

future to propose some new results in this matter.

Appendix I

Each sample contains a mass m_D of Cu(II) dimer and a mass m_I of monomeric Cu(II) impurity. Let us note M_D , χ_g^D and χ_M^D and M_I , χ_g^I and χ_M^I the molar weights, the susceptibilities per gram, and the molar susceptibilities for the dimer and the impurity, respectively. The apparent susceptibility per gram χ_g of the sample is given by

$$\chi_g = \chi_g^D \frac{m_D}{m_D + m_I} + \chi_g^I \frac{m_I}{m_D + m_I}$$

and the apparent molar susceptibility χ_M is

$$\chi_M = \chi_M^D \frac{m_D}{m_D + m_I} + \chi_M^I \frac{M_D}{M_I} \frac{m_I}{m_D + m_I}$$

$$\chi_M = \chi_M^D (1 - \rho M_I/M_D) + \chi_M^I \rho$$

where $\rho = [m_I/(m_D + m_I)](M_D/M_I)$ can be determined for each sample from the low-temperature data, by assuming that χ_M^I follows a Curie law: $\chi_M^I = N\beta^2 g^2/4kT$. The ratio M_I/M_D can be determined only from the study of several samples by using a self-consistent procedure.

Appendix II

The calculation performed in this work is of extended Hückel type, with charge iteration on all the atoms and Madelung corrections. The actual terminal ligands are replaced by ammonia molecules. The atomic orbitals are simple Slater-type orbitals for hydrogen, nitrogen, oxygen, and copper except for metallic 3d orbitals for which we choose two-component orbitals. Orbital exponents for the nonmetallic atoms are chosen by using Slater's rules; 4s and 4p exponents for copper come from Burns,³¹ assuming a charge +1 on the transition ions in the complex. Exponents and relative weights for metallic 3d orbitals are taken from Richardson et al.³² The A_{μ} , B_{μ} , C_{μ} , and $g_{\mu\mu}$ parameters of the method are given in Table V. The K parameter of the Wolfsberg-Helmholz approximation is taken equal to 1.75.

Registry No. [Cu(C₆H₁₁NH₂)₂OH]₂(ClO₄)₂, 35637-92-4.

Supplementary Material Available: A listing of structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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Neutral and Cationic Rhodium Complexes of 2,6-Disubstituted Phenyl Isocyanides. Crystal Structure Analysis of Chlorotrakis(2,4,6-tri-*tert*-butylphenyl isocyanide)rhodium(I) and Estimation of Bulkiness in Isocyanide Substituent¹

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Received November 27, 1978

Reaction of [Rh(COD)Cl]₂ with 2,6-xylyl isocyanide gave Rh(C₉H₉N)₃Cl (**1a**) or [Rh(C₉H₉N)₄]Cl (**2a**), depending on the molar ratio of the starting compounds, whereas reaction with 2,4,6-tri-*tert*-butylphenyl isocyanide gave only Rh(C₁₉H₂₉N)₃Cl (**1g**). Treatment of **1g** with C₁₉H₂₉N in the presence of AgPF₆ led to formation of cationic [Rh(C₁₉H₂₉N)₄]PF₆ (**2g**). Compound **2a** has a tendency to self-associate in solution, but no association occurred in **2g**, due to steric hindrance of bulky isocyanide ligands. Compound **1g** crystallizes in space group *P* $\bar{1}$ with two molecules in a unit cell of dimensions $a = 14.750$ (5) Å, $b = 23.785$ (7) Å, $c = 10.193$ (5) Å, $\alpha = 104.71$ (2)°, $\beta = 104.65$ (2)°, and $\gamma = 71.59$ (1)°. Each phenyl ring of the isocyanide ligands lies in a plane perpendicular to the RhClC₃ plane. The steric bulkiness of isocyanides was estimated in terms of fan-shaped angles.

There has been recent interest in investigations of the ground- and excited-state physical and chemical properties of complexes in which metal(d⁸)-metal(d⁸) interactions are

present.² It has been reported that the planar rhodium isocyanide cations, Rh(RNC)₄⁺ (R = Ph, Et, CH₃, etc.), undergo self-association in solution presumably through direct met-

al-metal bonding.^{2a,3} We examined steric effects of the isocyanide substituent on such a metal-metal interaction. The complex, $[\text{Rh}(\text{C}_{19}\text{H}_{29}\text{N})_4][\text{PF}_6]$, having bulky 2,4,6-*tert*-butylphenyl isocyanide ligands, was found to have no tendency to self-associate. This was confirmed by an X-ray crystal structure analysis of neutral chlorotris(2,4,6-*tert*-butylphenyl isocyanide)rhodium(I). In connection with the above observation, we describe a consideration on estimation of steric bulkiness of isocyanide substituents. A preliminary account has appeared previously.⁴

Experimental Section

Melting points were taken on a Laboratory Devices Mel-Temp apparatus and were uncorrected. Infrared spectra were recorded on a Shimadzu IR-27G spectrophotometer. Proton magnetic resonance spectra were obtained on a JEOL C-60HL spectrometer, with tetramethylsilane as a reference. Electronic spectra were recorded by using Cary 14 and Shimadzu UV-180 spectrophotometers. Xylyl and mesityl isocyanide were prepared by a procedure described in the literature.⁵ $[\text{Rh}(\text{COD})\text{Cl}]_2$ was obtained by Chatt's method.⁶

Preparation of 2,4,6-Tri-*tert*-butylphenyl Isocyanide. The reaction was carried out under a nitrogen atmosphere. A mixture of 10 g (0.035 mol) of 2,4,6-tri-*tert*-butylphenylformamide⁷ and 180 mL of DMF was charged in three-necked round bottle. The solution consisting of 12 g (0.1 mol) of SOCl_2 and 50 mL of DMF was added dropwise to the mixture at -50°C . After the addition was complete, the bath was removed to allow the reaction temperature to rise to -30°C . After 30 min, 25 g (0.24 mol) of dry Na_2CO_3 was added to the mixture, and the flask contents were stirred for 2 h at room temperature. The reaction mixture was poured into ice water. The mixture was extracted with benzene, followed by washing with water and drying over anhydrous sodium sulfate. The mixture was purified by chromatography on alumina. Elution with benzene-hexane (1:4) gave a very pale orange solution. Crystallization by hexane gave the colorless title compound (6.13 g, 64.6%, mp 136°C): IR (CCl_4) 2098 cm^{-1} ; NMR (CDCl_3) δ 1.31 (s, *p-t*-Bu), 1.54 (s, *o-t*-Bu), 7.32 (s, aromatic proton); UV (CH_3CN) 218 (ϵ 5.44×10^3), 232 (ϵ 1.29×10^4), 251 (ϵ 9.8×10^3), 275 (ϵ 1.06×10^3), 284 (ϵ 9.5×10^2) nm. Anal. Calcd for $\text{C}_{19}\text{H}_{29}\text{N}$: C, 84.07; H, 10.77; N, 5.16. Found: C, 84.11; H, 10.82; N, 5.07.

Preparation of $\text{Rh}(\text{RNC})_3\text{X}$ and $[\text{Rh}(\text{RNC})_4][\text{PF}_6]$. The representative examples are described below.

$\text{Rh}(\text{C}_9\text{H}_9\text{N})_3\text{Cl}$. 2,6-Xylyl isocyanide ($\text{C}_9\text{H}_9\text{N}$) (0.14 g, 1.1 mmol) was added to a solution of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.1 g, 0.17 mmol) in CH_2Cl_2 (5 mL) at room temperature. After 30 min, hexane was added to the mixture to give the yellow crystalline compound $\text{Rh}(\text{C}_9\text{H}_9\text{N})_3\text{Cl}$ (**1a**): mp $178\text{--}180^\circ\text{C}$ dec; IR (KBr) $2145, 2105\text{ cm}^{-1}$; NMR (CDCl_3) δ 2.40 (s, 2 *o*- CH_3), 2.50 (s, 4 *o*- CH_3). Anal. Calcd for $\text{C}_{27}\text{H}_{27}\text{N}_3\text{ClRh}$: C, 61.13; H, 5.12; N, 7.90. Found: C, 60.97; H, 5.16; N, 8.21. Other related compounds were also prepared according to procedures similar to those described above.

$\text{Rh}(\text{C}_9\text{H}_9\text{N})_3\text{Br}$. mp $\sim 182^\circ\text{C}$ dec; IR (KBr) 2090 cm^{-1} . Anal. Calcd for $\text{C}_{27}\text{H}_{27}\text{N}_3\text{BrRh}$: C, 56.27; H, 4.72; N, 7.29. Found: C, 56.43; H, 4.73; N, 7.19.

$\text{Rh}(\text{C}_9\text{H}_9\text{N})_3\text{I}$. mp $\sim 160^\circ\text{C}$ dec; IR (KBr) 2088 cm^{-1} . Anal. Calcd for $\text{C}_{27}\text{H}_{27}\text{N}_3\text{IRh}$: C, 52.03; H, 4.37; N, 6.74. Found: C, 51.98; H, 4.37; N, 6.64.

$\text{Rh}(\text{C}_{10}\text{H}_{11}\text{N})_3\text{Cl}$. mp $206\text{--}209^\circ\text{C}$ dec; IR (KBr) 2108 cm^{-1} ; NMR (CDCl_3) δ 2.44 (s, 4 *o*- CH_3), 2.34 (s, 2 *o*- CH_3), 2.28 (s, 3 *p*- CH_3). Anal. Calcd for $\text{C}_{30}\text{H}_{33}\text{N}_3\text{ClRh}$: C, 62.78; H, 5.80; N, 7.32. Found: C, 62.79; H, 5.81; N, 7.39.

$\text{Rh}(\text{C}_{10}\text{H}_{11}\text{N})_3\text{Br}$. mp $204\text{--}206^\circ\text{C}$ dec; IR (KBr) $2095, 2053\text{ cm}^{-1}$; NMR (CDCl_3) δ 2.44 (b s, 6 *o*- CH_3), 2.29 (s, 3 *p*- CH_3). Anal. Calcd for $\text{C}_{30}\text{H}_{33}\text{N}_3\text{BrRh}$: C, 58.27; H, 5.38; N, 6.79. Found: C, 59.04; H, 5.51; N, 6.99.

$[\text{Rh}(\text{C}_{19}\text{H}_{29}\text{N})_4][\text{PF}_6]$. AgPF_6 (0.04 g, 0.16 mmol) was added to a mixture of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.04 g, 0.068 mmol) and 2,4,6-tri-*tert*-butylphenyl isocyanide (0.184 g, 0.68 mmol) in CH_2Cl_2 (5 mL) at room temperature. After 0.5 h, the precipitate was filtered off. *n*-Hexane was added to the filtrate to give the yellow complex $[\text{Rh}(\text{C}_{19}\text{H}_{29}\text{N})_4][\text{PF}_6] \cdot 1/2\text{CH}_2\text{Cl}_2$ (0.134 g, 72%, mp $275\text{--}278^\circ\text{C}$ dec): IR (KBr) $2148, 2129\text{ cm}^{-1}$; NMR (CDCl_3) δ 1.30 (s, *p-t*-Bu), 1.49 (b s, *o-t*-Bu), 5.29 (s, CH_2Cl_2), 7.32 (s, *m*- C_6H). Anal. Calcd for $\text{C}_{76.5}\text{H}_{77}\text{N}_4\text{PF}_6\text{ClRh}$: C, 66.77; H, 8.57; N, 4.07. Found: C, 66.26; H, 8.38; N, 3.93.

X-Ray Data Collection. Yellow needles of $\text{Rh}(\text{C}_{19}\text{H}_{29}\text{N})_3\text{Cl}$ were obtained by slow evaporation of a mixture of benzene and hexane. Preliminary photographs indicated that the complex crystallized in the triclinic system and the choice of the centrosymmetric triclinic space group $\bar{P}1$ was confirmed by the successful solution and refinement of the structure. Cell constants of $a = 14.750$ (5) Å, $b = 23.785$ (7) Å, $c = 10.193$ (5) Å, $\alpha = 104.71$ (2)°, $\beta = 104.65$ (2)°, and $\gamma = 71.59$ (1)° were determined from high-order reflections of a Rigaku four-circle automated diffractometer ($T = 23^\circ\text{C}$, λ 0.71069 Å). The calculated density of 0.981 g/cm^3 ($M_r = 952.706$, $V = 3223.4\text{ Å}^3$, and $Z = 2$) agrees well with 0.97 g/cm^3 measured by flotation in an aqueous solution of potassium iodide.

The crystal with the following six faces of the forms $\{001\}$, $\{010\}$, and $\{110\}$ was mounted such that the c axis was nearly parallel to the ϕ axis of a Rigaku four-circle diffractometer. The perpendicular distances to each of these faces were 0.63, 0.39, and 0.13 mm, respectively. Intensity data were collected by using graphite monochromatized Mo $K\alpha$ radiation and a 2θ - ω scan technique. The intensity of a reflection, I , and its esd, $\sigma(I)$, were calculated as outlined previously.⁸ Five-second stationary background counts were taken at the lower and upper limits of each scan. Three standard reflections were monitored before every 100 measurements. A total of 7819 independent intensities in the range $2\theta \leq 50^\circ$ were measured. The 6922 reflections for which $|F_o| > 3\sigma(|F_o|)$ were used in the solution and refinement of the structure. Intensities were corrected for Lorentz and polarization effects. The linear absorption coefficient is 3.65 cm^{-1} and the calculated transmission factors varied from 0.86 to 0.96. No correction for absorption was made.

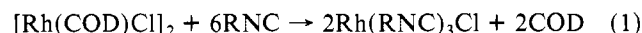
Solution and Refinement of Structure. The rhodium and chloride atoms were located from a three-dimensional Patterson map.⁹ A subsequent Fourier map phased by the two atoms gave the positions of all the remaining heavier atoms. Five cycles of a block-diagonal least-squares refinement of all the positional and isotropic thermal parameters resulted in the residual factors $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$ of 13.8 and 16.6%, respectively. Further six cycles of a refinement with anisotropic thermal parameters converged to $R_1 = 7.85\%$ and $R_2 = 12.16\%$. In these refinements, the $\sum w(|F_o| - |F_c|)^2$ function was minimized, where a weighting scheme of the form $w^{1/2} = 1.0$ for $|F_o| \leq 40.0$ and $w^{1/2} = 40.0/|F_o|$ for $|F_o| > 40.0$ was employed. No unusual trends were observed in an analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of either $(\sin \theta)/\lambda$ or $|F_o|$. In the final cycles of a refinement, no positional parameter exhibited shifts of more than 0.24 times its estimated standard deviation. The standard deviation of an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$, was 3.1, where the numbers of reflections (m) and refined parameters (n) were 6922 and 559, respectively. Anomalous dispersion effects for Rh and Cl were included in the calculation of F_c by using $\Delta f'$ and $\Delta f''$ calculated by Cromer.¹⁰ The atomic scattering factors were from the usual tabulation.¹¹ No attempt was made to locate hydrogen atoms.

A list of observed and calculated structure factor amplitudes is available.¹² The final atomic coordinates and thermal parameters are listed in Table I.

Results and Discussion

Preparation and Characterization of Rhodium Complexes.

When $[\text{Rh}(\text{COD})\text{Cl}]_2$ was treated with isocyanide having ortho-substituted phenyl groups (2,4,6-tri-*tert*-butylphenyl-2,4,6-mesityl or -2,6-xylyl) in 1:6 molar ratio at room temperature, the neutral yellow complex **1** was formed in quantitative yield (eq 1). The ^1H NMR spectra of **1** showed



the presence of two kinds of nonequivalent isocyanide groups in a 1:2 intensity ratio. The infrared spectra showed two absorption bands for the $\text{N}\equiv\text{C}$ stretching frequency, indicating a C_2 symmetry of the molecule. Bromide and iodide derivatives were obtained by metathetic reactions of **1** with potassium bromide or iodide. The neutral complex **1a** was readily converted to the known cationic complex **2a**, $[\text{Rh}(\text{C}_9\text{H}_9\text{N})_4]\text{Cl}$,¹³ when treated with 2,6-xylyl isocyanide (eq 2). On



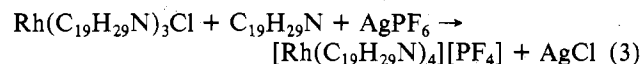
the other hand the reaction of **1g** with bulkier 2,4,6-tri-

Table I. Final Atomic Parameters and Standard Deviations^a

ATOM	X	Y	Z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Rh	0.2165(1)	0.2132(0)	0.0960(1)	3.4(0)	3.4(0)	3.7(0)	-0.9(0)	2.0(0)	-0.4(0)
Cl	0.3622(2)	0.2054(1)	0.1260(4)	4.1(1)	9.5(2)	12.1(2)	-2.6(1)	4.5(1)	-3.4(2)
N(1)	0.2626(5)	0.3368(3)	0.2962(7)	4.8(3)	3.1(3)	3.5(3)	-1.1(2)	1.3(2)	-0.4(2)
N(2)	-0.0668(5)	0.2275(3)	0.0422(7)	3.6(3)	4.3(3)	3.9(3)	-1.0(2)	1.8(2)	0.7(2)
N(3)	0.2694(5)	0.0871(3)	-0.0905(7)	4.1(3)	3.2(3)	3.7(3)	-0.8(2)	2.8(2)	-0.4(2)
C(1)	0.2131(6)	0.2916(4)	0.2169(9)	4.1(4)	4.1(4)	3.9(4)	-1.1(3)	1.1(3)	0.5(3)
C(2)	0.2018(6)	0.3912(3)	0.3885(8)	3.6(3)	3.1(3)	3.2(3)	-1.1(2)	1.9(3)	-0.5(3)
C(3)	0.2122(6)	0.3909(3)	0.5308(8)	4.5(4)	3.3(3)	3.3(4)	-1.2(3)	1.7(3)	0.1(3)
C(4)	0.2039(6)	0.4465(4)	0.6189(9)	4.6(4)	4.1(4)	3.9(4)	-1.1(3)	1.9(3)	0.1(3)
C(5)	0.1696(6)	0.5061(4)	0.5727(9)	4.7(4)	3.5(4)	4.2(4)	-0.9(3)	3.4(3)	-0.4(3)
C(6)	0.1851(6)	0.4961(4)	0.4323(9)	4.8(4)	3.9(4)	4.2(4)	-0.9(3)	3.3(3)	0.1(3)
C(7)	0.1912(6)	0.4422(3)	0.3377(8)	4.2(4)	3.4(3)	3.3(3)	-0.8(3)	2.3(3)	0.2(3)
C(8)	0.0836(6)	0.2211(3)	0.0630(8)	4.6(4)	3.4(3)	3.3(3)	-0.9(3)	2.8(3)	0.1(3)
C(9)	-0.1018(6)	0.2406(3)	0.0280(8)	3.1(3)	3.5(3)	3.5(3)	-0.8(2)	1.7(3)	0.0(3)
C(10)	-0.1614(6)	0.2709(3)	-0.0788(9)	4.2(4)	3.6(4)	3.6(4)	-1.1(3)	2.0(3)	0.4(3)
C(11)	-0.2604(6)	0.2876(4)	-0.0825(9)	3.9(4)	4.4(4)	4.2(4)	-0.7(3)	1.1(3)	0.6(3)
C(12)	-0.3005(6)	0.2740(4)	0.0119(9)	3.5(4)	4.4(4)	4.2(4)	-0.8(3)	2.4(3)	-0.1(3)
C(13)	-0.2398(6)	0.2467(4)	0.1097(9)	3.4(3)	4.1(4)	4.2(4)	-0.9(3)	1.5(3)	0.3(3)
C(14)	-0.1400(6)	0.2235(3)	0.1204(9)	4.0(4)	3.8(4)	3.1(3)	-0.9(3)	1.7(3)	0.5(3)
C(15)	0.2448(6)	0.1333(4)	-0.0227(9)	3.7(4)	4.1(4)	3.8(4)	-1.0(3)	2.5(3)	0.3(3)
C(16)	0.3000(5)	0.0328(3)	-0.1805(8)	3.8(3)	3.1(3)	3.2(3)	-0.7(2)	3.0(3)	-0.3(3)
C(17)	0.3277(6)	-0.0207(3)	-0.1311(8)	3.8(3)	3.4(3)	3.3(3)	-0.6(3)	2.3(3)	0.5(3)
C(18)	0.3531(6)	-0.0756(4)	-0.2252(9)	4.4(4)	4.0(4)	3.6(4)	-1.1(3)	3.3(3)	0.1(3)
C(19)	0.3511(6)	-0.0744(3)	-0.3645(9)	3.8(4)	3.7(4)	4.2(4)	-0.6(3)	4.0(3)	-0.2(3)
C(20)	0.3278(6)	-0.0203(4)	-0.4081(9)	4.8(4)	4.0(4)	3.8(4)	-0.9(3)	3.5(3)	0.4(3)
C(21)	0.3025(6)	0.0349(3)	-0.3175(9)	4.5(4)	3.3(3)	3.6(4)	-0.7(3)	2.7(3)	0.5(3)
C(22)	0.2319(8)	0.3340(4)	0.5491(10)	8.0(6)	4.8(5)	3.4(4)	-2.2(4)	0.6(4)	0.9(3)
C(23)	0.3240(10)	0.2885(5)	0.5512(13)	8.7(8)	5.2(6)	6.9(7)	1.1(5)	0.7(6)	2.1(5)
C(24)	0.1436(12)	0.3061(6)	0.5325(14)	12.2(10)	7.5(7)	7.7(7)	-5.8(7)	2.9(7)	2.0(6)
C(25)	0.2446(12)	0.3497(6)	0.7518(12)	14.1(11)	7.3(7)	3.9(5)	-2.9(7)	1.9(6)	2.4(5)
C(26)	0.1895(8)	0.4409(4)	0.1852(9)	7.5(6)	5.3(5)	3.1(4)	-1.9(4)	2.2(4)	0.7(3)
C(27)	0.2877(9)	0.3986(6)	0.1435(11)	7.0(6)	8.7(7)	4.3(5)	-2.4(5)	6.6(4)	-0.5(5)
C(28)	0.1002(9)	0.4214(6)	0.0903(11)	7.7(7)	9.7(8)	4.1(5)	-3.3(6)	-2.3(4)	2.2(5)
C(29)	0.1629(12)	0.5048(6)	0.1623(13)	15.1(12)	6.7(7)	5.2(6)	-3.9(7)	5.5(7)	2.1(5)
C(30)	0.1771(9)	0.5609(4)	0.6749(11)	8.5(7)	4.2(5)	5.7(5)	-1.8(4)	6.9(5)	-1.4(4)
C(31)	0.2368(18)	0.5525(7)	0.8147(16)	24.2(21)	6.9(8)	5.9(8)	-4.5(11)	-3.8(10)	-2.3(6)
C(32)	0.2025(17)	0.6067(6)	0.6238(19)	24.0(20)	6.1(7)	11.7(11)	-8.6(10)	20.7(12)	-3.2(7)
C(33)	0.0739(14)	0.5842(9)	0.6912(29)	10.0(11)	11.9(13)	26.4(25)	-2.2(10)	25.0(14)	-10.4(15)
C(34)	-0.1199(7)	0.2852(4)	-0.1887(10)	5.3(5)	5.1(5)	4.4(4)	-1.4(4)	2.0(3)	1.7(4)
C(35)	-0.2055(9)	0.3158(6)	-0.2971(13)	7.1(7)	10.9(9)	6.6(7)	-1.7(6)	0.3(5)	5.9(7)
C(36)	-0.0611(9)	0.2263(5)	-0.2683(11)	8.2(7)	6.5(6)	4.6(5)	-1.0(5)	7.0(5)	0.3(4)
C(37)	-0.0566(9)	0.3291(5)	-0.1199(13)	7.8(7)	5.9(6)	7.2(6)	-3.3(5)	3.0(5)	1.7(5)
C(38)	-0.0748(7)	0.1870(4)	0.2315(10)	4.6(4)	4.5(4)	5.4(5)	-0.8(3)	2.6(4)	1.8(4)
C(39)	-0.0113(9)	0.1252(5)	0.1601(14)	8.1(7)	4.9(5)	8.0(7)	0.3(5)	6.3(6)	1.6(5)
C(40)	-0.0165(8)	0.2244(5)	0.3403(11)	6.1(6)	7.9(7)	4.3(5)	-2.5(5)	-1.7(4)	1.7(4)
C(41)	-0.1367(8)	0.1711(6)	0.3117(12)	6.7(6)	8.4(7)	6.5(6)	-1.7(5)	4.2(5)	3.9(5)
C(42)	-0.4113(6)	0.2951(4)	0.6050(11)	3.5(4)	5.9(5)	5.7(5)	-1.3(3)	1.6(3)	0.6(4)
C(43)	-0.4530(10)	0.3602(6)	-0.0181(24)	5.8(7)	6.6(8)	23.7(20)	1.6(6)	10.1(9)	5.2(10)
C(44)	-0.4573(9)	0.2551(7)	-0.1199(19)	4.6(6)	11.1(10)	12.8(11)	-3.1(6)	-1.3(6)	-2.7(9)
C(45)	-0.4356(10)	0.2879(10)	0.1349(18)	4.9(6)	22.1(19)	9.6(10)	0.3(9)	7.5(6)	3.5(11)
C(46)	0.2802(8)	0.0946(4)	-0.3685(10)	7.1(6)	4.0(4)	4.6(5)	-1.4(4)	3.6(4)	1.1(3)
C(47)	0.1715(9)	0.1334(5)	-0.3585(13)	6.0(6)	5.1(5)	8.1(7)	0.3(4)	2.3(5)	2.6(5)
C(48)	0.3566(9)	0.1245(5)	-0.2818(12)	7.6(6)	5.3(5)	7.2(6)	-3.0(5)	3.5(5)	1.4(5)
C(49)	0.2905(11)	0.0824(5)	-0.5210(12)	12.0(10)	6.4(6)	4.8(5)	-2.5(6)	6.2(6)	1.8(5)
C(50)	0.3295(7)	-0.0224(4)	0.0195(9)	5.9(5)	4.9(4)	3.8(4)	-1.1(4)	3.7(3)	0.6(3)
C(51)	0.4022(8)	0.0110(5)	0.1189(10)	6.8(6)	8.1(7)	3.7(4)	-2.6(5)	-0.1(4)	0.5(4)
C(52)	0.2264(8)	0.0043(5)	0.0561(12)	6.1(6)	8.0(7)	5.7(5)	-1.5(5)	7.4(4)	0.6(5)
C(53)	0.3652(10)	-0.0903(5)	0.0435(12)	10.7(9)	5.2(5)	5.8(6)	-0.8(5)	6.2(6)	2.5(5)
C(54)	0.3787(7)	-0.1324(4)	-0.4682(10)	5.3(5)	4.4(4)	4.8(5)	-1.0(3)	4.8(4)	-0.9(3)
C(55)	0.2947(10)	-0.1333(6)	-0.5989(14)	9.0(8)	7.4(7)	6.1(6)	-0.5(6)	-0.5(6)	-2.2(5)
C(56)	0.417(10)	-0.1353(6)	-0.5115(17)	8.8(8)	6.5(7)	12.6(10)	-1.9(6)	18.3(8)	-2.4(6)
C(57)	0.3932(10)	-0.1902(4)	-0.4117(13)	9.2(7)	3.7(4)	8.2(7)	-1.4(4)	8.1(6)	-0.4(4)

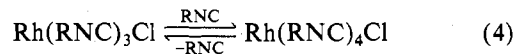
^a The form of the anisotropic thermal parameters is $\exp[-1/4(B_{11}h^2a^* + B_{22}k^2b^* + B_{33}l^2c^* + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}kib^*c^*)]$.

tert-butylphenyl isocyanide (C₁₉H₂₉N) led to recovery of the starting compound. The cationic complex **2g**, [Rh(C₁₉H₂₉N)₄][PF₆], was isolated as a PF₆ salt by treating **1g** with C₁₉H₂₉N in the presence of AgPF₆ (eq 3).



In the ¹H NMR spectra of **1** and **2** the resonances due to the *o*-methyl groups of **1a** and **2a** showed the sharp singlets δ 2.40 (2 CH₃) and 2.50 (4 CH₃) for **1a** and δ 2.46 for **2a**, respectively, but those due to the ortho *tert*-butyl groups of **1g** and **2g** showed slightly broad singlets, δ 1.29 and 1.54 for **1g** and δ 1.49 for **2g**, respectively. The ¹H NMR spectrum of a mixture of **1g** and C₁₉H₂₉N in a 1:1 molar ratio showed the presence of only one kind of isocyanide. The electronic spectrum of the aforementioned 1:1 mixture in CH₃CN was closely similar to that of **2g**, suggesting the presence of the cationic species in the system in question. This spectroscopic

behavior suggests the presence of a rapid equilibrium as shown in eq 4.



In the low-temperature ¹H NMR spectra of **2g** and the 1:1 mixture of **1g** and C₁₉H₂₉N, the signal due to ortho *tert*-butyl groups broadened on cooling. An effect of the line width of the aforementioned signal to temperatures is listed in Table II and Figure 1. On the other hand, no line broadening of the signal due to the ortho methyl groups was observed even at -63 °C in the ¹H NMR spectra of **1a** and **2a**. These are explained in terms of hindered rotation of sterically crowded 2,4,6-tri-*tert*-butylphenyl isocyanide ligand, supported by the presence of an interaction between cis-positioned isocyanide ligands in the X-ray crystallographic examination (vide infra).

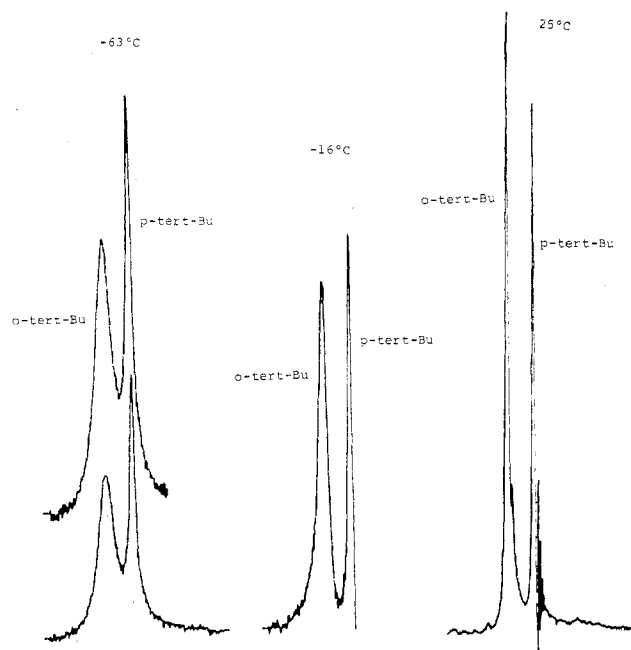
Electronic Spectra of Rhodium(I) Complexes. The electronic spectral data are compiled in Table III. The low-energy transition which appeared at ca. 400 nm was identified as

Table II. The Line Width of Ortho *tert*-Butyl Groups^a

compound	temp, °C	line width, Hz
[Rh(C ₁₉ H ₂₉ N) ₄][PF ₆], 2g	23	1.5
	-16	4.2
	-63	8.4
Rh(C ₁₉ H ₂₉ N) ₃ Cl-C ₁₉ H ₂₉ N	23	1.8
	-16	1.8
	-63	10.2

^a Measured in CDCl₃.Table III. Electronic Spectra of Rh(RNC)₃X and [Rh(RNC)₄]X in CH₃CN

no.	compound	λ _{max} , nm (ε _{max}) at 25 °C
1a	Rh(C ₉ H ₉ N) ₃ Cl	444 (250), 403 (3200), 333 (39 700), 235 (68 000)
1b	Rh(C ₉ H ₉ N) ₃ Br	435 (390), 389 (1250), 322 (31 000), 238 (36 000)
1c	Rh(C ₉ H ₉ N) ₃ I	430 (430), 393 (2100), 321 (28 000), 234 (44 000)
1d	Rh(C ₁₀ H ₁₁ N) ₃ Cl	447 (460), 391 (3400), 327 (32 000), 243 (43 000)
1e	Rh(C ₁₀ H ₁₁ N) ₃ Br	440 (320), 389 (3000), 327 (32 000), 241 (47 000)
1g	Rh(C ₁₉ H ₂₉ N) ₃ Cl	469 (975), 438 (1630), 398 (10 900), 331 (21 100), 274 (32 400), 266 (34 500), 221 (28 200)
2a	[Rh(C ₉ H ₉ N) ₄]Cl	440 (489), 404 (3830), 337 (36 200), 318 (29 500), 242 (12 100), 239 (137 000)
2g	[Rh(C ₁₉ H ₂₉ N) ₄][PF ₆]	536 (1680), 465 (1160), 417 (23 200), 345 (25 300), 248 (31 500) ^a
	Rh(C ₁₉ H ₂₉ N) ₃ Cl-C ₁₉ H ₂₉ N	474 (1090), 415 (3350), 334 (37 700), 276 (54 900), 265 (53 400), 209 (77 100) ^a

^a Measured in H₂O-MeOH (10:1).Figure 1. Variable-temperature ¹H NMR spectra of [Rh(C₁₉H₂₉N)₄][PF₆] (2g).

$d_{z^2}-\pi^*$ metal to ligand charge-transfer absorption. The positions of these transitions are sensitive to the isocyanide substituent. The absorption bands moved to lower energy in the sterically crowded order of the substituent: 2,4,6-tri-

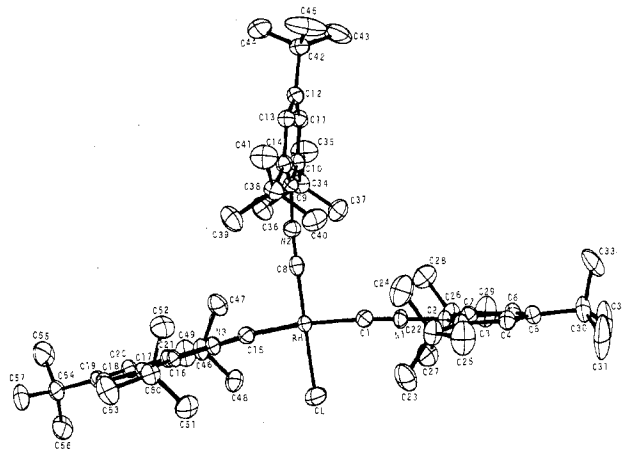


Figure 2. Perspective view of nonhydrogen atoms showing the numbering scheme.

Table IV. Selected Bond Lengths Angles and Interatomic Distances

Bond Lengths (Å)			
Rh-C(1)	1.947 (9)	C(8)-N(2)	1.175 (12)
Rh-C(8)	1.860 (10)	N(2)-C(9)	1.399 (11)
Rh-C(15)	1.959 (8)	C(15)-N(3)	1.142 (10)
Rh-Cl	2.334 (3)	N(3)-C(16)	1.398 (10)
C(1)-N(1)	1.160 (11)		
N(1)-C(2)	1.392 (10)		
Bond Angles (deg)			
Cl-Rh-C(1)	87.8 (3)	Rh-C(1)-N(1)	174.8 (9)
Cl-Rh-C(15)	86.2 (3)	C(1)-N(1)-C(2)	179.8 (9)
C(1)-Rh-C(8)	92.3 (4)	Rh-C(8)-N(8)	178.5 (8)
C(8)-Rh-C(15)	93.7 (4)	C(8)-N(8)-C(9)	174.1 (9)
Cl-Rh-C(8)	177.2 (3)	Rh-C(15)-N(3)	174.0 (8)
C(1)-Rh-C(15)	174.0 (4)	C(15)-N(3)-C(16)	175.9 (9)
Interatomic Distances (Å)			
C(24)-C(40)	3.38 (2)	N(2)-C(36)	3.06 (1)
C(28)-C(37)	3.62 (2)	N(2)-C(37)	3.06 (2)
C(36)-C(47)	3.64 (2)	N(2)-C(39)	3.03 (2)
C(39)-C(52)	3.96 (2)	N(2)-C(40)	3.10 (2)
N(1)-C(23)	3.04 (2)	N(3)-C(47)	3.05 (2)
N(1)-C(24)	3.07 (2)	N(3)-C(48)	3.08 (2)
N(1)-C(27)	3.04 (2)	N(3)-C(51)	3.05 (1)
N(1)-C(28)	3.06 (2)	N(3)-C(52)	3.05 (2)

tert-butylphenyl (469 nm) < 2,4,6-mesityl (447 nm) ≈ 2,6-xylyl (444 nm) for Rh(RNC)₃Cl. This tendency is in good agreement with the result in which the lowest transition energy decreases with bulkiness of the phosphorus ligands (L) in the electronic spectra of NiBr₂L₂.¹⁴

Tetrakis(isocyanide)rhodium(I) cations have been found to exhibit oligomerization in solution.³ The metal-metal transition appeared at ca. 500 nm. The spectrum of 2a in acetonitrile appeared at ca. 400 nm assignable to a monomeric species. The spectrum in MeOH-H₂O (1:10) showed a new band at 536 nm, which is assigned to a dimeric species by analogy to that³ in [Rh(RNC)₄]₂²⁺. This phenomenon is similar to the solvent-dependent one of Rh(*t*-BuNC)₄⁺. On the other hand the electronic spectra of [Rh(C₁₉H₂₉N)₄][PF₆] or Rh(C₁₉H₂₉N)₃Cl-C₁₉H₂₉N in CH₃CN and MeOH-H₂O (1:10) appeared at ca. 470 nm, which is assigned to monomeric species. No changes of the spectra occur in the concentration range from 1.9 × 10⁻² to 4.8 × 10⁻⁵ M. This is explained in terms of steric hindrance of bulky isocyanide ligands. The X-ray crystallographic examination explained fully the results of electronic spectra (vide infra).

Crystal Structure of Rh(C₁₉H₂₉N)₃Cl. Figure 2 is a perspective view of the Rh(C₁₉H₂₉N)₃Cl molecule. Important bond distances and angles are given in Table IV. The geometry around the rhodium atom is square planar as shown in Table V. The angles C(1)-Rh-C(8) = 92.3 (3)° and

Table V. Least-Squares Planes and Distances of Atoms from Their Respective Planes^a

plane		distance from the plane	
atom	distance, Å	atom	distance, Å
(1) Plane through the RhCIC ₃ Atoms			
0.0423X - 0.4317Y + 0.9010Z = -2.8755			
Rh	0.016	C(25)	3.95
Cl	-0.032	C(29)	-3.58
C(1)	0.026	C(35)	-3.94
C(8)	-0.037	C(49)	-3.93
C(15)	0.026	C(53)	3.60
(2) Plane through the Phenyl Ring			
0.9842X - 0.1623Y - 0.0712Z = 3.7734			
C(2)	-0.025	C(23)	1.38
C(3)	0.020	C(24)	-1.21
C(4)	-0.000	C(27)	1.40
C(5)	-0.015	C(28)	-1.17
C(6)	0.011		
C(7)	0.009		
(3) Plane through the Phenyl Ring			
0.3031X + 0.8613Y + 0.4077Z = 4.2516			
C(9)	0.029	C(36)	-1.35
C(10)	-0.022	C(37)	1.18
C(11)	-0.004	C(39)	-1.30
C(12)	0.023	C(40)	1.28
C(13)	-0.016		
C(14)	-0.010		
(4) Plane through the Phenyl Ring			
0.9997X + 0.0227Y + 0.0107Z = 4.4821			
C(16)	-0.018	C(47)	-1.20
C(17)	-0.001	C(48)	1.41
C(18)	0.020	C(51)	1.33
C(19)	-0.020	C(52)	-1.23
C(20)	0.002		
C(21)	0.017		

^a The equation of each plane is defined by $Ax + By + Cz = D$, where x , y , and z are the orthogonal coordinates measured in Å units along the crystallographic a^* , b , and c axes, respectively.

Table VI. Dihedral Angles between the RhCIC(1)C(8)C(15) Plane and the Phenyl Rings of Ligands

phenyl ring	dihedral angle, ^a deg
C(2)C(3)C(4)C(5)C(6)C(7)	92.7
C(9)C(10)C(11)C(12)C(13)C(14)	90.5
C(16)C(17)C(18)C(19)C(20)C(21)	92.4

^a Calculated from the equation of each plane defined by $Ax + By + Cz = D$, which was shown in Table V.

C(8)-Rh-C(15) = 93.7 (4)° are larger than the angles C(1)-Rh-Cl = 87.3 (3)° and C(15)-Rh-Cl = 86.2 (3)°, which may minimize repulsive interaction between two neighboring isocyanide ligands. The configuration of the molecule is of particular interest. The dihedral angles between the Rh-C(1)-C(8)-C(15)-Cl plane and the planes of the phenyl rings of each ligand are 92.7, 90.5, and 92.4°, respectively (Table VI). Thus, each phenyl ring is closely perpendicular to the RhC₃Cl plane. This configuration seems to minimize steric hindrance between phenyl rings having bulky *tert*-butyl groups at the 2 and 6 positions. Two methyl groups of ortho *tert*-butyl groups were arranged symmetrically to the C≡N-Ph plane of each coordinated isocyanide ligand to minimize repulsive interaction. Even though the distances between the aforementioned two methyl groups and isocyanide nitrogen atom are ca. 3.0 Å, indicating the intramolecular interaction in the isocyanide ligand, this conformation seems to minimize repulsive interaction (Table IV). A similar conformation may be presented in uncoordinated 2,4,6-tri-*tert*-butylphenyl isocyanide. The distances of 3.38-3.96 Å between the nearest methyl groups of *tert*-butyl groups in the cis-positioned isocyanide ligands are shorter than that of the

Table VII. Mean Lengths of M-C, C≡N, and N-C Bonds and Other Bond Lengths and Angles

mean lengths ^a		other bond lengths and angles ^b		
bond	length, Å	bond	length, Å	angle, deg
M-C	1.92	C=C	1.39	sp ² 120
C≡N	1.17	C-C	1.54	sp ³ 109.5
N-C	1.46	C-H	1.09	
other data ^b				group dist, Å
van der Waals radii			CH ₃	2.0
			H	1.2
half-thickness of aromatic nucleus				1.85

^a From X-ray crystallographic data (35 examples) of the isocyanide complexes.¹⁶ ^b "Handbook of Chemistry and Physics", 51st ed., R. C. Weast, Ed., The Chemical Rubber Co., Cleveland, pp D-141 and F-154.



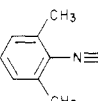
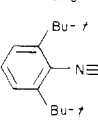
van der Waals radii, 4.0 Å, also indicating the presence of steric interaction (Table IV). This interaction is related with the result that the line width of the signal due to the ortho *tert*-butyl groups of **2g** increases with lowering of temperatures in the temperature-dependent NMR spectra, since a more sterically crowded structure is considered for complex **2g**. Generally, the Rh-Rh distances observed in the Rh(0) or Rh(II) compounds where there is a conventional single bond or a Rh-Rh interaction are shorter than 3.2 Å. For example, the Rh-Rh distance in [Rh(CO)(PPh₃)₂]₂ is 2.630 Å,¹⁵ that in Rh₂(DMG)₂(PPh₃)₂·H₂O·C₃H₇OH is 2.936 Å,¹⁶ and that in [Rh₂(PhNC)₈][BPh₄]₂ is 3.193 (0) Å.^{3d} On the basis of the distances (ca. 3.6-4.0 Å) between the RhC₃Cl plane and the outer carbon atoms (C(25), C(29), C(35), C(41), C(49), or C(53)) of the methyl groups in the ortho *tert*-butyl groups, the intermolecular Rh-Rh distance of **2c** in the solution does not fall within ca. 8 Å. Thus, the Rh-Rh interaction cannot occur.

Estimation of Bulkiness in Isocyanide. The quantitative estimation of steric effects in the phosphorus ligands has been made on the basis of ligand cone angles (θ) of space-filling CPK molecular models.¹⁷ The quantitative value of steric effects in the isocyanide ligands cannot be estimated by the apex angle of an aforementioned cylindrical cone because the structure of an isocyanide does not always have cylindrical symmetry. We tried to estimate steric effects of isocyanide by the planar wideness. The following three suppositions were taken for estimation of bulkiness: (1) On the basis of the X-ray crystallographic data (35 examples) which have been known hitherto, the mean distances of M-C, C≡N, and N-C bonds were determined¹⁸ and other bond lengths and angles used generally acknowledged values. The values are listed in Table VII. (2) The M-C≡N-C bond is linear. (3) The substituents are folded to give a maximum angle.

In light of the above-mentioned suppositions, the fan-shaped angles of wideness and thickness (the estimation values of bulkiness), being calculated by drawing of the plane of projection which was obtained by the right angle projection, are listed in Table VIII. Examples of drawing are shown in Figures 3 and 4. Table VIII also shows the fan-shaped angles of 2,4,6-tri-*tert*-butylphenyl isocyanide which were obtained from a X-ray crystallographic determination of **1g**. Both values agreed relatively.

The phenyl rings of **2g** cannot be in the same plane with the RhC₄ plane, because the fan-shaped angle of 2,4,6-tri-*tert*-butylphenyl isocyanide is 141°; the sum of the fan-shaped angles is 141 × 4 = 564°. Formation of the four-coordinated complex would be possible by having the structure so that the planes of the phenyl rings lie in the perpendicular plane to the RhC₄ plane; the sum of the fan-shaped angles is 93 × 4 = 372°. Since the distance between the outer atoms of ortho *tert*-butyl groups of 2,4,6-tri-*tert*-butylphenyl isocyanide, in

Table VIII. Fan-Shaped Angles of Isocyanide^a

isocyanide	angle 1, deg (wide- ness)	angle 2, deg (thick- ness)	angle s, deg (wide- ness)	angle 2, deg (thick- ness)
	77	48		
	91.5	50.5 ^c		
	106	53		
	141	93	133 ^b	109 ^b
			133	108
			132	106
CH ₃ N≡C	52	52		
C ₂ H ₅ N≡C	64	52		
<i>t</i> -BuN≡C	70	68		

^a Since the cone angle of CO is estimated as $\sim 95^\circ$,¹⁷ one should fully consider an estimation of isocyanide as having a fan-shaped angle which is smaller than 90° . ^b Calculated from X-ray crystallographic data of Rh(C₁₉H₂₉N)₃Cl (**1g**). ^c Fan-shaped angles are mean values of fan-shaped angles of phenyl and 2,6-xylyl isocyanide.

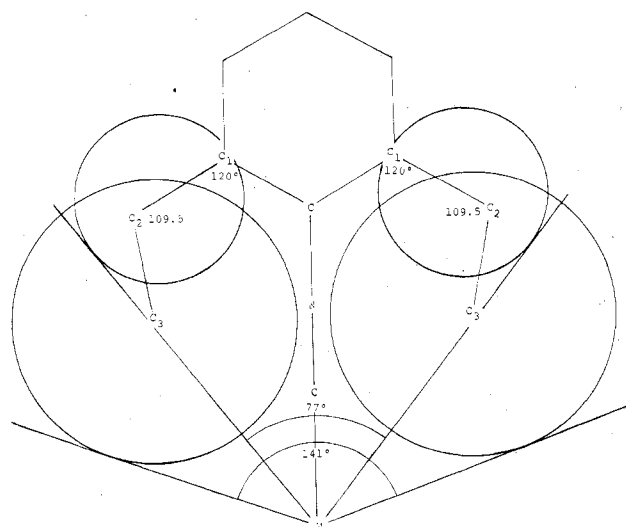


Figure 3. Drawing of fan-shaped angle 1 (wideness) of phenyl and 2,6-di-*tert*-butylphenyl isocyanide. In 2,6-di-*tert*-butylphenyl isocyanide a tertiary carbon (C₂) and one methyl carbon (C₃) of the *tert*-butyl group are arranged in the same plane as the phenyl ring. The circles show the van der Waals radii.

this case, is calculated to be ca. 4.2 Å from the drawing (Figure 3), it is clear that the metal-metal interaction cannot occur in complex **2g**.

It has been found by an X-ray crystallographic study that the planes of the phenyl rings of [Rh₂(*p*-CH₃C₆H₄NC)₈I₂]²⁺ lie very nearly in the RhC₄ coordination plane and the distance of Rh-Rh bond is 2.785 Å.¹⁹ This structure behavior is shown to be possible from the fan-shaped angle of the phenyl isocyanide (77°) and the value of half of the thickness (1.85 Å) of the phenyl group. In the X-ray determination of [Rh₂(PhNC)₈][BPh₄]₂, the phenyl rings lie out of the RhC₄ plane, and this conformation causes the metal-metal distance (3.193 (0) Å) to be longer.^{3d}

The fan-shaped angles 1 (wideness) and 2 (thickness) of 2,6-xylyl isocyanide (106 and 53°, respectively) fall between those of phenyl isocyanide and 2,6-di-*tert*-butylphenyl iso-

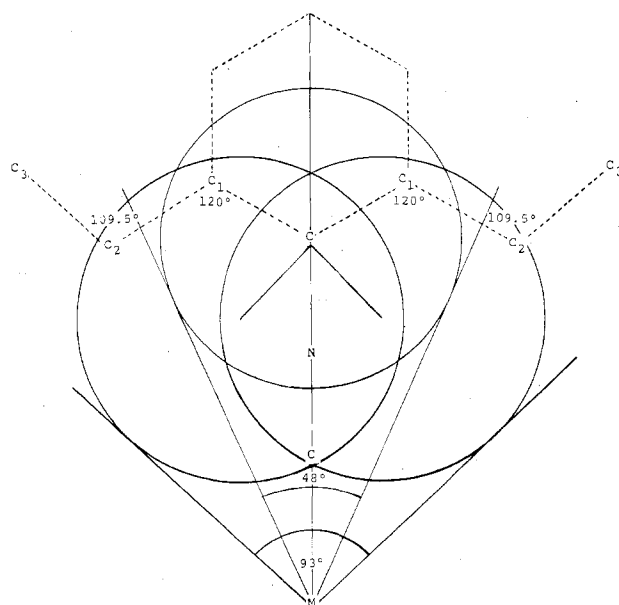


Figure 4. Drawing of fan-shaped angle 2 (thickness) of phenyl and 2,6-di-*tert*-butylphenyl isocyanide. 2,6-Di-*tert*-butylphenyl isocyanide is arranged as shown by the dotted line; a tertiary carbon (C₂) and one methyl carbon (C₃) of the *tert*-butyl group lie in the same plane as the phenyl ring. The solid line is a view which rotated the molecular arrangement (as shown in the dotted line) to 90° .

cyanide. Thus, observation of self-association in complex **2a** occurs probably by having the conformation in which the planes of the phenyl rings twist slightly from the RhC₄ coordination plane. In this case, the metal-metal distance would be longer than that of [Rh₂(PhNC)₈][BPh₄]₂ and the metal-metal interaction would be weaker.

Acknowledgment. Y. Y. thanks the Ministry of Education, Japan (Scientific Research Grant No. 354182), for generous research support. We thank Miss. K. Kobayashi and Dr. T. Sakurai of this Institute for the permission to use the computer program READ80.

Registry No. **1a**, 65255-55-2; **1b**, 65255-56-3; **1c**, 65255-57-4; **1d**, 69855-39-6; **1e**, 69847-31-0; **1g**, 69867-68-1; **2a**, 61754-48-1; **2a** (dimer), 69847-32-1; **2g**, 69847-34-3; [Rh(COD)Cl]₂, 12308-49-5; 2,4,6-tri-*tert*-butylphenyl isocyanide, 69847-28-5; 2,4,6-tri-*tert*-butylphenylformamide, 69847-29-6.

Supplementary Material Available: A listing of structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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$(\eta^3\text{-Triphenylcyclopropenyl})\text{tricarbonscobalt}$

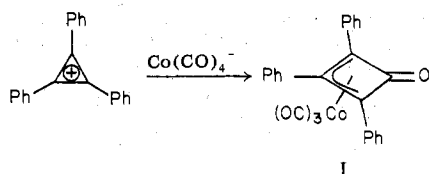
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Received December 4, 1978

Reaction of triphenylcyclopropenium fluoroborate with octacarbonyldicobalt gives the title compound. It is also obtained, in low yield, by using decacarbonyltricobalt anion. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 13.343$ (3) Å, $b = 10.284$ (2) Å, $c = 14.975$ (3) Å, $\beta = 108.84$ (2)°, and $Z = 4$. The molecule has pseudo- C_{3v} symmetry with ring Co-C and C-C bond distances averaging 2.01 (1) and 1.42 (1) Å, respectively, confirming its place as the final member of the now-complete cobaltatetrahedrane family.

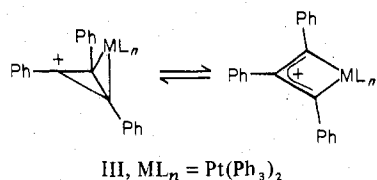
Introduction

In 1962, Coffey¹ reported the reaction of triphenylcyclopropenyl bromide with tetracarbonylcobaltate(-I) anion. The product was later shown to be the oxocyclobutenyl complex, I.^{2,3} Other reactions of cyclopropenyl compounds with

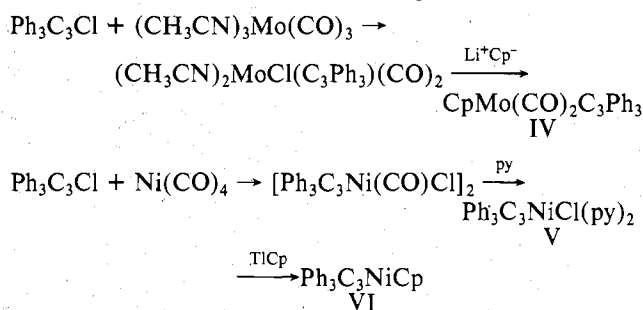


transition-metal anions have likewise failed to yield cyclopropenyl complexes: cyclopentadienyldicarbonylferrate,⁴ cyclopentadienyltricarboxymolybdate,⁴ and pentacarbonylmanganate⁵ anions gave products of one-electron transfer; ethylene trichloroplatinate(II)⁶ and hexacarbonylvanadate gave only saltlike precipitates. Photolysis of the triphenylcyclopropenium hexacarbonylvanadate gave, however, (triphenylcyclopropenyl)pentacarbonylvanadium,⁷ II.

Reactions of cyclopropenyl compounds with neutral transition-metal compounds, however, have resulted in a variety of complexes. Reactions of tris(dibenzylideneacetone)dipalladium⁸ and carbonylchlorotris(trimethyl phosphite)iridium⁹ gave metallacyclobutenyl systems from oxidative addition to a C-C bond. Ethylenebis(triphenylphosphine)platinum(0) gave an unsymmetrical π complex, III, with the platinum directly bonded to only two of the carbons of the three-membered ring (2.09 Å), the third distance being much longer (2.48 Å).¹⁰ This interesting structure is conceptually related to the metallacyclobutenyls by a sigmatropic ring opening:



Neutral metal carbonyls have also reacted to form cyclopropenyl complexes¹¹⁻¹⁴ ($Ph = C_6H_5$; $py = C_5H_5N$)



That V and VI are η^3 -cyclopropenyl complexes was shown by X-ray crystallography.^{15,16} II and IV may, by virtue of their stoichiometries, also be η^3 -cyclopropenyl complexes, but the unexpected structure of III should lead to caution in making structural assignments based on the available data.

Beyond the general interest in η^3 -cyclopropenyl complexes exemplified in the above studies, a cobalt tricarbonyl complex derives further interest from its membership in the cobaltatetrahedrane family, which also includes the known dodecacarbonyltetracobalt, methylnonacarbonyltricobalts,¹⁷ (alkyne)hexacarbonyldicobalts,¹⁸ and the tetrahedranes themselves, an example of which has just been reported.¹⁹ Synthesis of a cyclopropenyltricarbonscobalt derivative completes the family.

Experimental Section

All reactions, filtrations, and transfers were done under nitrogen with Schlenk-type glassware. Solvents were degassed with nitrogen before use. Sodium tetracarbonylcobaltate,²⁰ triphenylcyclopropenium fluoroborate,²¹ and sodium decacarbonyltricobaltate²² were prepared according to literature methods. Octacarbonyldicobalt was used as obtained from Strem Chemicals.

Reaction of Triphenylcyclopropenium Fluoroborate, VII, with Sodium Decacarbonyltricobaltate. A three-neck flask fitted with a reflux condenser and a Nujol gas-exit bubbler, nitrogen inlet, and syringe stopper was flushed with nitrogen and then charged with 0.81 g (2.28