also thank J. Blank and R. Minard for obtaining mass spectra.

Registry No. 1, 106865-70-7; **2a**, 106865-74-1; **2b**, 93756-36-6; 3, 106865-71-8; **4a**, 106865-75-2; **4b**, 106865-72-9; **5**·PPN, 111583-10-9; **6**, 116184-62-4; **7**, 46134-83-2; **13**, 116184-67-9; **16a**, 116184-68-0; **16b**, 116184-70-4; **17**, 116184-69-1; [PPN][Cp(CO)$_2$Re—C{O}Tol], 116184-64-6; Cp′(CO)$_2$Mn=C{OMe}Tol, 116184-65-7; CO, 630-08-0.

Supplementary Material Available: Tables of anisotropic temperature factors, complete bond lengths and bond angles, and calculated hydrogen atom positions (4 pages); a list of structure factors (11 pages). Ordering information is given on any current masthead page.

Formation of Indolenine Derivatives from Dicobalt Octaisocyanide and Carbon Polyhalide[1]

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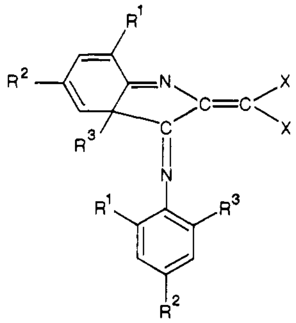
Reactions of dicobalt octaisocyanide with carbon tetrahalides (CCl$_4$ or CBr$_4$) gave indolenine derivatives and CoX$_2$(RNC)$_4$ (R = 2,6-Me$_2$C$_6$H$_3$, 2,4,6-Me$_3$C$_6$H$_2$, 2,6-Me$_2$-4-BrC$_6$H$_2$, 2,4-*t*-Bu$_2$-6-MeC$_6$H$_2$; X = Cl, Br). Benzyl bromide reacted with dicobalt octakis(2,6-xylyl isocyanide) to afford 1,6-diphenyl-2,3,4,5-tetrakis(*N*-2,6-xylylimino)hexane and CoBr$_2$(2,6-Me$_2$C$_6$H$_3$NC)$_4$. The reaction path for formation of indolenine derivatives is discussed.

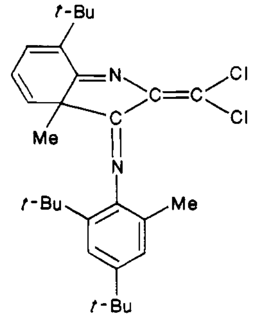
Dicobalt octacarbonyl has been widely used as a catalyst or precursor of a stoichiometric reagent in organic synthesis.[2] Dicobalt octaisocyanide also can be used in analogy to Co$_2$(CO)$_8$.[3] Previously we reported that Co$_2$(RNC)$_8$ behaves as a catalyst for the preparation of diiminoindazoles and indazolines from azo compounds and isocyanides.[4] In this paper, we describe the formation of indolenine derivatives from Co$_2$(RNC)$_8$ and carbon tetrahalides.

When carbon tetrachloride was added to a mixture of dicobalt octakis(2,6-xylyl isocyanide) and 2,6-xylyl isocyanide in benzene at room temperature, the reaction proceeded readily to give a green precipitate, identified as CoCl$_2$(2,6-Me$_2$C$_6$H$_3$NC)$_4$ (**2a**). Chromatography of the yellow solution gave indolenine derivative **1a**, identified by comparison with the melting point and infrared and ^{1}H NMR spectra of the authentic compound.[5]

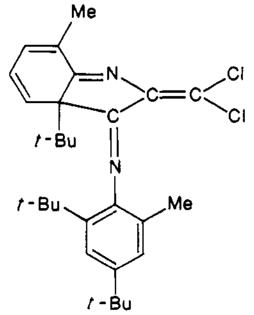
Similar reactions occurred to give the corresponding indolenine derivatives when Co$_2$(2,4,6-Me$_3$C$_6$H$_2$NC)$_8$ and Co$_2$(2,6-Me$_2$-4-BrC$_6$H$_2$NC)$_8$ were used. Carbon tetrabromide was also employed in the reaction with Co$_2$(2,6-Me$_2$C$_6$H$_3$NC)$_8$ in place of carbon tetrachloride. In the case of the reaction of dicobalt octakis(2,4-di-*tert*-butyl-6-methylphenyl isocyanide) with CCl$_4$, the cyclization is expected to occur in either ipso position occupied by the 2-*tert*-butyl or the 6-methyl group (1e-A or 1e-B). The



1a: R^1 = R^3 = Me, R^2 = H, X = Cl
b: R^1 = R^2 = R^3 = Me, X = Cl
c: R^1 = R^3 = Me, R^2 = Br, X = Cl
d: R^1 = R^3 = Me, R^2 = H, X = Br
e: R^1 = R^2 = *t*-Bu, R^3 = Me, X = Cl



1e-A



1e-B

^{1}H NMR spectrum showed two peaks at δ 1.28 and 2.13, each corresponding to three protons of the methyl groups. The resonance at δ 1.28 falls in the range of chemical shifts of methyl protons bound to a sp^3 carbon atom, suggesting the structure 1e-A. Thus, the position of cyclization seems to be controlled by steric factors.

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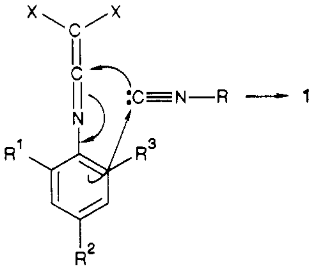
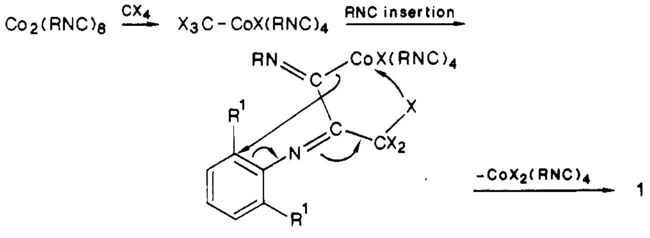
Two possible pathways are considered for the formation of indolenine derivatives. The first consists of the formation of a dihalocarbene (or a carbenoid) in a reaction $Co_2(RNC)_8$ with carbon tetrahalide, accompanied by addition of dihalocarbene to free or coordinated isocyanide to give the dihaloketenimine. The formation of carbene or carbenoid in the reaction of low-valent transition-metal complexes with polyhalogen compounds has been reported.[6] The reaction may be accomplished by a 1,4-cycloaddition of isocyanide to the ketenimine. The process

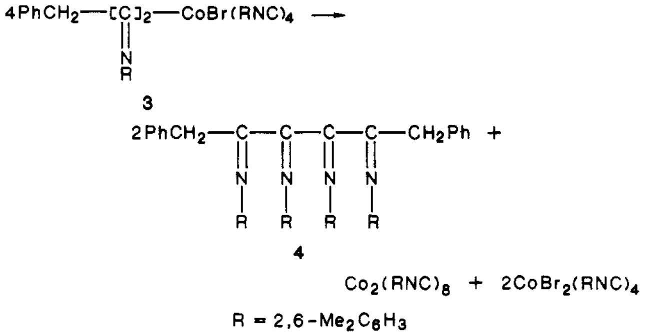


through the ketenimine intermediate has been reported by Obata et al.[5] The second possible process is an initial oxidative addition of the polyhalogen compound to $Co_2(RNC)_8$ and subsequent double insertion of isocyanide molecules into the cobalt–carbon bond affording an intermediate species. This type of successive insertion reaction is well-known.[7] The reaction is completed by an internal transfer of chlorine to the cobalt atom leading to cyclization.



In an attempt to investigate the path, the reaction of $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ with CCl_4 was carried out in the presence of cyclohexene. The only isolable compound was the indolenine derivative and 7,7-dichloronorcarane was not obtained. Since the reaction of cyclohexyl isocyanide with dichlorocarbene in the presence of water has been reported to give *N*-cyclohexyıdichloroacetoamide,[8] the reaction was also carried out in the presence of a small amount of water. If a ketenimine is a real intermediate in this reaction, *N*-2,6-xylyldichloroacetoamide should be isolated, but the only isolated organic compound was the indolenine derivative.

The reaction of $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ with $PhCH_2Br$ gave $CoBr_2(2,6\text{-}Me_2C_6H_3NC)_4$ (**2d**) and yellow crystals of (**4**), formulated as $(PhCH_2)_2(2,6\text{-}Me_2C_6H_3NC)_4$ on the basis of a mass spectrum. The infrared spectrum of 4 showed the presence of carbon–nitrogen double bonds near 1600 cm^{-1}. The ^1H NMR spectrum showed three relatively broad peaks for methyl and methylene protons at δ 1.67, 1.97, and 3.72. The ^{13}C NMR spectrum showed each two signals for ortho methyl and imino carbons: δ_c 18.15 and 18.56 for the former and δ_c 164.88 and 165.09 for the latter. The benzylic carbon appeared as a singlet at δ_c 40.80.



These spectroscopic data suggested that 4 is 1,6-diphenyl-2,3,4,5-tetrakis(*N*-2,6-xylylimino)hexane. This compound is considered to be the product of a coupling reaction of the intermediate **3** accompanied by a disproportionation reaction.

These results suggest that the second pathway is likely to be operative, although the first path through the ketenimine intermediate cannot be excluded completely. Since $CoX_2(RNC)_4$ is reduced with sodium amalgam to give $Co_2(RNC)_8$, the cobalt values can be recycled.

Experimental Section

Isocyanides and dicobalt octaisocyanide were prepared according to literature procedures.[3,9] All reactions were carried out under an atmosphere of nitrogen. Infrared spectra were recorded on a Shimazu spectrometer. ^1H NMR spectra were recorded on a Varian HA-100B spectrometer, and the ^{13}C NMR spectrum was measured on a JEOL GX-400 spectrometer, using tetramethylsilane as a reference. The mass spectra were measured on a Niphon denshi type JPS-1S mass spectrometer with a direct-inlet system.

Reaction of $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ with CCl_4. To a reddish brown solution of $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ (0.48 g, 0.41 mmol) and 2,6-xylyl isocyanide (0.32 g, 2.4 mmol) in benzene (10 mL) was added carbon tetrachloride (0.42 g, 3.4 mmol) in benzene (5 mL) at room temperature. After the solution was stirred for 2 h, the green precipitate (0.49 g, 91%) of $CoCl_2(2,6\text{-}Me_2C_6H_3NC)_4$ (**2a**) was filtered and identified by comparison with an authentic sample.[3] The yellow filtrate was chromatographed on alumina. Eluting with hexane gave unreacted isocyanide. The second elution with benzene gave a yellow solution. Removal of the solvent and crystallization of the residue from ether gave 0.13 g (46%) of the indolenine derivative **1a**, mp 137 °C (lit.[5] mp 135.5 °C); ^1H NMR ($CDCl_3$) δ 1.19 (s, Me), 1.93 (s, Me), 2.15 (s, 2Me), 5.5–6.4 (m, 3 H, olefinic protons), 6.85–7.2 (m, 3 H, aromatic protons); IR (KBr) 1687, 1630, 1590 cm^{-1} (C=N and C=C). Anal. Calcd for $C_{19}H_{18}N_2Cl_2$: C, 66.10; H, 5.25; N, 8.11; Cl, 20.54. Found: C, 66.06; H, 5.26; N, 8.06; Cl, 20.49.

The following compounds were obtained by a procedure similar to that described above.

1b (32%): mp 146–147 °C (lit.[5] mp 148 °C); ^1H NMR ($CDCl_3$) δ 1.17 (s, Me), 1.68 (s, Me), 1.91 (s, 2Me), 2.30 (s, Me), 5.35 (b, H), 6.21 (b, H), 6.85 (b, 2 H); IR (KBr) 1686, 1630 cm^{-1} (C=N and C=C). Anal. Calcd for $C_{21}H_{22}N_2Cl_2$: C, 67.56; H, 5.94; N, 7.50. Found: C, 68.15; H, 5.93; N, 7.66.

2b (93%): mp 234 °C dec; IR (KBr) 220 cm^{-1} (N≡C). Anal. Calcd for $C_{40}H_{44}N_4Cl_2Co$: C, 67.60; H, 6.24 N, 7.89. Found: C, 67.33; H, 6.89; N, 7.93.

1c (34%): mp 185 °C; IR (KBr): 1684, 1618 (sh), 1602 cm^{-1} (C=N and C=C). Anal. Calcd for $C_{19}H_{16}N_2Br_2Cl_2$: C, 45.36; H, 3.21; N, 5.57. Found: C, 45.45; H, 3.19; N, 5.41.

1d (52%): mp 121–122 °C (lit. mp 120 °C); IR (KBr) 1613, 1600 cm^{-1} (C=N and C=C). Anal. Calcd for $C_{19}H_{18}N_2Br_2$: C, 52.56; H, 4.71; N, 6.45. Found: C, 52.66; H, 4.68; N, 6.39. Complex 2d was identified as $CoBr_2(2,6\text{-}Me_2C_6H_3NC)_4$ (94%) by comparison with an authentic sample.[3,6]

1e (53%): mp 189 °C; ^1H NMR ($CDCl_3$) δ 0.83, 1.19, 1.30, 1.33 (s, *t*-Bu), 1.29, 2.13 (s, Me), 5.0–6.4 (c, olefinic protons), 7.0-7.3

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(aromatic protons); IR Nujol 1672, 1630 cm^{-1}. Anal. Calcd for $C_{33}H_{46}N_2Cl_2$: C, 73.18; H, 8.56; N, 5.17. Found: C, 73.20; H, 8.97; N, 5.44.

2e (91%): IR (KBr) 2196 cm^{-1} (C≡N). Anal. Calcd for $C_{64}H_{92}N_4Cl_2Co$: C, 73.40; H, 8.86; N, 5.35. Found: C, 73.11; H, 9.00; N, 5.55.

Reaction of $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ with Benzyl Bromide. To a solution of **1a** (0.48 g, 0.4 mmol) and 2,6-xylyl isocyanide (0.54 g, 4.12 mmol) in benzene (10 mL) was added benzyl bromide (0.33 g, 1.93 mmol) in benzene (5 mL) at room temperature. After 1 h, the green solid (0.58 g, 95.2%) of **2d** was filtered. The yellow filtrate was chromatographed on alumina. Eluting with hexane gave a pale yellow solution, from which 2,6-xylyl isocyanide was recovered. The second elution with benzene gave a yellow solution. The removal of the solvent and crystallization of the residue from hexane gave yellow crystals (0.36 g, 62.2%) of **4**: mp 153 °C; mass spectrum, *m/e* (mol wt 706.9); IR (KBr) 1670, 1630 cm^{-1} (C═N); ^{1}H NMR ($CDCl_3$) δ 1.67 (b s, Me), 1.97 (b s, Me), 3.72 (b s, CH_2), 6.5–7.6 (aromatic protons); ^{13}C NMR ($CDCl_3$) δ 18.15, 18.58 (CH_3), 40.80 (CH_2), 125.23, 125.65 (outer and inner orthocarbons in aromatic carbons), 134.17 (CH_2C), 123.30, 123.61, 126.61, 127.58, 127.82, 128.17, 129.70 (other aromatic carbons), 147.19 (outer and inner NC, accidental degeneracy), 164.86, 165.09 (outer and inner imino *C*).

Registry No. 1a, 57116-94-6; **1b**, 57116-97-9; **1c**, 116785-56-9; **1d**, 57116-95-7; **1e**, 116785-57-0; **2a**, 67662-53-7; **2b**, 116840-41-6; **2d**, 64707-32-0; **2e**, 116840-42-7; **4**, 64694-36-6; CCl_4, 56-23-5; CBr_4, 558-13-4; $CO_2(2,4,6\text{-}Me_3C_6H_2NC)_8$, 67662-51-5; $CO_2(2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2NC)_8$, 67662-52-6; $CO_2(2,6\text{-}Me_2C_6H_3NC)_8$, 64707-28-4; $2,4,6\text{-}Me_3C_6H_2NC$, 57116-96-8; $2,6\text{-}Me_2\text{-}4\text{-}BrC_6H_2NC$, 24139-49-9; dicobalt octakis(2,4-di-*tert*-butyl-6-methylphenyl isocyanide), 116862-77-2; 2,6-xylyl isocyanide, 2769-71-3; 2,4-di-*tert*-butyl-6-methylphenyl isocyanide, 98264-36-9; benzyl bromide, 100-39-0.

Communications

Conformationally Rigid η^3-Cyclopropenyl Complexes of Ruthenium(IV). Crystal and Molecular Structure of $[Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3Ph_3)Br_2]$

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Received June 24, 1988

Summary: Oxidative addition reactions of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}COD)X]$ (COD = 1,5-cyclooctadiene, X = Cl, Br) or tetrameric $[\{Ru(\eta^5\text{-}C_5Me_5)Cl\}_4]$ with triphenylcyclopropenyl halide salts affords high yields of the novel (η^3-cyclopropenyl)ruthenium(IV) complexes $[Ru(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_3Ph_3)X_2]$ (**5**, R = H, X = Cl; **6**, R = H, X = Br; **9**, R = Me, X = Cl). Metathetical replacement of chloride in **5** using bromide or iodide affords the dibromo and diiodo complexes **6** and **7**, respectively. Reaction of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}COD)Cl]$ with triphenylcyclopropenyl bromide affords the mixed chloro–bromo complex $[Ru(\eta^5\text{-}C_5R_5)(\eta^3\text{-}C_3Ph_3)ClBr]$ (**8**) as well as the dichloro and dibromo complexes **5** and **6**, respectively. The X-ray crystal structure of the bromo derivative **6** confirms the (η^3-cyclopropenyl)metal bonding mode in the solid state: orthorhombic, *Pbca*, *a* = 20.759 (7) Å, *b* = 15.656 (5) Å, *c* = 15.584 (3) Å, *V* = 5066 (2) Å^3, *Z* = 8, D_{calcd} = 1.78 g cm^{-3}. In contrast to their fluxional isoelectronic analogue $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3Ph_3)(CO)_2]$ (**2**), $^{13}C\{^1H\}$ and ^{1}H NMR studies of **5–9** establish the conformational rigidity of the cyclopropenyl ligand in solution. Estimates of maximum (≤32 kJ mol^{-1} for **2**) and minimum (≥62 kJ mol^{-1} for **8**) values of $\Delta G^{\ddagger}$ for cyclopropenyl rotation are made from ^{13}C NMR data.

The metallacyclobutadiene/η^3-cyclopropenyl valence isomeric relationship and its possible importance in alkyne metathesis continue to stimulate considerable interest.[2] The synthesis and crystallographic characterization of a number of transition-metal η^3-cyclopropenyl complexes[3,4] have led to the suggestion[4b] that certain structural features pertaining to the metal–C_3 interaction might be correlated with the presence or absence of NMR time scale fluxionality in solution. This is illustrated by the related complexes **1**[4b] and **2**-**4**.[3a] In the formally d^2 W(IV) complex **1** the cyclopropenyl ring is conformationally rigid on the NMR time scale in solution at ambient temperature, and the solid-state structure shows a shorter distance from the metal to the C_3 ring centroid (1.991 Å) than to the C_5 ring centroid (2.046 Å).[4b] Contrasting behavior is exhibited by the formally d^4 M(II) complexes **2–4**, in which the cyclopropenyl rings rotate rapidly on the NMR time scale at −80 °C and the solid-state structures of **2** and **3** exhibit shorter distances to the C_5 centroid (**2**, 1.997 Å; **3**, 1.999 Å) than to the C_3 centroid (**2**, 2.055 Å; **3**, 2.067 Å).[3a] Unfortunately, while compounds **1** and **2–4** were the closest analogues available for structural and spectroscopic comparison, it was not clear whether the difference in formal d-electron configuration between the metals, steric effects due to different coordination numbers at the metal or different ring substituents, and/or the apparently tighter binding of the C_3 ring in complex **1** were responsible for the difference in rotational barriers between **1** and **2–4**. Here we report the synthesis and characterization of conformationally rigid, isostructural, and isoelectronic analogues of complexes **2–4**, which provide compelling evidence that none of the above factors correlates directly

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