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Synthesis and Reactions of Dicobalt Octaisocyanide[1,2]

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Reactions of $Co_2(CO)_8$ with RNC (R = 2,6-$(CH_3)_2C_6H_3$, 2,4,6-$(CH_3)_3C_6H_2$, 2,6-$(CH_3)_2$-4-BrC_6H_2) at 80–90 °C gave dicobalt octaisocyanide (**1**). Compound **1** is linked by a metal–metal bond and two isocyanide bridges and each cobalt carries three terminal isocyanide groups both in the solid state and in solutions. The ^1H NMR spectra showed the presence of intra- and intermolecular ligand exchange between bridging and terminal isocyanide ligands and between coordinated and free isocyanide ligands, respectively. The σ–σ^* transition energy of the metal–metal bond was lower by ca. 4300 cm^{-1} than that of $Co_2(CO)_8$. No reduction of **1** with Na–Hg occurred, this being consistent with the observation of a high negative value of the redox potential at −2.1 eV. The reaction with halogens gave $Co(RNC)_4X_2$ (X = Br, I). Treatment with $AgPF_6$ in the presence of RNC gave $[Co(RNC)_5][PF_6]$.

Metal carbonyls have been well-known for a variety of metals. They are very important as catalysts for several organic synthesis. Dicobalt octacarbonyl, $Co_2(CO)_8$, has been used as a catalyst of the hydroformylation of olefins and the carbonylation of various organic compounds.[3] In addition to utility as a catalyst, $Co_2(CO)_8$ exhibits interesting and unusually complex characteristics in its structure.[4]

Isocyanide resembles carbon monoxide in forming a wide range of zerovalent transition-metal complexes, e.g., Ni, Pd, Pt, Cr, Mo, W, etc.[5] Recently Stone and his co-workers have reported that the reduction reaction of pentakis(*tert*-butyl isocyanide)cobalt(I) hexafluorophosphate with potassium amalgam gives dicobalt octakis(*tert*-butyl isocyanide), which was confirmed by X-ray structural determination.[6]

Independently we found that the substitution reaction of $Co_2(CO)_8$ with excess isocyanide produced the zerovalent cobalt complexes of isocyanides, which were interesting in comparison with $Co_2(CO)_8$. We describe the synthesis and some reactions of the zerovalent cobalt complexes of isocyanides. A preliminary account has appeared previously.[7]

Results and Discussion

Preparation of Dicobalt Octaisocyanide and Its Related Complexes. The methods developed for the preparation of zerovalent cobalt complexes of isocyanide, $Co_2(RNC)_8$, are (1) the carbon monoxide displacement reactions of $Co_2(CO)_8$ or $Co_4(CO)_{12}$ with isocyanides and (2) the reductive reactions of $Co(RNC)_4X_2$ with Na–Hg.

Interaction of an excess of 2,6-xylyl isocyanide with $Co_2(CO)_8$ at room temperature led to the formation of $[Co(2,6\text{-}(CH_3)_2C_6H_3NC)_5][Co(CO)_4]$, which is known as a product of the base reaction (eq 1). This type of complex

$$Co_2(CO)_8 + 5(2,6\text{-}(CH_3)_2C_6H_3NC) \rightarrow [Co(2,6\text{-}(CH_3)_2C_6H_3NC)_5][Co(CO)_4] + 4CO \quad (1)$$

has been reported by Sacco[8] and Hieber et al.[9] However, the reaction at 80–90 °C resulted in further evolution of carbon monoxide to give the dimeric, reddish brown complex **1a**, $Co_2[2,6\text{-}(CH_3)_2\text{-}C_6H_3NC]_8$, in relatively high yield (eq 2).

$$[Co(2,6\text{-}(CH_3)_2C_6H_3NC)_5][Co(CO)_4] + 3C_9H_9N \rightleftarrows Co_2[2,6\text{-}(CH_3)_2C_6H_3NC]_8 + 4CO \quad (2)$$

Reaction 2 is reversible. Thus, the reaction of **1a** with carbon monoxide (30 kg/cm^2) proceeded with disproportionation to Co(I) and Co(−I) to afford $[Co(2,6\text{-}(CH_3)_2C_6H_3NC)_5][Co(CO)_4]$. The corresponding zerovalent complexes from analogous reactions with mesityl and 4-bromo-2,6-xylyl isocyanides were also generated. Reaction of the polynuclear compound $Co_4(CO)_{12}$ with an excess of 2,6-xylyl isocyanide (more than 16 mol) at room temperature led to the fragmentation of the cobalt cluster and substitution again to give the neutral compound $Co_2[2,6\text{-}(CH_3)_2\text{-}C_6H_3NC]_8$, **1a**.

Table I. Infrared Spectra of a Dicobalt Octaisocyanide, $Co_2[2,6\text{-}(CH_3)_2\text{-}4\text{-}XC_6H_2NC]_8$

		IR, cm^{-1} [a]	
X	medium	terminal N≡C	bridging N=C
Br	Nujol	2106, 2056 sh, 2034	1687 sh, 1672
	C_6H_5Cl	2126, 2092 sh, 2055, 2027, 1997	1684, 1678
	CH_2Cl_2	2132, 2092, 2070 sh, 2036, 1999	1689, 1677
H	KBr	2121, 2072 sh, 2044	1689, 1677
	C_6H_5Cl	2128, 2106, 2065, 2029, 1996	1686, 1673
CH_3	KBr	2116 sh, 2060, 2013	1663, 1653
	C_6H_5Cl	2106, 2066, 2042, 2022, 1998 sh	1669

[a] sh = shoulder band.

When dichlorotetrakis(2,6-xylyl isocyanide)cobalt(II) was treated with sodium amalgam in THF at room temperature, compound **1a** was obtained in a fairly good yield (eq 3).

$$Co[2,6\text{-}(CH_3)_2C_6H_3NC]_4Cl_2 \xrightarrow[THF]{Na\text{-}Hg} Co_2[2,6\text{-}(CH_3)_2C_6H_3NC]_8 \quad (3)$$

Compounds of type **1** are reddish brown or brown crystalline solids and are air sensitive even in the solid state. They are soluble in aromatic hydrocarbons but poorly soluble in alcohols.

Structure and Spectral Properties. It is known that the structure of dicobalt octacarbonyl, $Co_2(CO)_8$, is of C_{2v} point group symmetry in the solid and involves a pair of bridging CO groups.[10] In solutions, the presence of two forms without bridging CO groups together with the CO bridging form mentioned above is evident in the infrared spectra.[4] Recently, the structure of dicobalt octakis(*tert*-butyl isocyanide), $Co_2[(CH_3)_3CNC]_8$, in the crystal has been determined by X-ray structural measurement, in which the Co_2C_8 skeleton closely resembles that of $Co_2(CO)_8$.[6] However, the characteristics of the structure have not been described in detail.

The infrared spectrum of **1a** in Nujol showed three absorptions assignable to the terminal isocyanide groups at 2106, 2056 (sh), and 2034 cm^{-1} and two due to the bridging isocyanide groups at 1687 (sh) and 1672 cm^{-1} (Figure 1). The spectrum in chlorobenzene at 23 °C showed five absorptions due to the terminal NC stretching at 2126, 2092 (sh), 2055, 2027, and 1997 cm^{-1} and two due to the bridging ones at 1684 and 1678 cm^{-1} (Figure 1). Upon cooling of the mixture to −80 °C the spectrum in C_6H_5Cl remained unchanged (Figure 1). The spectrum in CH_2Cl_2 also exhibited a pattern similar to that in C_6H_5Cl. The infrared spectra of the other zerovalent cobalt complexes were in agreement with that of **1a**.

The infrared spectra of these complexes are consistent with the structure of $Co_2(CN\text{-}t\text{-}Bu)_8$ as found by Stone et al.,[6] in which the cobalt atoms are linked by a metal-to-metal bond

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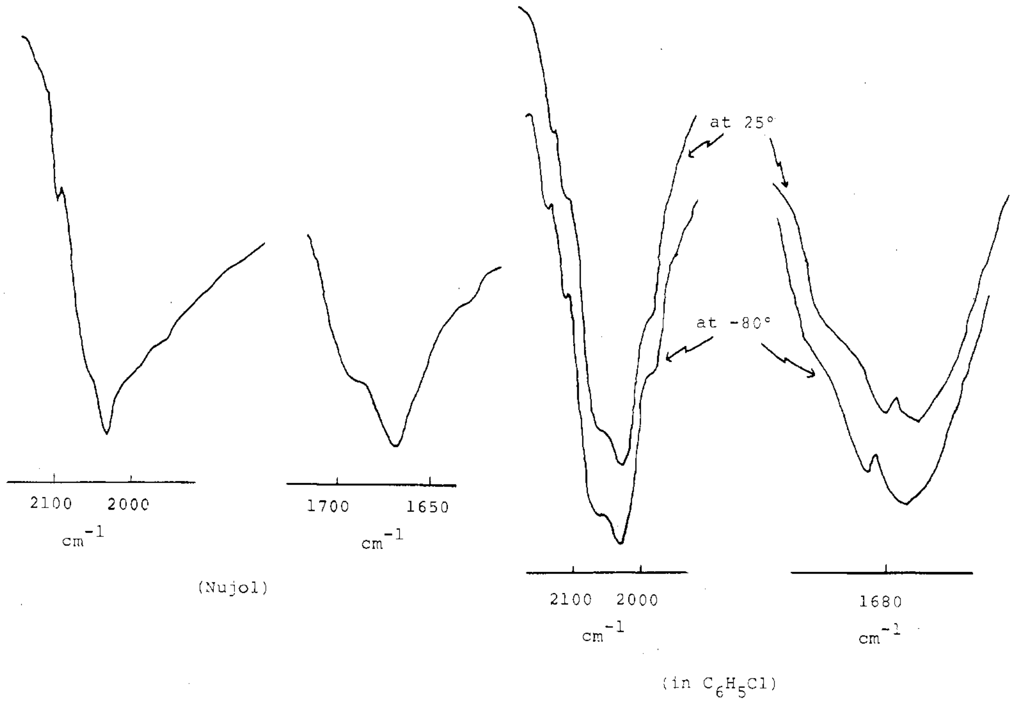
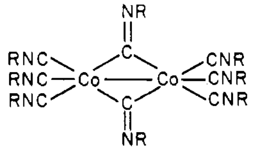


Figure 1. Infrared spectra of $Co_2(C_9H_9N)_8$ (Nujol and chlorobenzene) at +25 and -80 °C.

and two isocyanide bridges and each cobalt carries three terminal isocyanide groups.



A salient infrared spectral feature is that the CN bands ascribable to the bridging isocyanide ligands appear at lower energy regions than those of other complexes containing the bridging isocyanide ligand. Regions typical of M–M bridging ligands which have been observed in $(\eta\text{-}C_5H_5)_2Fe_2(CO)_3(CNR)$,[11] $(\eta\text{-}C_5H_5)_2Fe_2(CNR)_2(CO)_2$,[12] and $[\eta\text{-}C_5H_5Ni(CNR)]_2$[12b,13] are from 1704 to 1870 cm^{-1}. The low-energy absorption may result from coordination to low-valent metals.

One would have expected to see at least two sets of methyl resonances in the proton NMR spectrum. The spectrum of **1a** in C_6H_5Cl showed only one sharp singlet at δ 2.23.[14] The singlet broadened at low temperatures, but complete separation of the broad signal still was not observed at -90 °C. The spectrum in CD_2Cl_2 also showed only one singlet. Furthermore, the ortho-methyl resonances showed only one sharp singlet in the proton NMR spectra of **1b** and **1c**. Thus, these NMR spectra are very likely due to fluxionality between bridging and terminal isocyanide ligands in solution.

A similar phenomenon has been observed in the ^{13}C NMR spectra of $Co_2(CO)_8$, which exhibits one ^{13}C resonance between 20 and -150 °C.[4e,15]

Ligand exchange of **1a** with free 2,6-xylyl isocyanide in C_6H_5Cl was examined by variable-temperature NMR spectroscopy. The chemical shifts of free and coordinated isocyanides were independent of concentration within the limits of error (±0.2 Hz) at the line positions between 10 and 30% concentration. It was also shown that the chemical shift of free isocyanide was independent of temperatures between 23 and 150 °C. The chemical shifts of each ortho-methyl resonance of free 2,6-xylyl isocyanide and $Co_2[2,6\text{-}(CH_3)_2C_6H_3NC]_8$ in a mixed system are independent of the ratio of concentration, suggesting the absence of the ligand exchange. On warming of a mixed system, the two methyl resonances of the free coordinated isocyanides broadened and coalesced at 127 °C. The broad singlet sharpened at higher temperatures. This change is reversible.

Table II. Approximate Coalescene Temperatures, Rate Constants, and Free Energies for $Co_2[2,6\text{-}(CH_3)_2\text{-}4\text{-}XC_6H_2NC]_8$[a]

X	coalescence temp, °C	k, s^{-1}	ΔG^*, kcal/mol
Br	135	20.6	21.8
H	127	21.5	21.3
CH_3	118	24.0	21.2

[a] Measured in chlorobenzene.

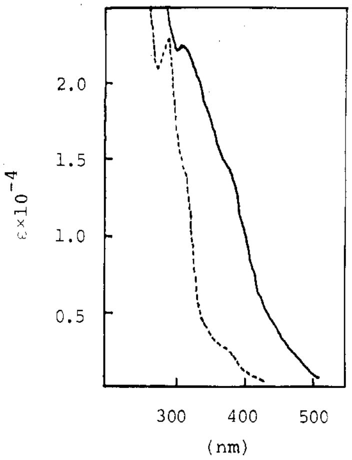


Figure 2. Electronic spectra of $Co_2(C_9H_9N)_8$ in cyclohexane at 298 K (—) and of $Co_2(CO)_8$[19] in 2-methylpentane at 50 K (---).

The rate of ^{14}CO exchange with $Co_2(CO)_8$ is immeasurably rapid at room temperature.[16] This low exchange rate for the isocyanide complexes is probably due to the steric effect of the bulky isocyanide ligands. The electronic effect for the coalescence temperatures was also observed. Table II shows approximate coalescence temperatures of para-substituted xylyl isocyanide complexes decrease in the order Br, H, CH_3. This is consistent with the decrease of π-acceptor ability of the isocyanide ligand.

The σ–σ^* assignment of the intense near-UV band in

$M_2(CO)_{10}$ (M = Mn, Tc, Re)[17,18] and $M_2(CO)_8$ (M = Co)[19] having a two-electron metal–metal σ bond has been widely adopted. The homolytic cleavage of the metal–metal bond is a very important photoprocess and is related to the σ–σ^* transition.

The electronic spectrum of **1a** in cyclohexane together with that of $Co_2(CO)_8$ is shown in Figure 2. The σ–σ^* transition of the bridged form of $Co_2(CO)_8$ in 2-methylpentane occurred at 35 460 cm^{-1} (282 nm). By analogy with the interpretation of the electronic spectrum of $Co_2(CO)_8$, the band at 31 200 cm^{-1} (320 nm) is assigned to the σ–σ^* transition. The energy of the σ–σ^* transition in **1a** is lower by 4260 cm^{-1} than that of the bridged species of $Co_2(CO)_8$.

Replacement of carbon monoxide by isocyanide results in increased localization of π-electron density on the cobalt atoms, which, in turn, would increase d_π–d_π repulsive interactions and weaken the metal–metal bond.

The effect of ligand substitution on the energy of the σ–σ^* transition has been well documented for the $Co_2(CO)_8$ dimer. The σ–σ^* transition decreased in energy from 28 570 cm^{-1} (350 nm) in nonbridged $Co_2(CO)_8$ to 27 780 cm^{-1} (360 nm) in $Co_2(CO)_6(P(OMe)_3)_2$ and 25 450 cm^{-1} (393 nm) in $Co_2(CO)_6(PPh_3)_2$.[19] This order is consistent with decrease of π-acceptor ability of the substituted ligands. A similar behavior in the σ–σ^* transition energy is observed in the isocyanide complexes $Co_2[4\text{-X-}2,6\text{-}(CH_3)_2C_6H_2NC]_8$, i.e., a shift from 31 800 cm^{-1}, for X = Br, to 31 200 cm^{-1}, for X = H, and 30 100 cm^{-1}, for X = CH_3. The plot of the σ–σ^* transition energy of **1** against the Hammett σ_p value of the para substituent of ligands is shown in Figure 3; a linear variation is observed. It can be concluded that the σ–σ^* transition energy is predominantly influenced by the capacity of the ligand to transfer electrons to the metals. An increase of electron density on the metal atoms would then shift σ–σ^* transition energy toward a smaller value.

Reactions. Dicobalt octacarbonyl, $Co_2(CO)_8$, is readily reduced with sodium amalgam to produce sodium tetracarbonylcobaltate, $NaCo(CO)_4$, which is an important precursor in the synthesis of various alkyl-, aryl-, and aroylcobalt complexes.[20] However, a similar reduction of dicobalt octaisocyanide **1** did not occur and **1** was recovered quantitatively. Metal anions with all isocyanide ligands have not been observed hitherto, although those having CO as the sole ligand have been isolated for the various metals.[21] This difference may be due to the steric hindrance of bulky isocyanide ligands and to the relatively high electron density on the cobalt atoms, arising from high electron-releasing ability of isocyanide. Thus, an increase of the electronic density on the metal atoms will cause the metal to accept an extra electron with more difficulty, and the reduction potential will have a more negative value. In the preliminary measurement of the reduction potential complex **1a** has a higher negative value (−2.1 eV) than does $Co_2(CO)_8$ (−0.4 eV[22]), suggesting difficulty of the reduction of **1a**.

By contrast, facile oxidation reactions of the isocyanide complexes can be expected because of the high electron density on the metals. The reactions of **1a** with bromine and iodine occurred readily at room temperature to afford $Co[2,6\text{-}(CH_3)_2C_6H_3NC]_4X_2$ (X = Br or I).

When **1a** was treated with $AgPF_6$ in the presence of 2,6-xylyl isocyanide at room temperature, a cleavage of the metal–metal bond occurred and complex **2**, $[Co(2,6\text{-}(CH_3)_2C_6H_3NC)_5][PF_6]$, was formed together with metallic silver (eq 4).

$$\mathbf{1a} + 2(2,6\text{-}(CH_3)_2C_6H_3NC) + 2AgPF_6 \rightarrow 2[Co(2,6\text{-}(CH_3)_2C_6H_3NC)_5][PF_6] + Ag \quad (4)$$

A similar type of oxidation of the zerovalent complexes $Cr(RNC)_6$ to $Cr(RNC)_6^{n+}$ (n = 1, 2) has been accomplished by using $AgPF_6$.[23] The infrared spectrum of **2** showed the terminal isocyanide groups at 2200 and 2213 cm^{-1}. The characteristic absorption bands due to the PF_6 anion were observed between 800 and 900 cm^{-1}. The NMR spectrum in $CDCl_3$ showed only one sharp singlet at δ 2.47 for the ortho-methyl protons.

It has been reported that the similar type of complex $[Co(t\text{-}BuNC)_5][PF_6]$ has a trigonal-bipyramidal structure.[24] Accordingly the structure of the aforementioned complexes is considered to be similar. The singlet due to the ortho-methyl resonances in the proton NMR spectrum would result from fluxionality between the two axial and the three equatorial ligands.

The reactions of **1a** with HBF_4 or $HClO_4$ took place in the presence of 2,6-xylyl isocyanide to give the similar type of complexes $Co[2,6\text{-}(CH_3)_2C_6H_3NC]_5X$ (X = BF_4, ClO_4). The NMR spectrum of each complex again showed only one singlet of the ortho-methyl protons. A resonance arising from metal hydride species was not observed.

Experimental Section

General Procedures and Physical Measurements. The reactions were carried out under an atmosphere of nitrogen. Melting points were taken on a Laboratory Devices Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Shimazu IR-27G obtained on JEOL C-60HL and Varian HA-100B spectrometers, using tetramethylsilane as a reference. Electronic spectra of the complexes were recorded using a Cary 17 spectrophotometer. The reduction potential was made at 13 °C using a spectrochemistry system. Dry DMF was used as a solvent with solutions 3 × 10^{-4} M in complex. Tetrabutylammonium perchlorate (0.2 M) was employed as the base electrolyte.

Materials. Isocyanides were prepared by procedures described in the literature.[25] Dicobalt octacarbonyl[26] and tetracobalt dodecacarbonyl[27] were prepared according to published methods. The other chemicals and solvents obtained commercially were reagent grade quality or equivalent. They were used as received.

Variable-Temperature NMR and Infrared Spectra Studies. $Co_2(RNC)_8$ or $Co_2(RNC)_8$ and RNC were dissolved in chlorobenzene and sealed under a nitrogen atmosphere in a 5-mm NMR tube. Temperatures were calibrated using the chemical shift separation obtained from an ethylene glycol solution at high temperatures and using that obtained from a methanol solution at low temperatures.

The cool-cell for measurement of infrared spectra at low temperatures was kindly supplied by Miss M. Goto of Tokyo University. Temperatures were calibrated by a thermocouple.

Preparation of $[Co(2,6\text{-}(CH_3)_2C_6H_3NC)_5][Co(CO)_4]$. To a solution of $Co_2(CO)_8$ (0.12 g, 0.35 mmol) in toluene (10 mL) was added 2,6-xylyl isocyanide (0.33 g, 2.5 mmol) at room temperature. After 20 min, the resulting yellow crystalline solid was filtered off and then washed with hexane; yield 0.28 g (93%). Anal. Calcd for $Co_2C_{49}H_{45}N_5O_4$: C, 66.44; H, 5.12; N, 7.91. Found: C, 66.31; H, 5.10; N, 7.95.

Preparation of $Co_2(RNC)_8$. Two representative reactions are described below.

(a) $Co_2[2,6\text{-}(CH_3)_2C_6H_3NC]_8$ from $Co_2(CO)_8$ and 2,6-Xylyl Isocyanide. A mixture of $Co_2(CO)_8$ (0.15 g, 0.44 mmol) and 2,6-xylyl isocyanide (0.56 g, 4.4 mmol) in toluene (10 mL) was heated at 80 °C for 1 h. The resulting reddish brown solution was chromatographed on alumina (the height of alumina was about 3 cm), benzene being used as an eluant. Removal of the solvent and crystallization of the residue from benzene–hexane at room temperature gave $Co_2[2,6\text{-}(CH_3)_2C_6H_3NC]_8$ (0.35 g, 68.5%; mp 194–196 °C (decomposed under nitrogen)) as reddish brown crystals. ^1H NMR (in C_6H_5Cl): δ 2.23 (s, CH_3). Anal. Calcd for $Co_2C_{72}H_{72}N_8$: C, 74.09; H, 6.22; N, 9.60. Found: C, 74.12; H, 6.21; N, 9.75. By using a strictly analogous procedure, 0.39 g (80%; mp 123 °C dec) of $Co_2[2,4,6\text{-}(CH_3)_3C_6H_2NC]_8$ was obtained from $Co_2(CO)_8$ (0.13 g, 0.38 mmol) and mesityl isocyanide (0.73 g, 5.0 mmol). ^1H NMR (in C_6H_5Cl): δ 2.35 (s, ortho CH_3), 2.11 (s, para CH_3). Anal. Calcd for $Co_2C_{80}H_{88}N_8$: C, 75.10; H, 6.93; N, 8.76. Found: C, 75.30; H, 6.82; N, 8.83.

A 0.42-g amount (67%; mp 139–142 °C dec) of $Co_2[2,6\text{-}(CH_3)_2\text{-}4\text{-}BrC_6H_2NC]_8$ was obtained from $Co_2(CO)_8$ (0.12 g, 0.35 mmol) and p-bromo-2,6-xylyl isocyanide (0.71 g, 3.4 mmol). ^1H NMR (in

Table III. Electronic Spectra of $Co_2[2,6-(CH_3)_2-4-XC_6H_2NC]_8$:[a] Effect of Ligand Substitution on the Energy of the the σ-σ^* Transition

X	σ-σ^*, cm^{-1}	ϵ, M^{-1} cm^{-1}
Br	31 800 (314 nm)	19 980
H	31 200 (320 nm)	22 000
CH_3	30 100 (334 nm)	21 300

[a] Measured in cyclohexane at 298 K.

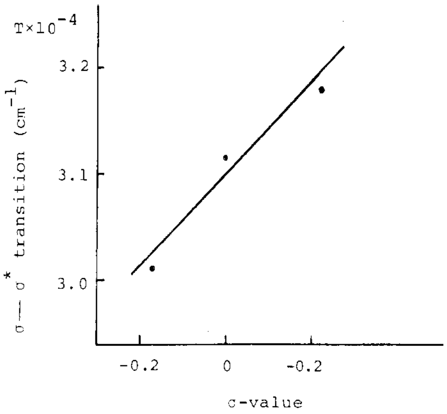


Figure 3. Correlation between the σ–σ^* transition energy and Hammett values (σ).

C_6H_5Cl): δ 2.18 (s, CH_3). Anal. Calcd for $Co_2C_{72}H_{64}N_8Br_8$: C, 48.08; H, 3.59; N, 6.23. Found: C, 48.27; H, 3.63; N, 6.45.

(b) $Co_2[2,6-(CH_3)_2C_6H_3NC]_8$ from $Co[2,6-(CH_3)_2C_6H_3NC]_4Cl_2$ and Sodium Amalgam. A mixture of dichlorotetrakis(2,6-xylyl isocyanide)cobalt(II) (1.1 g, 1.67 mmol), excess ~1% sodium amalgam, and THF (30 mL) was stirred at room temperature. The green color of the starting compound in solution became reddish brown. After 1 h, the THF solution was separated and then the solvent was removed in vacuo. The residue was chromatographed on alumina using benzene as an eluant. Removal of the solvent and crystallization of the residue from benzene–hexane gave the title compound (0.39 g, 40%).

Reactions of $Co_2[2,6-(CH_3)_2C_6H_3NC]_8$ (1a). (a) With Bromine. To a solution of **1a** (0.1 g, 0.086 mmol) in benzene (10 mL) was added bromine (0.016 g, 0.1 mmol) in benzene (5 mL) at 10 °C. After 1 h, the reaction solution produced a green crystalline product, $Co[2,6-(CH_3)_2C_6H_3NC]_4Br_2$, which was removed by filtration, washed with benzene, and then dried in vacuo (93%; mp 195–197 °C dec). IR (KBr): 2193 and 2134 (terminal NC) cm^{-1}. Anal. Calcd for $CoC_{36}H_{36}N_4Br_2$: C, 58.16; H, 4.88; N, 7.54. Found: C, 57.99; H, 4.84; N, 7.56.

(b) With Iodine. By using an analogous procedure to that of (a), $Co[2,6-(CH_3)_2C_6H_3NC]_4I_2$ (95%; mp 210–217 °C dec) was obtained as dark yellow crystalline solid from **1a** (0.1 g, 0.09 mmol) and iodine (0.025 mmol). IR (KBr): 2175 and 2118 (terminal NC) cm^{-1}. Anal. Calcd for $CoC_{36}H_{36}N_4I_2$: C, 51.63; H, 4.33; N, 6.69. Found: C, 51.53; H, 4.35; N, 6.63.

(c) With $AgPF_6$. To a solution of **1a** (0.25 g, 0.21 mmol) and 2,6-xylyl isocyanide (0.13 g, 1.0 mmol) in benzene (10 mL) was added $AgPF_6$ (0.11 g, 0.44 mmol) at room temperature. After 1 h, the solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2. The solution was filtered through the glass filter (3G3). Hexane was added and the solution was kept at room temperature. The complex $[Co(2,6-(CH_3)_2C_6H_3NC)_5][PF_6]$ (0.22 g, 61%; mp 126 °C dec) was obtained as the yellow crystals. IR (KBr): 2200 and 2113 (terminal NC) cm^{-1}. ^1H NMR (in $CDCl_3$): δ 2.47 (s, CH_3) and 7.1–7.3 (c, C_6H_3). Anal. Calcd for $CoC_{45}H_{45}N_5PF_6$: C, 62.86; H, 5.28; N, 8.15. Found: C, 63.12; H, 5.22; N, 8.59.

(d) With HBF_4. To a solution of **1a** (0.2 g, 0.17 mmol) in benzene (10 mL) was added 42% HBF_4 (0.5 mL) at room temperature. After 2 h, the resulting yellow crystals, $[Co(2,6-(CH_3)_2C_6H_3NC)_5][BF_4]$ (mp 118–120 °C dec), were filtered off. The crude product was recrystallized from CH_2Cl_2–ether at –30 °C. The complex obtained contained $^1/_2$ $(C_2H_5)_2O$. IR (KBr): 2198 and 2110 (terminal NC) cm^{-1}. ^1H NMR (in CD_2Cl_2): δ 1.14 (t, CH_3, 7 Hz), 2.43 (s, ortho CH_3), 3.43 (q, CH_2, 7 Hz), and 7.1–7.3 (c, C_6H_3). Anal. Calcd for $CoC_{47}H_{50}BF_4O_{1/2}$: C, 67.31; H, 6.01; N, 8.35. Found: C, 67.37; H, 5.93; N, 8.06.

(e) With $HClO_4$. By using an analogous procedure to that of (c), $[Co(2,6-(CH_3)_2C_6H_3NC)_5][ClO_4]$ (89%; mp 105–108 °C dec) was obtained as yellow crystals from **1a** (0.2 g, 0.17 mmol) and 60% $HClO_4$ (1 mL). IR (KBr): 2132 and 2089 (terminal NC) cm^{-1}. ^1H NMR (in $CDCl_3$): δ 2.46 (s, ortho CH_3), 7.20 (c, C_6H_3). Anal. Calcd for $CoC_{45}H_{45}N_5ClO_4$: C, 66.38; H, 5.57; N, 8.60. Found: C, 66.43; H, 5.74; N, 8.44.

(f) With Carbon Monoxide. A mixture of **1a** (0.3 g, 0.26 mmol) and 30 kg/cm^2 of CO in benzene (10 mL) in a 200-mL stainless steel autoclave was kept at 40 °C for 8 h. The mixture was cooled to room temperature. A yellow crystalline solid was observed, being identified as $[Co(2,6-(CH_3)_2C_6H_3NC)_5][Co(CO)_4]$ (0.12 g, 52%) by comparison of the infrared spectrum of this complex with that of the authentic sample.

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Registry No. **1a**, 64707-28-4; **1**(X = CH_3), 67662-51-5; **1**(X = Br), 67662-52-6; $[Co(2,6-(CH_3)_2C_6H_3NC)_2][Co(CO)_4]$, 64707-30-8; $Co_2(CO)_6$, 10210-68-1; $Co[2,6-(CH_3)_2C_6H_3NC]_4Cl_2$, 67662-53-7; $Co[2,6-(CH_3)_2C_6H_3NC]_4Br_2$, 64707-32-0; $Co[2,6-(CH_3)_2C_6H_3NC]_4I_2$, 64727-87-3; $[Co(2,6-(CH_3)_2C_6H_3NC)_5][PF_6]$, 67710-94-5; $[Co(2,6-(CH_3)_2C_6H_3NC)_5][BF_4]$, 67710-95-6; $[Co(2,6-(CH_3)_2C_6H_3NC)_2][ClO_4]$, 67710-70-7.

References and Notes

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