BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3411—3415 (1973)

Isocyanide-phosphine Complexes of Cobalt(I)

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(Received February 8, 1973)

Diamagnetic penta-coordinate Co(I) complexes of formula, $[Co(p\text{-}CH_3C_6H_4NC)_4(PPh_3)]X$ (**1**) and $[Co(p\text{-}CH_3C_6H_4NC)_3(PPh_3)_2]X$ (**2**) ($X=Cl^-, Br^-, I^-, ClO_4^-, BPh_4^-$) were obtained from $CoX(PPh_3)_3$ or $CoX_2(PPh_3)_2$. Their ^1H NMR spectra served to deduce the trigonal bipyramidal structure. The aromatic ring proton NMR spectra and the IR CN stretching absorptions of radial modes were discussed in terms of the dπ-pπ back bonding.

Recently isocyanide transition metal complexes have resumed considerable attention. Much of the impetus for the current research may stem from the unique property of isocyanide ligands which are capable of stabilizing a wider range of metal valency states than the isoelectronic molecule, carbon monoxide. Both the CN functional group and the substituent provide spectroscopic information valuable for structural assignments and for discussions on the nature of the metal-ligand bonding. Another interesting property is the reducing ability. Thus Co(I) complexes $[Co(RNC)_5]X$ are accessible from Co(II) halides by treating with an excess of RNC (R=alkyl or aryl). We were interested in comparing the structural chemistry in a series of $[Co(RNC)_{5-n}L_n]^+$. When our study was commenced no mixed complexes of this series were known except for $[Co(p\text{-}CH_3C_6H_4NC)_3(PPh_3)_2]^+$ which was reported without detail.[2] After completion of the work,[3] a paper describing $[Co(t\text{-}BuNC)_4AsPh_3]^+$, $[Co(t\text{-}BuNC)_3(PPh_3)_2]^+$ and others appeared,[4] but failed to report the preparation of $[Co(RNC)_4PPh_3]^+$. We were able to synthesize two types $[Co(RNC)_3(PPh_3)_2]^+$ and $[Co(RNC)_4PPh_3]^+$ ($R=p\text{-}CH_3C_6H_4-$) in addition to the known pentakis complex. Their stabilities and well-defined IR and NMR spectra enabled us to deduce their molecular structure to be isostructural (trigonal bipyramid). The series $[Co(RNC)_{5-n}L_n]^+$ (n=0, 1, 2) consitutes a system relevant for the study of the nature of isocyanide coordination to a low-valent metal. In view of the unusual ^1H NMR spectrum of the aromatic ring protons of free $p\text{-}CH_3C_6H_4NC$, which is due to the magnetic anisotropy of the C≡N– group, ^1H NMR spectra of the coordinated isocyanide deserve scrutiny.

Experimental

Materials. Commercial chemicals were used without further purification. *para*-Tolylisocyanide was prepared by the formamide–potassium *t*-butoxide method.[5] Compounds $[CoCl_2(PPh_3)_2]$[6] and $[CoCl(PPh_3)_3]$[7] were prepared by the procedures given in literature.

Instruments. The infrared spectra were measured with a Hitachi-Perkin Elmer Model 225 as Nujol mulls between CsI discs and in acetone solution in 0.1 mm NaCl cells. Proton nuclear magnetic resonance spectra were measured with a 100 MHz. Model JNM 4H-100 of JEOL using TMS as internal standard.

Syntheses of Compounds. *Tetrakis-*p*-tolylisocyanide-triphenylphosphinecobalt (I) chloride*: $CoCl(PPh_3)_3$ (1.2 g, 1.434 mmol) and *p*-tolylisocyanide (0.75 g, 6.4 mmol) were mixed in 100 ml of benzene at 5—10 °C under nitrogen atmosphere to give a yellow solution containing dark residue. The filtered solution was concentrated and treated with hexane affording a yellow powder. The powder was washed with hexane and dried under vacuum. Yield 0.6 g, 50% (calculated from the cobalt). Mp 80 °C (decomposition). Found: C, 71.27; H, 5.57; N, 6.59; Cl, 4.18%. Calcd for $C_{50}H_{43}ClN_4PCo$: C, 72.77; H, 5.25; N, 6.79; Cl, 4.30%.

*Tetrakis-*p*-tolylisocyanide-triphenylphosphinecobalt (I) Perchlorate*: A solution of $[Co(p\text{-}CH_3C_6H_4NC)_4PPh_3]Cl$ in cold ethanol

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[1] For review see L. Malatesta, *Progr. Inorg. Chem.*, **1**, 288 (1959); L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," J. Wiley, London (1969), pp. 131—143.

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and a solution of $[Co(p\text{-}CH_3C_6H_4NC)_4PPh_3]_2[CoCl_4]$ in cold methanol were treated separately with an excess of $NaClO_4$ affording the same compound. The product was washed with water and cold methanol, and dried under vacuum. Yellow crystals, mp 144—146 °C (decomposition). Λ_M=24.9 mho cm^2 mol^{-1} (10^{-3} M nitrobenzene solution at 21 °C). Found: C, 67.61; H, 5.19; N, 6.47; Cl, 4.02%. Calcd for $C_{50}H_{43}ClN_4O_4PCo$: C, 67.53; H, 4.87; N, 6.30; Cl, 3.99%.

Tetrakis-p-*tolylisocyanide-triphenylphosphinecobalt(I) Tetraphenylborate*: A solution of $[Co(p\text{-}CH_3C_6H_4NC)_4PPh_3]Cl$ in ethanol was treated at 10 °C with an excess of $NaBPh_4$ affording yellow crystals. The product was washed with cold ethanol and dried under vacuum. Mp 90—92 °C (decomposition). Λ_M=16.2 mho cm^2 mol^{-1} (10^{-3} M nitrobenzene solution at 21 °C). Found: C, 79.16; H, 5.62; N, 4.94%. Calcd for $C_{74}H_{63}BN_4PCo$: C, 80.14; H, 5.73; N, 5.05%.

Tetrakis-p-*tolylisocyanide-triphenylphosphinecobalt(I) Tetrachlorocobaltate* (II): A suspension of 3.5 g of $CoCl_2(PPh_3)_2$ (5.36 mmol) in 30 ml of acetone was treated with 4 g of *p*-tolylisocyanide (33.2 mmol) at room temperature. The mixture was stirred for a few minutes affording a yellow-green solution; green crystals were formed by addition of a small portion of hexane. The product was washed with acetone and dried under vacuum. Yield 1.7 g, 53.5% (based on the cobalt). Mp 106—108 °C (decomposition). Found: C, 67.59; H, 5.38; N, 6.06; Cl, 8.11%. Calcd for $C_{100}H_{86}Cl_4N_8P_2Co_3$: C, 67.47; H, 4.87; N, 6.29; Cl; 7.96%.

Tris-p-*tolylisocyanide-bis-triphenylphosphinecobalt(I) chloride*: Method (a): The above yellow solution obtained after the filtration of $[Co(p\text{-}CH_3C_6H_4NC)_4PPh_3]_2[CoCl_4]$ was treated with another portion of hexane affording yellow crystals. The product was washed with hexane and dried under vacuum. Yield 0.45 g, 8.7%. Method (b): A mixture of 0.5 g of $[Co(p\text{-}CH_3C_6H_4NC)_4PPh_3]Cl$ (0.61 mmol) and 0.2 g of PPh_3 (0.76 mmol) was dissolved in hot benzene; the filtered solution afforded yellow crystals on cooling. The product was washed with benzene and dried under vacuum. Mp 175 °C. Λ_M=25.8 mho cm^2 mol^{-1} (10^{-3} M nitrobenzene solution at 21 °C). Found: C, 73.87; H, 5.81; N, 4.31; Cl, 3.75%. Calcd for $C_{60}H_{51}ClN_3P_2Co$: C, 74.26; H, 5.30; N, 4.33; Cl, 3.65%.

Tris-p-*tolylisocyanide-bis-triphenylphosphinecobalt(I) bromide*: A mixture of 1.5 g of $CoBr_2(PPh_3)_2$ (2.09 mmol) and 1.5 g of *p*-tolylisocyanide (12.8 mmol) in 15 ml of acetone was stirred at room temperature to give a yellow solution and a small amount of green residue. The filtered solution was treated with hexane to afford yellow crystals. Yield 0.4 g, 18.8%. Mp 192—194 °C. Λ_M=24.7 mho cm^2 mol^{-1}. (10^{-3} M nitrobenzene solution at 21 °C). Found: C, 70.60; H, 5.32; N, 4.18; Br, 8.30%. Calcd for $C_{60}H_{51}BrN_3P_2Co$: C, 71.01; H, 5.07; N, 4.14; Br, 7.87%.

Tris-p-*tolylisocyanide-bis-triphenylphosphinecobalt(I) iodide*: A mixture of 1.5 g of $CoI_2(PPh_3)_2$ (1.8 mmol) and 1.1 g of $p\text{-}CH_3C_6H_4NC$ (9.4 mmol) in 20 ml of acetone was stirred at room temperature to give a brown solution. On being left to stand, brown crystals of the known Co(II) complex, $Co(p\text{-}CH_3C_6H_4NC)_4I_2$, were formed (1.0 g, 71% of the cobalt). The filtered solution was treated with hexane to afford orange crystals of the product. Yield 0.35 g, 18.3%. Mp 195 °C. Λ_M=21.9 mho cm^2 mol^{-1} (10^{-3} M nitrobenzene solution at 21 °C). Found: C, 66.31; H, 5.16; N, 3.87%. Calcd for $C_{60}H_{51}IN_3P_2Co$: C, 67.87; H, 4.84; N, 3.96%. The compound $Co(p\text{-}CH_3C_6H_4)_4I_2$ was identified by its elemental analysis and mp.

Tris-p-*tolylisocyanide-bis-triphenylphosphinecobalt(I) perchlorate*: Method (a): A solution of $[Co(p\text{-}CH_3C_6H_4NC)_3(PPh_3)_2]Cl$ in ethanol was treated at room temperature with an excess of $NaClO_4$, affording yellow-orange crystals. Method (b): A solution of $[Co(p\text{-}CH_3C_6H_4NC)_4PPh_3]_2[CoCl_4]$ in methanol was heated to boliling point and treated with an excess of $NaClO_4$; on cooling orange crystals of the product were formed. The product was washed with water and cold ethanol and dried under vacuum. Mp 205 °C. Λ_M= 24.7 mho cm^2 mol^{-1} (10^{-3} M nitrobenzene solution at 21 °C). Found: C, 69.12; H, 5.33; N, 4.09; Cl, 3.68%. Calcd for $C_{60}H_{51}ClN_3O_4P_2Co$: C, 69.67; H, 4.97; N, 4.06; Cl, 3.43%.

Tris-p-*tolylisocyanide-bis-triphenylphosphinecobalt(I) tetraphenylborate*: A solution of $[Co(p\text{-}CH_3C_6H_4NC)_3\ (PPh_3)_2]Cl$ in ethanol was treated at room temperature with an excess of $NaBPh_4$ to afford yellow crystals. The product was washed with ethanol and dried under vacuum. Mp 183 °C. Λ_M=15.7 mho cm^2 mol^{-1} (10^{-3} M nitrobenzene solution at 21 °C). Found: C, 81.03; H, 6.07; N, 3.36%. Calcd for $C_{84}H_{71}BN_3P_2Co$: C, 80.44; H, 5.71; N, 3.35%.

Results and Discussion

Preparation. Penta-coordinated Co(I) complexes of formula $[Co(RNC)_4P]X$ and $[Co(RNC)_3P_2]X$ (RNC=$p\text{-}CH_3C_6H_4NC$, P=PPh_3) were prepared from phosphine-halide complexes of Co(I) or Co(II). The complex $[Co(RNC)_4P]Cl$ is readily obtainable by treating the tetrahedral, green Co(I) complex, $CoCl(PPh_3)_3$,7) with a slight excess of *p*-tolylisocyanide (RNC/Co=4.5) in benzene at 5—10 °C; it was isolated in about 50% yield in the form of yellow powder, air-stable, moderately soluble in benzene and very soluble in polar solvents. The cation $[Co(RNC)_4P]^+$ was also produced by treating the tetrahedral Co(II) complex $CoCl_2(PPh_3)_2$6) with an excess of the isocyanide (RNC/Co=6.2) in acetone at room temperature, and isolated as the tetrachlorocobaltate salt. The complex salts $[Co(RNC)_4P]Y$ ($Y=ClO_4^-$, X^-, and BPh_4^-) were obtained by metathetic exchange of the chloride anion in an alcoholic solution. The IR and NMR spectra indicate that the tetrakis-isocyanide-mono-phosphine complex salts obtained by both methods are always contaminated with a small amount (10—25%) of impurities which are a mixture of $[Co(RNC)_3P]X$ and $[Co(RNC)_5]X$ in an approximately equimolar amount. All these compounds form yellow, air-stable crystals and behave in solution as uni-univalent electrolytes (Λ_M=16—25 mho cm^2 mol^{-1} in nitrobenzene at 21 °C). They melt with decomposition at relatively low temperature (80—146 °C) indicating thermal instability of the cation $[Co(RNC)_4P]^+$ in comparison with $[Co(RNC)_3P_2]^+$. Consistent with the formal oxidation state Co(I), they are diamagnetic, normal chemical shift values being observed for the proton NMR spectra.

The reaction of $CoCl_2(PPh_3)_2$ with $p\text{-}CH_3C_6H_4NC$ produced, besides $[Co(RNC)_4P]_2CoCl_4$, the tris-isocyanide-bis-phosphine complex $[Co(RNC)_3P_2]Cl$ in a low yield. The corresponding bromide complex $[Co(RNC)_3P_2]Br$ was similarly obtained by starting from $CoBr_2(PPh_3)_2$ and the isocyanide in a molar ratio of 1 : 6.1; in this case we were unable to detect the formation of the $[Co(RNC)_4P]^+$ cation.

The reaction of $CoI_2(PPh_3)_2$ with $p\text{-}CH_3C_6H_4NC$ in acetone proceeds differently producing only a small amount (18%) of the expected compound $[Co(RNC)_3P_2]I$, the predominant reaction product being the known Co(II) complex $Co(RNC)_4I_2$.[8] This result is in contrast to the successful reduction of $CoI_2(PR_3)_2$ with carbon monoxide leading to $CoI(CO)_2(PR_3)_2$.[9]

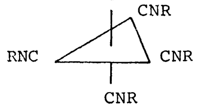
The cation $[Co(RNC)_4P]^+$ is readily transformed into a very stable cation $[Co(RNC)_3P_2]^+$ by reaction with an excess of phosphine. Thus $[Co(RNC)_3P_2]Cl$ was obtained by treating $[Co(RNC)_4P]Cl$ with PPh_3 in benzene as an insoluble product. The tris-isocyanide-bis-triphenylphosphine complexes were isolated in a form of orange yellow crystals, which are also diamagnetic and uni-univalent electrolytes in solution. They show high melting points (175—205 °C) and unusual stability against oxygen and reducing agents.

Failure of isolation of pure $[Co(RNC)_4P]X$ suggests the presence of equilibrium (1) in solution. Thus an acetone solution containing equimolar amounts of $[Co(RNC)_3P_2]ClO_4$ and $[Co(RNC)_5]ClO_4$ was prepared (at 22 °C) to follow reaction (1) with ^1H NMR.

$$2[Co(RNC)_4P]^+ \rightleftharpoons [Co(RNC)_3P_2]^+ + [Co(RNC)_5]^+ \qquad (1)$$

The spectrum indicates that $[Co(RNC)_4P]ClO_4$ is formed in about 70% yield within 5 min after the mixing and that the concentration of $[Co(RNC)_4P]ClO_4$ remains practically constant after 2 days. The equilibrium is apparently favorable for the formation of $[Co(RNC)_4P]^+$. However, an accurate measurement of this equilibrium would be hampered as the following observation implies. When $NaClO_4$ was added to an ethanol solution of $[Co(RNC)_4P]_2CoCl_4$ the least soluble complex $[Co(RNC)_3P_2]ClO_4$ (100% purity) was slowly precipitated out, whereas the addition of $NaClO_4$ to the cold (below 10 °C) methanol solution caused rapid precipitation of $[Co(RNC)_4P]ClO_4$ (about 90% purity).

Structure. The ^1H NMR spectrum of complex $[Co(CH_3C_6H_4NC)_5]ClO_4$[10] shows a singlet absorption at τ 7.58 (15 H) assignable to the methyl protons and a slightly broad singlet at τ 2.68 (20 H) due to the ring protons (Fig. 1). An infrared study on $[Co(C_6H_5NC)_5]ClO_4$[11] suggested the molecular structure to be trigonal bipyramid. Later the stereochemistry for $[Co(CH_3NC)_5]ClO_4$ was established by a single-crystal X-ray analysis.[12] By analogy the same stereochemistry may be assumed for $[Co(p\text{-}CH_3C_6H_4NC)_5]ClO_4$. Unexpectedly the ^1H NMR spectrum shows only one sharp singlet resonance for the methyl protons implying the stereochemical non-rigidity in solution[4] or the rapid ligand exchange.[4a]



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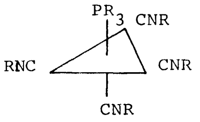

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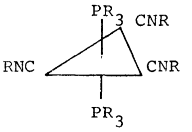

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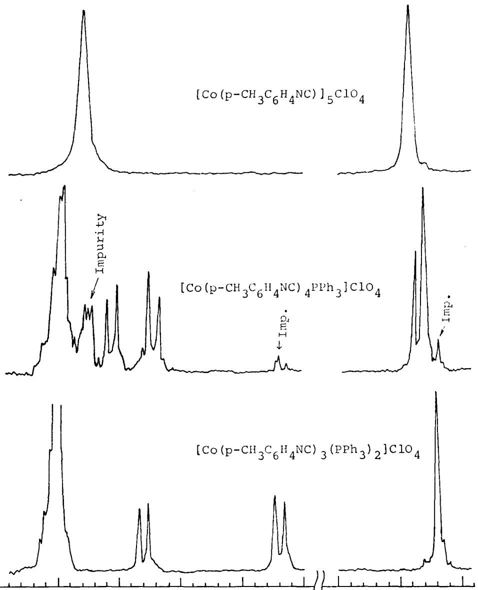

Fig. 1. NMR spectra of *p*-tolylisocyanide Co(I) complexes.

The NMR spectrum of $[Co(RNC)_3P_2]ClO_4$ shows a singlet at τ 7.80 (~9 H), and two doublet resonances with coupling constant 8 Hz due to ring protons at τ 4.28 (~6 H) and τ 3.17 (~6 H). In addition to resonances a complex peak (~30 H) appeared at τ 2.46, which is assignable to the ring protons of the triphenylphosphines (Fig. 1). The observation of one sharp singlet for the methyl protons suggests equivalence with respect to the isocyanide ligation. Consistent with this is the AB type resonance for the isocyanide ring protons. Thus the complex is deduced to have a trigonal bipyramidal structure with the two phosphine ligands at axial positions (III).

The NMR spectrum of the $[Co(RNC)_4P]^+$ cation was somewhat complicated owing to the contamination of $[Co(RNC)_5]^+$ and $[Co(RNC)_3P_2]^+$. Subtraction of the absorptions due to the latter two leaves a spectrum showing two singlets for the methyl protons at τ 7.68 (~9 H) and 7.62 (~3 H), and three doublet resonances for ring protons at τ 3.25 (*J* 8 Hz, 6 H), 2.90 (*J* 8 Hz, 6 H), and 2.70 (*J* 5 Hz, 4 H). Based on the coupling schemes and the intensity data, the ring proton resonances at τ 3.25 and τ 2.90 (12 H), a typical AB type spectrum for *para*-disubstituted aromatic ring protons, are assigned to those of three equivalent *p*-tolylisocyanide ligands and the one at τ 2.70 (~4 H) with *J*=5 Hz to the ring protons of the axial isocyanide ligand. The assignment is supported by the intensity ratio (3/1) for the methyl protons. Thus a trigonal bipyramidal structure (II) is also confirmed.

It may be of interest to examine the infrared spectra. Table 1 summarized the CN stretching absorptions measured in Nujol mull and in acetone solution. The CN stretching frequencies of $[Co(PhNC)_5]^+$ have been reported by Cotton and Parish,[11] who observed with a rock-salt prism two CN stretching bands corresponding

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[8] L. Malatesta, A. Sacco, and L. Mattiello, *Gazz. Chim. Ital.*, **83**, 499 (1953).

[9] M. Bressan, B. Corain, P. Rigo, and A. Turco, *Inorg. Chem.*, **9**, 1733 (1970).

[10] L. Malatesta and A. Sacco, *Z. Anorg. Allgem. Chem.*, **273**, 247 (1953).

[11] F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, **1960**, 1440.

[12] F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **4**, 318 (1965).

Fig. 2. IR spectra in the CN stretching region of *p*-tolylisocyanide Co(I) complexes. ——: [Co(*p*-$CH_3C_6H_4NC)_5$]ClO_4, ----: [Co(*p*-$CH_3C_6H_4NC)_4$ (PPh_3)]ClO_4, —·—: [Co(*p*-$CH_3C_6H_4NC)_3$ $(PPh_3)_2$]ClO_4.

to the E′ and A_2'' modes. Our solution spectrum (Fig. 2) for $[Co(RNC)_5]^+$ measured with a grating spectrometer also shows two strong CN bands as expected for the trigonal bipyramidal configuration. If $[Co(RNC)_4P]^+$ has C_{3v} symmetry, it will require three CN stretching bands ($2A_1$ and E). Two medium and one strong absorptions are observable; the intensity data suggest that the band at 2088 cm^{-1} corresponds to E mode vibration and the other two bands of medium intensity to A_1 mode. For the isostructural (C_{3v}) penta-coordinate carbonyl complexes of a formula $ML(CO)_4$, where M is Fe or Co and L is PR_3, SiR_3, SnR_3, GeR_3, *etc*, the carbonyl stretching band of the lowest frequency was assigned to E mode and the two higher bands to A_1 mode.[13] The cation $[Co(RNC)_3P_2]^+$ of D_{3h} symmetry should show only one CN stretching (E′). The strong band at 2067 cm^{-1} is presumably assignable to E′ mode vibration. In addition to the fundamental vibration a medium intensity band appears at 2035 cm^{-1}. Very weak additional bands also occur for $[Co(RNC)_4P]^+$ and $[Co(RNC)_5]^+$. Observation of more bands than required by the group theory is not uncommon for complexes ligated by CO, C≡N$^-$, or RNC.[14] A rationale could be a combination or overtone band whose intensity is gained by Fermi resonance with the fundamental, a deviation from the idealized symmetry[11] which renders the totally symmetric mode slightly infrared active, or a ^{13}C isotopic band. We have no proof at the moment for discernment of these effects. However, we regard the weak absorptions to be non-fundamental. Despite complications, an important feature is observable from Fig. 2. The most intense bands corresponding to either E or E′ mode are the radial modes, decrease in wave numbers along the series: $[Co(RNC)_5]^+ > [Co(RNC)_4P]^+ > [Co(RNC)_3P_2]^+$. The decrease in CN stretching frequencies is explicable in terms of the increase in back donation to the equatorial isocyanide ligands due to the increase in number of the more electron-donating PPh_3 molecule.[15a] This view receives further support from the NMR spectroscopic study below.

NMR Spectra. Free *p*-tolylisocyanide in $CDCl_3$ shows a sharp signal at τ 7.66 which is due to the methyl protons and a somewhat broader signal at τ 2.8 whose top splits slightly into doublet (*J* 2 Hz). In *para*-disubstituted benzenes additivity of the substituents effect on the chemical shift of the ring protons are generally recognized and interpreted in terms of pi-electron densities.[15,16] However, no report along this line has been made on the aromatic isocyanides. Further we are unable to locate the isocyanide group in the Hammett scale. As the electron-attracting property is apparent,[17] it is unlikely that CH_3– and C≡N– groups are comparable with respect to the overall electronic effect (mesomeric plus inductive effect). The proximity between the chemical shifts for H_o and H_m appears to be a fortuitous result derived from the substituent electronic effect plus the neighbor

TABLE 1. IR SPECTRA[a] OF THE COMPLEXES IN THE $\nu_{C\equiv N}$ STRETCHING REGION

Compound[b]	Nujol mull	Acetone solution
$[Co(RNC)_3P_2]Cl$	2083(vs), 2058(vs), 2035(vs)	2067(vs), 2035(m)
$[Co(RNC)_3P_2]Br$	2083(vs), 2060(vs), 2035(vs)	2067(bs), 2035(m)
$[Co(RNC)_3P_2]I$	2083(vs), 2059(vs), 2035(vs)	2067(vs), 2035(m)
$[Co(RNC)_3P_2]ClO_4$	2083(vs), 2057(vs), 2033(vs)	2067(vs), 2035(m)
$[Co(RNC)_3P_2]BPh_4$	2064(vs), 2030(s)	2067(vs), 2037(m)
$[Co(RNC)_4P]Cl$	2165(m), 2122(m), 2080(vs, br), 2030(m)	2169(m), 2122(m), 2088(vs), 2035(vw)
$[Co(RNC)_4P]ClO_4$	2167(m), 2118(m), 2083(vs, br), 2033(w)	2168(m), 2120(m), 2088(vs), 2035(vw)
$[Co(RNC)_4P]BPh_4$	2164(m), 2115(m), 2080(vs, br), 2033(m)	2168(m), 2115(m), 2088(vs), 2035(vw)
$[Co(RNC)_4P]_2[CoCl_4]$	2168(s), 2120(s), 2080(vs, br), 2035(m)	2168(m), 2120(m), 2087(vs), 2035(w)[c]
$[Co(RNC)_5]ClO_4$	2147(s), 2097(vs), 2035(m)	2146(s), 2105(vs)

a) vs=very strong, s=strong, m=medium, w=weak, vw=very weak, br=broad
b) R=$CH_3C_6H_4$ c) chloroform solution

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13) J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *J. Chem. Soc., Ser. A*, **1968**, 1199.

14) F. A. Cotton and F. Zingales, *J. Amer. Chem. Soc.*, **83**, 351 (1961).

15) J. S. Martin and B. P. Dailey, *J. Chem. Phys.*, **39**, 1722 (1963).

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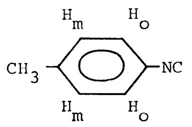
17) I. Ugi, "Isonitrile Chemistry," Academic Press, New York (1971), pp. 217—222.



magnetic anisotropy. Thus the known empirical equation (1)[15] for the substituent electronic effects, should be modified into Eq. (2) to accommodate the latter effect,[18-21] where σ_o is the chemical shift for H_o, σ_M the magnetic screening constant, and α determines the contribution.

$$\sigma_E = d_o(R_1) + \gamma(R_1)d_m(R_4) \qquad (1)$$

$$\sigma_o = \sigma_E + \alpha\sigma_M \qquad (2)$$

The chemical shift for H_m may be expressed by an equation analogous to Eq. (1), since the neighbor anisotropy decreases with the cube of distance.[22] An interesting fact is a nearly linear correlation between the NC stretching frequencies (E or E′ mode) and the chemical shifts of ring protons. The H_m or H_o proton shows a regular up-field shift in the series $[Co(RNC)_{5-n}P_n]^+$ (n=0, 1, 2). The $\Delta\nu$ (difference with respect to ν_{NC} of free p-$CH_3C_6H_4NC$) and $\Delta\tau$ (difference with respect to τ values of free p-$CH_3C_6H_4NC$) values for n=0, 1, 2 are respectively 26, 43, 64 (cm^{-1}) and −0.12, 0.45, 1.48 (ppm) for H_m; $\Delta\tau$ values for H_o are −0.12, 0.10, and 0.37 (*vide infra* for the assingment). These values reasonably satisfy relation $\Delta\tau = k\Delta\nu$. Since vibronic characteristics of a bond are not influenced by the magnetic property, the linear correlation implies either a negligible contribution of term $\alpha\sigma_M$ or a linear dependency of the magnetic term upon the electronic term σ_E. Although it is difficult to assess the absolute value of term $\alpha\sigma_M$ (and the two factors may be inseparable), a qualitative discussion can be given as follows. The magnetic field due to electric currents at an acetylenic or an isocyanide group[19,23] is expected to decrease with increase in electron drainage into the anti-bonding π orbital. This is understandable if we consider an effective overlap of pπ orbitals of a CN group with those of the aromatic ring, which occurs only with one of the two orthogonal pπ double bonds of the CN group. The overlap leads to a delocalized system $M{=}C{\equiv}N{=}$Aryl, thus relating to the effectiveness of the metal-ligand π-back bonding. The axial symmetry of a triple bond responsible for the magnetic anisotropy will readily be destroyed with inequal participation of the pπ bonds in the delocalized system $M{=}C{\equiv}N{=}$Aryl. Interaction of moiety M–C≡N– with the aromatic ring attached was demonstrated explicitly by unpaired spin density in some paramagnetic metal complexes.[24] Coefficient α decreases linearly with increase in dπ-pπ back bonding, and the abnormal ^1H NMR spectrum of p-$CH_3C_6H_4NC$ relaxes dramatically to that of $[Co(RNC)_4P]^+$ or $[Co(RNC)_3P_2]^+$ typical for *para*-disubstituted benzenes.

It is evident that the contribution of σ_M in free p-$CH_3C_6H_4NC$ renders the chemical shift for H_o higher than that for the coordinated isocyanide molecule bringing up the chemical shift of H_o near to that of H_m. If this is the case, the two ring proton resonances in $[Co(RNC)_4P]^+$ and $[Co(RNC)_3P_2]^+$ can be assigned; *i.e.*, the higher field resonance to H_m and the lower one to H_o. A slight downfield shift (−0.12 ppm relative to free(p-$CH_3C_6H_4NC$) observed for the ring protons in $[Co(p\text{-}CH_3C_6H_4NC)_5]^+$ is also explicable in terms of a σ-type donation from the isocyanide ligand to the Co(I) ion.

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