

**$(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{CNC}_6\text{H}_{11})\text{Cl}_2$.
A Mixed Arene–Isocyanide Complex**

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Received February 2, 1978

Isocyanide complexes containing arene or olefinic neutral ligands are few in number because displacement of the coordinated organic moiety generally occurs when an excess of an isocyanide ligand is left to react with a metal π -complex [1]. To our knowledge only arene–isocyanide complexes of the type $\text{Cr}(\text{CO})_2(\pi\text{-arene})(\text{CNR})$ (arene = benzene, dimethylterephthalate, mesitylene, hexamethylbenzene) have been reported [2] and some of them are not isolated in pure state; the complexes $[(\pi\text{-mesitylene})\text{Mn}(\text{CO})_2(\text{CNR})]\text{PF}_6$ ($\text{R} = \text{Et}$, CPh_3) have been obtained [3] by attack of the Lewis acids $[\text{Et}_3\text{O}]^+$ and $[\text{Ph}_3\text{C}]^+$ on the cyanide ligand in $(\pi\text{-mesitylene})\text{Mn}(\text{CO})_2\text{CN}$.

We have found that, by refluxing a benzene suspension of $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$ with an excess of cyclohexylisocyanide, a salmon pink solid was formed. This, on the basis of analytical results and characteristic spectroscopic i.r. and ^1H n.m.r. data, could be formulated as $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{CNC}_6\text{H}_{11})\text{Cl}_2$; in fact, the ^1H n.m.r. spectrum in CDCl_3 shows besides a broad multiplet in the range 8–8.7 τ , due to cyclohexylisocyanide ligand, a singlet at 4.18 τ due to benzene π -bonded to ruthenium atom; in the i.r. spectrum the $\nu(\text{CN})$ band is observed at 2222 cm^{-1} and the $\nu(\text{Ru-Cl})$ are at 302 and 275 cm^{-1} .

Unlike what is observed in the reaction with cyclohexylisocyanide, $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$ reacts with CNR ($\text{R} = \text{C}_6\text{H}_5$, $\text{C}_6\text{H}_4\text{CH}_3\text{-p}$), in refluxed benzene suspension to give $\text{Ru}(\text{CNR})_4\text{Cl}_2$. Complexes of this type have been obtained by Malatesta *et al.* [4] by boiling in alcohol a mixture of RuCl_3 or RuBr_3 with an excess of the appropriate isocyanide ligand; by this method a mixture of *cis* and *trans* isomers of dihalogenotetrakis(isocyanide)ruthenium(II), which in some cases could not be separated, were obtained [5]. Starting from $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$ only the *trans*-form $\text{Ru}(\text{CNR})_4\text{Cl}_2$ ($\text{R} = \text{Ph}$, $p\text{-CH}_3\text{C}_6\text{H}_4$, C_6H_{11}) was obtained; the proposed structures are assigned on the basis of the i.r. spectra in the $\nu(\text{CN})$ and $\nu(\text{Ru-Cl})$ region. In fact these products show a single $\nu(\text{CN})$ and $\nu(\text{Ru-Cl})$ band as expected for the *trans*-form (D_{4h} symmetry).

The formation of $\text{Ru}(\text{CN})_4\text{Cl}_2$ complexes occurs probably by displacement of the coordinated η^6 -arene from the intermediate $(\eta^6\text{-benzene})\text{Ru}(\text{CNR})\text{Cl}_2$. The complex $(\eta^6\text{-benzene})\text{Ru}(\text{CNC}_6\text{H}_{11})\text{Cl}_2$ can

be obtained probably owing to its little solubility in benzene. It is interesting that the complex *trans*- $\text{Ru}(\text{CNC}_6\text{H}_{11})_4\text{Cl}_2$ is also obtained in the reaction of $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$ with $\text{CNC}_6\text{H}_{11}$ and this confirms that $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{CNR})\text{Cl}_2$ complexes are intermediate in the reactions studied.

The coordinated cyclohexylisocyanide ligand is displaced by triphenylphosphine from $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{CNC}_6\text{H}_{11})\text{Cl}_2$, in refluxing benzene solution, to give $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)\text{Cl}_2$ [6].

Experimental

The complex $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$ and the isocyanide ligands are prepared according to literature methods [6, 7]. I.r. and ^1H n.m.r. spectra are recorded on Perkin-Elmer mod. 457 and Perkin-Elmer R 24 B spectrophotometers respectively. Elemental analyses were by Bernhardt Mikroanalytisches Laboratorium, Germany. All reactions were carried out under oxygen-free dinitrogen.

(\eta^6-Benzene)dichlorocyclohexylisocyanideruthenium(II), (\eta^6-C_6H_6)Ru(CNC_6H_{11})Cl_2 and Dichlorotetra(cyclohexylisocyanide)ruthenium(II), Ru(CNC_6H_{11})_4Cl_2

To a suspension of $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$ (0.50 g, 0.99 mmol) in benzene, a solution of $\text{CNC}_6\text{H}_{11}$ (0.40 g, 3.66 mmol) in the same solvent was added and the mixture was refluxed for about 30 min. A salmon-pink solid was formed; this was collected on a buckner, washed several times with benzene and dried in air to give the pure product $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{CNC}_6\text{H}_{11})\text{Cl}_2$. $\nu(\text{CN})$ 2222 cm^{-1} vs; $\nu(\text{RuCl})$ 302 and 275 cm^{-1} s; $\tau(\text{C}_6\text{H}_6)$ 4.18; $\tau(\text{C}_6\text{H}_{11})$ 8–8.7 multiplet (CDCl_3). Found: C 43.33, H 4.71, N 3.75, Cl 19.66. Calcd. for $\text{C}_{13}\text{H}_{17}\text{Cl}_2\text{NRu}$: C 43.46, H 4.76, N 3.89, Cl 19.73%.

The benzene solution was partially evaporated under reduced pressure; by adding hexane a yellow solid was obtained. This was filtered off, washed with hexane and crystallized from dichloromethane–hexane. $\nu(\text{CN})$ 2150 cm^{-1} vs br; $\nu(\text{Ru-Cl})$ 300 cm^{-1} s; $\tau(\text{C}_6\text{H}_{11})$ 7.65–8.7 multiplet (CDCl_3). Found: C 55.32, H 7.33, N 9.16, Cl 11.56. Calcd. for $\text{C}_{28}\text{H}_{44}\text{Cl}_2\text{N}_4\text{Ru}$: C 55.25, H 7.28, N 9.20, Cl 11.65%.

Dichlorotetra(p-tolylisocyanide)ruthenium(II), Ru(p-CH_3C_6H_4NC)_4Cl_2

To a suspension of $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$ (0.42 g, 0.84 mmol) in benzene, a solution of $p\text{-CH}_3\text{C}_6\text{H}_4\text{NC}$ (0.59 g, 5.04 mmol) in the same solvent was added. The reaction mixture was gently warmed and the progress of the reaction was followed by i.r. spectroscopy. After ca. 4 h the solution was filtered

and the solid residue characterized as the starting material $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$. The solvent was then removed leaving a yellow brown solid; this was washed several times with diethyl ether and crystallized from dichloromethane–pentane to give the product as yellow solid. The yield increases using an excess of the isocyanide ligand. $\nu(\text{CN})$ 2138 cm^{-1} vs (CH_2Cl_2) ; $\nu(\text{RuCl})$ 305 cm^{-1} s; $\tau(\text{CH}_3)$ 7.66 (CDCl_3). Found: C 60.07, H 4.46, N 8.70, Cl 11.12; Calcd. for $\text{C}_{32}\text{H}_{28}\text{Cl}_2\text{N}_4\text{Ru}$: C 60.00, H 4.40, N 8.74, Cl 11.07%.

Dichlorotetra(phenylisocyanide)ruthenium(II), Ru-(C₆H₅NC)₄Cl₂

This was prepared similarly and was obtained as yellow solid. $\nu(\text{CN})$ 2135 cm^{-1} vs (CH_2Cl_2) ; $\nu(\text{RuCl})$ 300 cm^{-1} s; $\tau(\text{C}_6\text{H}_5)$ 2.5–3.0 multiplet (CDCl_3). Found: C 57.61, H 3.47, N 9.64, Cl 12.10; Calcd. for $\text{C}_{28}\text{H}_{20}\text{N}_4\text{Cl}_2\text{Ru}$: C 57.54, H 3.45, N 9.58, Cl 12.13%.

Acknowledgements

We thank the CNR–Rome for financial support.

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