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# Studies of the Interaction of Isocyanides with Transition-metal Complexes.[1] XXVI. The Preparation of Octakis(aryl isocyanide)dirhodium

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**Synopsis.** The treatment of a mixture of $[\mathrm{Rh(cod)Cl}]_2$ and aryl isocyanide with sodium amalgam afforded octakis(aryl isocyanide)dirhodium. A structure with two bridging and six terminal isocyanide ligands was deduced from the IR spectrum in comparison with that of the known cobalt analog. The temperature-dependent $^1$H NMR spectrum of this complex suggested harder intramolecular and easier intermolecular ligand exchanges than those of the corresponding cobalt analog.

Previously Green *et al.*[2] and also the present authors[3] reported the synthesis of dinuclear zerovalent $\mathrm{Co_2(RNC)_8}$ either by the reduction of alkyl and aryl isocanide complexes of cobalt(I) and cobalt(II) by the alkali metal amalgam, or by the substitution reaction of $\mathrm{Co_2(CO)_8}$ or $\mathrm{Co_4(CO)_{12}}$ with aryl isocyanide. Spectroscopic and X-ray crystallographic analyses showed that the molecule consists of two bridging and six terminal isocyanide ligands and that the molecule is fluxional in a solution. For comparison we attempted to prepare related rhodium complexes and to examine their structural features.

## Results and Discussion

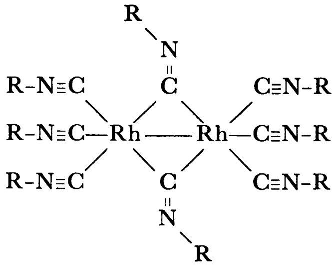
The treatment of dichloro-bis($\eta^4$-1,5-cyclooctadiene)dirhodium(I) and 2,6-xylyl isocyanide with a sodium amalgam in THF at room temperature led to formation of zerovalent octakis(2,6-xylyl isocyanide)dirhodium (**1a**) in a moderate yield:

$$[\mathrm{Rh(cod)Cl}]_2 + 8\,\mathrm{RNC} \xrightarrow{\mathrm{Na/Hg}} \mathrm{Rh_2(RNC)_8}.$$

**1a—c**

Yellow crystals of **1a** which contain benzene as a solvate are fairly stable in the solid state and can be kept in a refrigerator under an inert-gas atmosphere. In contrast, $\mathrm{Rh_2(CO)_8}$ has only been characterized spectroscopically under a high pressure of carbon monoxide[4] and also in a low-temperature matrix (*ca.* 35 K).[5] No isocyanide cluster complexes, such as $\mathrm{Rh_4(RNC)_{12}}$ and $\mathrm{Rh_6(RNC)_{16}}$ corresponding to the known binary carbonyl clusters were formed, probably for steric reasons. The use of mesityl or 2,6-dimethyl-4-bromophenyl isocyanide also afforded similar complexes (**1b**: 2,4,6-$\mathrm{Me_3C_6H_2NC}$; **1c**: 2,6-$\mathrm{Me_2}$-4-$\mathrm{BrC_6H_2NC}$).

The IR spectrum of **1a** in nujol shows characteristic absorptions assignable to the terminal isocyanide groups [2125(sh), 2090(sh), 2070(s), and 1995(sh) cm$^{-1}$] and to the bridge-bonded isocyanide groups [1672(m) and 1653(s) cm$^{-1}$]. The IR spectrum in a solution also shows a similar absorption pattern. These spectra were similar to those of the known cobalt analog, $\mathrm{Co_2(2,6\text{-}Me_2C_6H_3NC)_8}$, and suggest that **1a** has a dimeric structure consisting of two bridging and six terminal isocyanide ligands.



It has been known that binary rhodium carbonyl exists in the bridge-bonded form, and there is no evidene for the non-bridged form.[4,5]

The $^1$H NMR spectrum of **1a** in PhCl at the ambient temperature shows only one sharp singlet, at $\delta$ 2.30, which is assigned to methyl protons. This simple spectrum implies a rapid intramolecular ligand exchange between bridging and terminal isocyanide ligands. Similar behavior has also been observed in the case of the cobalt analog. However, the sharp singlet at $\delta$ 2.30 broadened on cooling and at *ca.* −33 °C splitted into two signals in an intensity ratio of 3:1, showing slow intramolecular ligand exchange; this was in contrast to the case of the cobalt analog, which showed rapid ligand exchange even at −90 °C. The intermolecular ligand exchange with added 2,6-xylyl isocyanide was also observed. The spectrum at 14 °C showed two sharp, separated signals, at $\delta$ 2.30 and 2.17, due to coordinated and uncoordinated isocyanides respectively. No intermolecular ligand exchange occurs below this temperature, as is indicated by the sharpness of the two separated singlets. The two signals become broad on warming and coalesce to a broad singlet at 40 °C. The spectrum at 60 °C shows a sharp singlet, suggeting rapid intermolecular exchange. This temperature-dependent NMR behavior is reversible. The coalescence temperature of intermolecular exchange in the cobalt analog is 127 °C. Thus, the intramolecular ligand exchange is harder, and the intermolecular exchange is easier in **1a** than in the cobalt analog. The thermodynamic data for the ligand-exchange processes of **1a**, **1b**, and **1c** are listed in Table 1.

The electronic spectra of **1a** in cyclohexane, together with that of $\mathrm{Co_2(2,6\text{-}Me_2C_6H_3NC)_8}$, are shown in Fig. 1. The band at 29670 cm$^{-1}$ (337 nm) is assigned to the $\sigma$-$\sigma^*$ transition by analogy with the electronic spectrum of $\mathrm{Co_2(2,6\text{-}Me_2C_6H_3NC)_8}$. The energy of the $\sigma$-$\sigma^*$ transition in **1a** is lower by 8790 cm$^{-1}$ than that of $\mathrm{Rh_2(CO)_8}$.[5] This difference can be associated with the weaker $\pi$-acid character of isocyanide than that of carbon monoxide. The

TABLE 1. APPROXIMATE COALESCENCE TEMPERATURES, RATE CONSTANTS, AND FREE ENERGIES FOR $Rh_2(2,6\text{-}Me_2\text{-}4\text{-}XC_6H_2NC)_8$[a]

| X | Intermolecular | | | Intramolecular | | |
|---|---|---|---|---|---|---|
| | $T_c$/°C | $k$/s$^{-1}$ | $\Delta G^*$/kcal m$^{-1}$ [b] | $T_c$/°C | $k$/s$^{-1}$ | $\Delta G^*$/kcal m$^{-1}$ [b] |
| Br | 50 | 34.2 | 16.6 | −25 | 20.4 | 12.8 |
| H | 40 | 31.1 | 16.1 | −28 | 13.0 | 12.9 |
| Me | 40 | 39.1 | 16.0 | | | |

a) Measured in PhCl. b) 1 cal = 4.184 J.

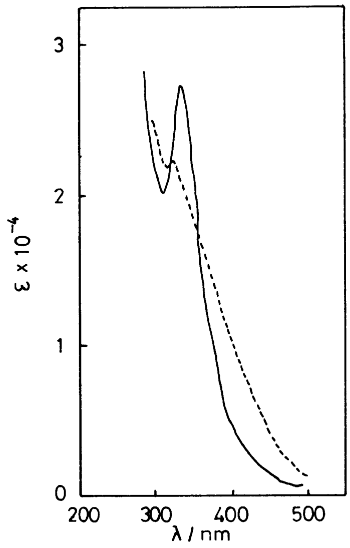


Fig. 1. Electronic spectra of $Rh_2(2,6\text{-}Me_2C_6H_3NC)_8$ (——) and $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ (----) in cyclohexane

isocyanide ligand promotes the accumulation of d-electron density on the rhodium atoms and so increases the d-d repulsive energies. The $\sigma$-$\sigma^*$ transition band in the isocyanide complex red-shifts on passing from $Co_2(2,6\text{-}Me_2C_6H_3NC)_8$ to $Rh_2(2,6\text{-}Me_2C_6H_3NC)_8$; this is the reverse of the trend observed in binary carbonyls of cobalt and rhodium.[5]

## Experimental

The reactions were carried out under an atmosphere of nitrogen. The IR and electronic spectra were obtained on Shimadzu IR-27G and Shimadzu UV-180 spectrophotometers respectively. The $^1H$ NMR spectra were recorded on a Varian HA-100B spectrometer, using tetramethylsilane as a reference. The isocyanides[6] and $[Rh(cod)Cl]_2$[7] were prepared by procedures described in the literature. The tetrahydrofuran was distilled from sodium ketyl just before use.

*Octakis(2,6-xylyl isocyanide)dirhodium (**1a**).* A mixture of $[Rh(cod)Cl]_2$ (0.20 g) and 2,6-xylyl isocyanide (0.50 g) (mole ratio: *ca.* 1:9.4) in dry tetrahydrofuran (50 ml) was stirred at room temperature with an excess of the sodium amalgam (1%) for 0.5 h. The solution was then decanted, and the solvent was evaporated to dryness under reduced pressure. The residue was chromatographed on alumina (deactivated by $H_2O$ (10%), 2 cm×5 cm), using benzene as the eluent. The concentration of the orange eluate and the addition of hexane gave yellow crystals of the title cmpound containing a benzene molecule (0.36 g, 68%); mp *ca.* 120 °C (decomposing in a nitrogen filled capillary tube). Found: C, 70.29; H, 5.29; N, 8.42%. Calcd for $Rh_2C_{78}H_{78}N_8$: C, 70.26; H, 5.95; N 8.40%.

Similarly, octakis(2,6-dimethyl-4-bromophenyl isocyanide)dirhodium (**1c**) was obtained in a 24% yield; mp *ca.* 150 °C (decomposing in a nitrogen filled capillary tube). Found: C, 48.38; H, 3.75; N, 5.69%. Calcd for $Rh_2C_{78}H_{70}N_8Br_8$ (containing a benzene molecule): C, 47.69; H, 3.59; N, 5.70%.

For the preparation of the mesityl isocyanide analog (**1b**), the reaction mixture was chromatographed on alumina, using tetrahydrofuran as the eluent.

The subsequent concentration of the eluate gave yellow crystals of **1b** in a 60% yield; mp *ca.* 130 °C (decomposing in a nitrogen filled capillary tube). Found : C, 69.91; H 6.81; N 7.57%. Calcd for $Rh_2C_{84}H_{96}N_8O$ (containing a tetrahydrofuran molecule): C, 70.09; H,6.72;N,7.78%.

*Variable-temperature NMR.* A mixture of **1a** (388 mg) and 2,6-xylyl isocyanide (12 mg) was dissolved in chlorobenzene and sealed under a nitrogen atmosphere in a 5-mm NMR tube. The 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. Similar variable-temperature NMR spectra of **1b** and **1c** were also measured; the results are summarized in Table 1.

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