-$Et_2C_6H_3NC$ with PPh_3, $P(C_6H_4OMe\text{-}p)_3$, or $P(C_6H_4Cl\text{-}p)_3$ are listed in Table I with melting points (decomposition ranges), -N≡C IR frequencies, and electronic spectral values (λ_{max}, ϵ). New complexes containing $P(C_6H_4OMe\text{-}p)_3$ or $P(C_6H_4Cl\text{-}p)_3$ prepared for this study are indicated by an asterisk (elemental analyses provided upon request to the author). Methods of preparation and apparent substitution preference are considered first.

Whereas $[Co(CNR)_3(PPh_3)_2]X$ were typically prepared [1, 3] by reaction of 5:1 mole ratio PPh_3 with $[Co(CNR)_5]X$ in short (3–5 min) reaction periods, this procedure sufficed for only $[Co(CNC_6H_4Me\text{-}o)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$. Reaction of $P(C_6H_4OMe\text{-}p)_3$ with $[Co(CNC_6H_4Cl\text{-}p)_5]BF_4$ showed unexpected behavior. In a reaction of 5:1 mole ratio for 15 min the product, after two re-crystallizations from CH_2Cl_2/Et_2O, analyzed as $0.75[Co(CNC_6H_4Cl\text{-}p)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]BF_4$ + $0.25[Co(CNC_6H_4Cl\text{-}p)_4P(C_6H_4OMe\text{-}p)_3]BF_4$, and additional 4 hr-reaction with excess $P(C_6H_4OMe\text{-}p)_3$ was required to complete conversion to $[Co(CNC_6H_4Cl\text{-}p)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]BF_4$. Since the monosubstituted derivative is more soluble than the disubstituted, $[Co(CNC_6H_4Cl\text{-}p)_4P(C_6H_4OMe\text{-}p)_3]BF_4$ was prepared in even greater initial percentage. Thus $[Co(CNC_6H_4Cl\text{-}p)_4P(C_6H_4OMe\text{-}p)_3]BF_4$ appears to be more readily prepared than $[Co(CNC_6H_4Cl\text{-}p)_4PPh_3]ClO_4$ [1], in contradiction to triarylphosphines with electron-donating substituents favoring disubstitution. Reaction of $P(C_6H_4OMe\text{-}p)_3$ with $[Co(CNC_6H_4Cl\text{-}p)_5]BF_4$ in 1.1:1 mole ratio for 30 min (Method B [1]), however, also produced a mixture of mono- and disubstituted complex. Preference for mono- or disubstitution is apparently not strong, and pure $[Co(CNC_6H_4Cl\text{-}p)_4P(C_6H_4OMe\text{-}p)_3]BF_4$ could probably be obtained with sufficient patience. This is not true for $[Co(CNC_6H_4Cl\text{-}p)_4PPh_3]ClO_4$ [1] and probably not true for the reported $[Co(CNC_6H_4Me\text{-}p)_4PPh_3]ClO_4$ [4, 1].

Reaction of 5:1 mole ratio $P(C_6H_4Cl\text{-}p)_3$ with $[Co(CNR)_5]X$ produced monosubstituted derivatives whether reaction time was long, $[Co(CNC_6H_4Me\text{-}o)_4P(C_6H_4Cl\text{-}p)_3]ClO_4$ (1 hr), or short, $[Co(CNC_6H_4Cl\text{-}p)_4P(C_6H_4Cl\text{-}p)_3]BF_4$ (15 min). This confirms that $P(C_6H_4Cl\text{-}p)_3$ favors monosubstitution. Reactions involving 2,6-$Et_2C_6H_3NC$ also monosubstituted, $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(C_6H_4OMe\text{-}p)_3ClO_4$ and $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(C_6H_4Cl\text{-}p)_3]ClO_4$, further supporting the $[Co(CNC_6H_3Et_2\text{-}2,6)_5]X$ preference for monosubstitution. Disubstitution reactions involving $P(C_6H_4Cl\text{-}p)_3$ necessarily required starting with Co(II) [4–7]. The $[Co(CNC_6H_4Me\text{-}o)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$ and $[Co(CNC_6H_3Et_2\text{-}2,6)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$ could be prepared by direct reduction/ligand substitution [7] of the corresponding $[Co(CNR)_5](ClO_4)_2$. Since $[Co(CNC_6H_4Cl\text{-}p)_5]X_2$ has not been prepared in a pure state [2, 8], excess $Co(BF_4)_2\cdot 6H_2O$ (in C_2H_5OH) was reacted with 3:2 mole ratio CNC_6H_4Cl-*p* and $P(C_6H_4Cl\text{-}p)_3$ (in

0020-1693/83/$3.00

CH_2Cl_2), and crude product precipitated by dropwise addition of ether. After re-crystallization from CH_2Cl_2/Et_2O, a mixture of di- and monosubstituted product was still present, which was finally converted to pure $[Co(CNC_6H_4Cl\text{-}p)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]BF_4$ upon extended reaction with excess $P(C_6H_4Cl\text{-}p)_3$ (Method C [1]). Since reactions involving $CNC_6H_4Cl\text{-}p$ [1, 3] or Co(II) [7] have previously favored disubstitution, observation of any $[Co(CNC_6H_4Cl\text{-}p)_4\ P(C_6H_4Cl\text{-}p)_3]BF_4$ underscores the tendency of $P(C_6H_4Cl\text{-}p)_3$ to favor monosubstitution. The $[Co(CNC_6H_3Et_2\text{-}2,6)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$ was also prepared by reduction/ligand substitution reaction [7].

On the basis of product composition, then, the triarylphosphine with electron-withdrawing substituent, *i.e.* $P(C_6H_4Cl\text{-}p)_3$, apparently favors monosubstitution reactions much more strongly than does the unsubstituted triphenylphosphine. The triarylphosphine with electron-donating substituent, *i.e.* $P(C_6H_4OMe\text{-}p)_3$, however, seems to behave analogously to PPh_3 or even favor monosubstitution reactions slightly more strongly. Control of ligand substitution reaction by inductive effects of ligand substituents has not been clearly established here. The $[Co(CNC_6H_3Et_2\text{-}2,6)_5ClO_4$ monosubstitutes in all instances, supporting arylisocyanide steric control of these substitution reactions.

Melting (decomposition) ranges, ν(-N≡C) ir frequencies, and electronic spectral values (Table I) give further insight into the bond preference/stability of these complexes. No correlation between melting points of the complexes and of the triarylphosphine ligands is observed: $P(C_6H_4OMe\text{-}p)_3$, 120–124; PPh_3, 79; $P(C_6H_4Cl\text{-}p)_3$, 90–93 °C [9]. Since decomposition temperatures should be an approximate indication of relative stability, the disubstituted triarylphosphine complexes appear more stable than the corresponding monosubstituted, with the exception of $[Co(CNC_6H_3Et_2\text{-}2,6)_4PPh_3]ClO_4$. Since monosubstitution is the favored reaction with both $P(C_6H_4Cl\text{-}p)_3$ and $2,6\text{-}Et_2C_6H_3NC$, the complexes are examples for kinetic accessibility *vs.* thermodynamic stability. Complexes of PPh_3, both mono- and disubstituted, in general appear to be the most stable, and complexes of $P(C_6H_4Cl\text{-}p)_3$, the least stable. The decomposition temperature range for $[Co(CNC_6H_4Cl\text{-}p)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]BF_4$ is lower than expected which correlates with the reaction showing unexpected tendency for monosubstitution, and that for $[Co(CNC_6H_4Me\text{-}o)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$ is unexpectedly high which may indicate exceptional stability for this complex.

Since higher ν(-N≡C) values indicate less π^*-acceptance and/or more σ-donation by the RNC and consequently more π^*-acceptance by the substituting PR_3, experimental ν(-N≡C) (Table I)—best measured from the strongest band in the solution spectra (2065, 2070, 2073; 2048, 2061, 2067; 2040, 2045, 2048 cm^{-1})—are consistent with decreasing $d_\pi \rightarrow \pi^*$ acceptance in the expected order: $P(C_6H_4Cl\text{-}p)_3 > PPh_3 > P(C_6H_4OMe\text{-}p)_3$. Electron withdrawing/donating abilities of the *para*-substituents are apparently transferred to coordinating ability of the triarylphosphine P-atom. For mull spectra (which are anticipatedly less accurate), ν(-N≡C) are also in the expected order, except for $[Co(CNC_6H_4Me\text{-}o)_3(PPh_3)_2]ClO_4$ (unusually low) and $[Co(CNC_6H_3Et_2\text{-}2,6)_3(PPh_3)_2]ClO_4$ (higher than $[Co(CNR)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$). For monosubstituted complexes, $[Co(CNC_6H_3Et_2\text{-}2,6)_4L]ClO_4$, ν(-N≡C) for the strongest solution band increases (2074, 2078, 2082 cm^{-1}) for L = $P(C_6H_4OMe\text{-}p)_3$, PPh_3, $P(C_6H_4Cl\text{-}p)_3$, respectively, clearly indicating increasing $d_\pi \rightarrow \pi^*$ acceptance by the respective triarylphosphine. Significant decrease in ν(-N≡C) for monosubstituted complexes compared to corresponding disubstituted is seen in solution data for the complete series $[Co(CNR)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]X$, $[Co(CNR)_4P(C_6H_4Cl\text{-}p)_3]X$ (2073, 2091; 2067, 2090; 2042, 2079 cm^{-1}), but is also evident in all other IR data. The triarylphosphines are significantly weaker π^*-accepting ligands than arylisocyanides.

An alternative interpretation of ν(-N≡C) values for $[Co(CNC_6H_4Me\text{-}o)_3(PPh_3)_2]ClO_4$ is possible, with both mull and solution values abnormally low. Complexes with $o\text{-}MeC_6H_4NC$ frequently show two strong IR bands instead of the one intense band, with weak shoulders, characteristic of most disubstituted arylisocyanide complexes of Co(I), so assignment of the strongest band *vs.* a shoulder can be ambiguous. The IR discussion was based on accepting the 2061vs bands for ν(-N≡C) in solution, instead of 2047s(sh), and 2039s in mull, instead of ~2067m (Table I). Perhaps the values: 2044, 2039, 2049 cm^{-1} (mull) and 2048, 2047, 2053 cm^{-1} (solution); or 2065, 2067, 2078 cm^{-1} (mull) and 2062, 2061, 2067 cm^{-1} (solution) should be compared as ν(-N≡C) for $[Co(CNC_6H_4Me\text{-}o)_3L_2]ClO_4$, L = $P(C_6H_4OMe\text{-}p)_3$, PPh_3, $P(C_6H_4Cl\text{-}p)_3$, respectively. Now both sets of data seem to challenge the expected (established) order of π^*-accepting ability: $P(C_6H_4Cl\text{-}p)_3 > PPh_3 > P(C_6H_4OMe\text{-}p)_3$ assuming analogous coordination geometry throughout. IR data could be suggesting a different structure, due possibly to steric hindrance from *ortho*-substitution, but this would be the only evidence for structural differences. In this investigation then, it may not be the complexes with $P(C_6H_4OMe\text{-}p)_3$ that are necessarily 'out of place', but rather complexes with PPh_3 that are unusual.

Electronic spectra for five-coordinate Co(I) complexes with organoisocyanide ligands have been interpreted as d → π^* charge transfer bands [10–12] or as one d–d band and charge transfer bands [13, 5]. If the first transition—which is most accurately measurable—is metal-to-ligand charge transfer into a π^* molecular orbital based primarily on the equa-

TABLE I. Triarylphosphine Complexes of Pentakis(arylisocyanide)cobalt(I).

Compound[a]	M. pt.[b] (°C)	Isocyanide IR[c]		Electronic spectra[d]
		Nujol	CH_2Cl_2	
$[Co(CNR_1)_3L_2^a]BF_4^f$	188–191	2015m(sh) 2059vs(br) 2069m(sh) ~2129w	~2020m(sh) 2065vs ~2120vs(sh)	365(34,500) 310(35,000) ≈283sh ≈270sh 240(82,000)
$[Co(CNR_1)_3L_2^b]ClO_4$	241–244	2025m(sh) 2060vs 2085m(sh) 2133w	~2015m(sh) ~2027w(sh) $\}^{e}$ 2070vs ~2117vw	360(31,000) 284(36,000) ≈243sh 232(75,000)
$[Co(CNR_1)_3L_2^c]BF_4^f$	225–230	~2005w(br) 2063s(v,br) ~2123w	~2015w ~2026w 2073s ~2126w	351(32,500) 294(37,000) ≈252sh 241(101,000)
$[Co(CNR_1)_4L^c]BF_4^f$	190–193	~2017vw(sh) 2088vs(br) 2122w ~2145vw(sh) 2173m	~2013vw(sh) ~2025vw(sh) $\}^{e}$ 2091vs(br) 2125w 2177m	342(34,000) ≈267sh ≈263sh $\}^{e}$ 243(90,000)
$[Co(CNR_2)_3L_2^a]ClO_4^f$	235–239	~2025w(sh) 2044s ~2065m(sh) ~2110vw(sh)	2024w 2048s 2062s(sh) ~2110w(sh)	354(31,000) 307(38,000) ≈283sh 245br(85,000)
$[Co(CNR_2)_3L_2^b]ClO_4$	214–216	~2020w(sh) 2039s ~2067m(sh) 2119w	~2022w(sh) 2047s(sh) 2061vs ~2105w(sh)	349(30,000) ~293sh 283(43,000) 236(64,500)
$[Co(CNR_2)_3L_2^c]ClO_4^f$	208–213	~2043m(sh) 2049s 2078s 2118w	~2023w(sh) ~2053m(sh) 2067s ~2111vw(sh)	341(28,000) 291(46,000) 247(94,000)
$[Co(CNR_2)_4L^c]ClO_4^f$	183–188	~2025vw(sh) ~2057vw(sh) 2075s(br) ~2089s(sh) 2122w 2172m	~2022vw(sh) ~2050vw(sh) 2090vs 2121w ~2135vw(sh) 2170m	334(26,000) ≈287sh ≈268sh 238(81,000)
$[Co(CNR_3)_3L_2^a]ClO_4^f$	174–177	~1995vw(br) 2034s ~2039s(sh) 2102w	~1995w 2040s(br) ~2099vw	354(14,000) ≈312sh ≈285sh 251(85,000)
$[Co(CNR_3)_4L^a]ClO_4^f$	143–145	~2000vw(sh) 2070s(br) 2104w 2156m	~2000vw 2074s 2105w 2159m	337(23,000) ≈270sh 255(82,000)
$[Co(CNR_3)_3L_2^b]ClO_4$	189–195	~1997m(br) 2046vs(br)	~1999w(br) 2045vs ~2110vw(sh)	350(12,000) 286(52,000) 249(59,000)
$[Co(CNR_3)_4L^b]ClO_4$	195–204	~2000vw 2069s(br) ~2083m(sh) 2109w 2159m	~1999vw 2078s 2108w ~2128vw(sh) 2160m	335(20,000) 264(58,000) ~234(58,000)

(continued overleaf)

TABLE I *(continued)*

Compound[a]	M. pt.[b] (°C)	Isocyanide IR[c]		Electronic spectra[d]
		Nujol	CH_2Cl_2	
$[Co(CNR_3)_3L_2^c]ClO_4$[f]	173–175	~1990w(br) 2042vs ~2057m(sh) ~2106w(sh)	~1990vw 2048vs(br) ~2105w(sh)	~343(12,000) ~291sh(48,000) 245(90,000)
$[Co(CNR_3)_4L^c]ClO_4$[f]	141–144	~1999vw 2067vs(br) 2079s(br) 2110w 2159m	~1999vw 2082s ~2111w(sh) ~2127vw(sh) 2163m	331(21,000) ≈267sh 244(77,000)

[a] $R_1 = C_6H_4Cl$-*p*, $R_2 = C_6H_4Me$-*o*, $R_3 = C_6H_3Et_2$-2,6; $L^a = P(C_6H_4OMe\text{-}p)_3$, $L^b = PPh_3$, $L^c = P(C_6H_4Cl\text{-}p)_3$. [b] Melting range (uncorrected), decompositon. [c] The ν(-N≡C) in cm^{-1}, s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. [d] The $\lambda_{max}(\epsilon)$ in mμ (nm), ϵ without Gaussian resolution. [e] May be considered as one band. [f] New complexes prepared in this study.

torial arylisocyanides [10], electronic data are in accord with $d_\pi \rightarrow \pi^*$ accepting ability: $P(C_6H_4OMe\text{-}p)_3 < PPh_3 < P(C_6H_4Cl\text{-}p)_3 \ll RNC$. Weaker π^*-accepting ligands substituted for one or two RNC force the remaining RNC to become stronger π^*-accepting, thereby lowering the energy (increasing λ_{max}) for the first charge transfer. The λ_{max} of the first transitions for $[Co(CNR)_3(PR_3)_2]X$ (365, 360, 351; 354, 349, 341; 354, 350, 343 mμ) are consistent with this intepretation. The λ_{max} of the first transitions for $[Co(CNC_6H_3Et_2\text{-}2,6)_4L]ClO_4$ (337, 335, 331 mμ) are also in anticipated sequence and significantly lower than values for the corresponding $[Co(CNC_6H_3Et_2\text{-}2,6)_3L_2]ClO_4$ complexes. This again indicates how the RNC ligands in complexes disubstituted with ligands that are weaker π^*-acceptors must undergo more $d_\pi \rightarrow \pi^*$ acceptance than in monosubstituted complexes.

Substitution reactions in $[Co(CNR)_5]X$, R = *p*-ClC_6H_4, *o*-MeC_6H_4, 2,6-$Et_2C_6H_3$; with triarylphosphines, PR_3, R = Ph, *p*-ClC_6H_4, *p*-$MeOC_6H_4$; yield mono- or disubstituted products as expected, except for appearance of $[Co(CNC_6H_4Cl\text{-}p)_4P(C_6H_4OMe\text{-}p)_3]BF_4$. The PPh_3 seems to show unexpectedly greater reactivity and stability in some of its complexes, relative to the other triarylphosphines, but the order of $d_\pi \rightarrow \pi^*$ accepting ability: $P(C_6H_4Cl\text{-}p)_3 > PPh_3 > P(C_6H_4OMe\text{-}p)_3$ anticipated from inductive effects of the substituents is observed in all cases except for ν(-N≡C) in $[Co(CNC_6H_4Me\text{-}o)_3(PPh_3)_2]ClO_4$, which indicates excessive π^*-acceptance.

References

1 C. A. L. Becker, *J. Inorg. Nucl. Chem., 42,* 27 (1980).
2 C. A. L. Becker, *J. Inorg. Nucl. Chem., 37,* 703 (1975).
3 C. A. L. Becker, *Synth. React. Inorg. Met.-org. Chem., 4,* 213 (1974).
4 S. Otsuka and M. Rossi, *Bull. Chem. Soc. Japan, 46,* 3411 (1973).
5 J. W. Dart, M. K. Lloyd, R. Mason, J. A. McCleverty and J. Williams, *J. Chem. Soc., Dalton Trans.*, 1747 (1973).
6 E. Bordignon, U. Croatto, U. Mazzi and A. A. Orio, *Inorg. Chem., 13,* 935 (1974).
7 C. A. L. Becker, *Synth. React. Inorg. Met.-org. Chem., 9,* 445 (1979).
8 C. A. L. Becker, *Inorg. Chim. Acta, 27,* L105 (1978).
9 Strem Catalog No. 10, Strem Chemicals, Inc., Newburyport, MA, 1981.
10 C. A. L. Becker, *J. Orgnomet. Chem., 104,* 89 (1976).
11 C. A. L. Becker, *Inorg. Chim. Acta, 36,* L441 (1979).
12 C. A. L. Becker, *Inorg. Nucl. Chem. Lett., 16,* 297 (1980).
13 Y. Dartiguenove, M. Dartiguenove and H. B. Gray, *Bull. Soc. Chim. Fr., 12,* 4225 (1969).