

Synthesis of cyano-bridged bimetallic complexes of h^5 -indenyl ruthenium(II): Characterization and spectroscopic studies

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Abstract. Reactions of the cyanide complexes of the type $[(\text{Ind})\text{Ru}(\text{PPh}_3)_2\text{CN}]$ (**1**), $[(\text{Ind})\text{Ru}(\text{dppe})\text{CN}]$ (**2**), $[(\text{Cp})\text{Ru}(\text{PPh}_3)_2\text{CN}]$ (**3**), with the corresponding chloro complexes $[(\text{Ind})\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ (**4**), $[(\text{Ind})\text{Ru}(\text{dppe})\text{Cl}]$ (**5**), $[(\text{Cp})\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ (**6**), in the presence of NH_4PF_6 salt give homometallic cyano-bridged compounds of the type $[(\text{Ind})(\text{PPh}_3)_2\text{Ru}-\text{CN}-\text{Ru}(\text{PPh}_3)_2(\text{Cp})]\text{PF}_6$ (**7**), $[(\text{Ind})(\text{PPh}_3)_2\text{Ru}-\text{CN}-\text{Ru}(\text{PPh}_3)_2(\text{Ind})]\text{PF}_6$ where Ind = indenyl, $h^5\text{-C}_9\text{H}_7$, (**8**), $[(\text{Cp})(\text{PPh}_3)_2\text{Ru}-\text{CN}-\text{Ru}(\text{dppe})(\text{Ind})]\text{PF}_6$, dppe = $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ (**9**), $[(\text{Ind})(\text{dppe})\text{Ru}-\text{CN}-\text{Ru}(\text{PPh}_3)_2(\text{Ind})]\text{PF}_6$ (**10**) and $[(\text{Ind})(\text{dppe})\text{Ru}-\text{CN}-\text{Ru}(\text{PPh}_3)_2(\text{Cp})]\text{PF}_6$ (**11**) respectively. Reaction of complex **3** with $[(p\text{-cymene})\text{RuCl}_2]_2$ dimer gave a mixed dimeric complex $[(\text{Cp})\text{Ru}(\text{PPh}_3)_2-\text{CN}-\text{RuCl}_2(p\text{-cymene})]$ (**12**). All these complexes have been characterized by IR, ^1H , ^{13}C and ^{31}P NMR spectroscopy and C, H, N analyses.

Keywords. Cyano-bridged; h^5 -indenyl; bimetallic complexes; ruthenium.

1. Introduction

Linear cyanide-bridged bimetallic complexes of the type $\text{M}-\text{CN}-\text{M}$ have been extensively studied¹⁻⁶. Cyanide-bridged, dinuclear transition metal compounds are widely used in the areas of electron delocalization and charge transfer studies⁷⁻¹¹.

In our earlier work, we have studied the nucleophilic character of cyanide group in $[\text{CpRu}(\text{PPh}_3)_2\text{CN}]$ complexes and synthesized various cyanide-bridged bimetallic complexes^{2,3,12,13}. As an extension of this work, we have chosen $[(\text{Ind})\text{RuL}_2\text{CN}]$ complexes where we expect the cyanide group to exhibit more nucleophilic character because of high electron density on the metal in indenyl ruthenium complex compared to the cyclopentadienyl analogue¹⁴. We wish to report here the reactions of $[(\text{Ind})\text{RuL}_2\text{CN}]$ with various halide complexes of the type $[(\text{Ind})\text{RuL}_2\text{Cl}]$, $[(\text{Cp})\text{RuL}_2\text{Cl}]$ etc.

2. Experimental

Solvents were dried by standard methods. Infrared spectra were recorded as KBr pellets using a Perkin-Elmer model 983 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker ACF 300 spectrometer and referenced to external tetramethylsilane. ^{31}P $\{^1\text{H}\}$ NMR chemical shifts are reported relative to H_3PO_4 (85%). In the NMR spectra,

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chemical shifts are expressed with reference to TMS (^1H and ^{13}C). Coupling constants, J , are given in hertz. Elemental analyses were performed by the service center, Regional Sophisticated Instrumentation Centre, NEHU, Shillong.

$[(\text{Ind})\text{RuL}_2\text{CN}]^{15}$, $[(\text{Ind})\text{RuL}_2\text{Cl}]^{15}$, $[(h^6\text{-}p\text{-cymene})\text{RuCl}_2]_2^{16}$ and $[(\text{Cp})\text{RuL}_2\text{CN}]^{17}$ were prepared by literature methods. Rutheniumtrichloride trihydrate was obtained from Arrora Matthey (P) Limited and used as such.

2.1 Preparation of complexes

A typical reaction procedure was as follows for complexes $[(\text{Ar})\text{L}_2\text{Ru}-\text{CN}-\text{RuL}_2(\text{Ar}^1)]\text{PF}_6$, **7–11**.

A suspension of $[(\text{Ind})\text{RuL}_2(\text{CN})]$ (0.5 mmol), $[(\text{Ind})\text{RuL}'_2(\text{Cl})]$ (0.5 mmol), or $[(\text{Cp})\text{Ru}(\text{PPh}_3)_2(\text{Cl})]$ (0.5 mmol) ($\text{L} = \text{PPh}_3$ or $\text{L}_2 = \text{dppe}$) and NH_4PF_6 in methanol 20 ml was refluxed for 2 h. The initially light brown suspension turned into yellowish solution, which on cooling some of the complex was precipitated out. The yellow complex was separated out by filtration. The filtrate was concentrated to dryness. The compound was dissolved in dichloromethane and filtered. Addition of diethylether to the filtrate yielded yellowish precipitate, which was washed with diethylether and dried.

2.2 Preparation of $[(\text{Cp})(\text{PPh}_3)_2\text{Ru}-m\text{-CN}-\text{Ru}(h^6\text{-}p\text{-cymene})\text{Cl}_2]$

The complex $[(\text{Cp})\text{Ru}(\text{PPh}_3)_2(\text{CN})]$ (100 mg, 0.139 mmol) suspended in methanol (20 ml) was heated under reflux with $[(h^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$ (30 mg, 0.139 mmol) for four hours. The yellow orange solution was evaporated to dryness on a water bath and the residue was dissolved in dichloromethane (5 ml). Addition of diethylether to this solution resulted in an orange solid. This was filtered and washed with diethylether and dried in vacuum.

3. Results and discussion

Cyanide-bridged complexes are prepared by treatment of cyanide complexes with the corresponding chloride complexes in presence of NH_4PF_6 in methanol. Chloride complexes dissociate in methanol and form solvated cations¹² of the type $[(\text{Ind})\text{RuL}_2(\text{sol})]^+$. These cations act as electrophiles towards the cyanide complexes. The reactions take place very smoothly as below to give the products in good yield.



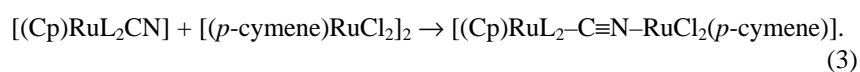
Ind = indenyl, $\text{L}_2 = (\text{PPh}_3)_2$, dppe = $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$



The crude products are purified by passing through a column (silica gel) using dichloromethane as eluent to yield the pure complexes, which are yellow in colour. These have been characterized by their n_{CN} stretching mode in infrared, which shifts to higher energies by about $5\text{--}25\text{ cm}^{-1}$ compared to the corresponding cyanide complexes^{2,3,18,19},

owing to the formation of a cyanide bridge. The ν_{CN} band shift to higher energy is explained²⁰ in terms of removal of electron density from the lowest filled CN $\sigma^*(s)$ orbital on the co-ordinating nitrogen of the cyanide group. Moreover, on bridge formation, there is simple mechanical constraint on CN motion imposed by the presence of the second metal centre which makes ν_{CN} shift to higher frequency²¹. This shift to higher frequency on bridging has also been explained on the basis of force field arguments²². The complexes have also shown characteristic IR bands for triphenylphosphine groups in the range of 1480, 1430, 1090, 740, 690, 520 cm^{-1} and a strong band is also observed for ν_{PF} at 840 cm^{-1} .

Complex **12** is formed by reaction of complex **3** $[(\text{Cp})\text{RuL}_2\text{CN}]$ and $[(p\text{-cymene})\text{RuCl}_2]_2$ dimer in the ratio of 2:1 in ethanol as follows.



Complex **12** exhibits a strong stretching band for ν_{CN} at 2112 cm^{-1} , indicating the shift of the band position by 44 cm^{-1} to higher energy compared to the starting cyanide complex $[(\text{Cp})\text{RuL}_2\text{CN}]$ (**3**), where ν_{CN} is at 2068 cm^{-1} . The ^1H NMR spectrum of the complex has shown characteristic peaks for the cyclopentadienyl and p -cymene groups (table 1, figure 1).

The proton NMR spectra of complexes **7**, **9**, **11** (table 1) show sharp signals due to Cp around δ 4.0 ppm, and a set of indenyl peaks around δ 4.3 ppm (doublet) and δ 5.0 ppm (triplet). In the case of complexes **8**, **10** we would expect two sets of indenyl proton peaks in the range 4 to 5 ppm, but we observe broad multiplets instead of two doublets and two triplets for two indenyl groups. All these complexes exhibit sharp signals in ^{31}P $\{^1\text{H}\}$ NMR spectra for triphenylphosphine and dppe ligands in the region of 47 and 85 ppm respectively (table 1) confirming the presence of these ligands. Signals

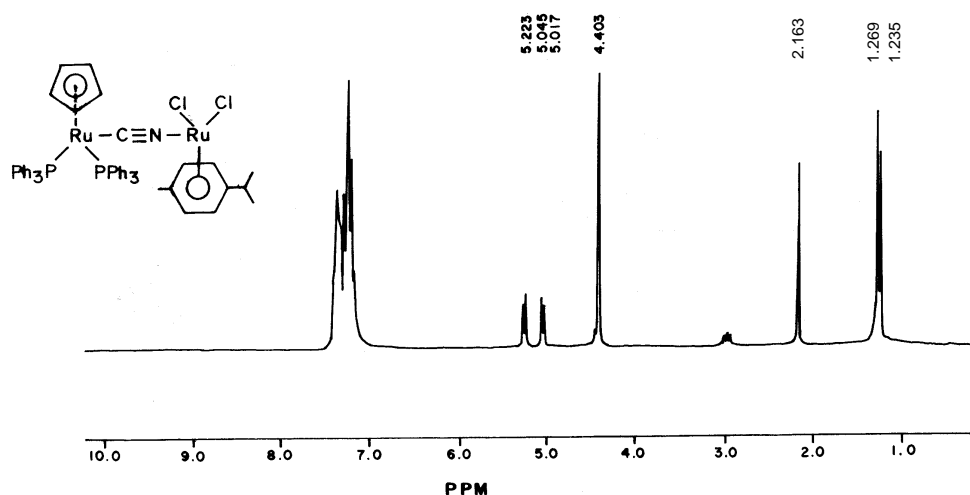


Figure 1. ^1H NMR spectrum of complex $[(\text{Cp})(\text{PPh}_3)_2\text{Ru-}m\text{-CN-Ru}(h^6\text{-}p\text{-cymene})\text{-Cl}_2]$ in CDCl_3 .

Table 1. Spectral data of cyanide bridged complexes: [(Ar)₂Ru–CN–RuL₂(Ar')]PF₆. All the complexes gave satisfactory C, H, and N data

	IR ^a ν_{CN} , ν_{PF} (cm ⁻¹)	¹ H NMR ^b , CDCl ₃ (d ppm)	¹³ C NMR ^c (d ppm)	³¹ P NMR (d ppm)
= indenyl, ' = Cp; L = L' = PPh ₃ (7)	2065, 839	4.05 (s, Cp), 4.4 (d, 2H, $J_{\text{H}} = 2.5$ Hz), 5.02 (t, 1H, $J_{\text{H}} = 2.0$ Hz), 6.9–7.2 (m, Ph, 64 H)	74, 82, 109, 123, 127–137, 177	42, 47 (Cp)
= Ar' = indenyl; = L' = PPh ₃ (8)	2078, 840	4.3 (d, 2H), 4.9 (t, 1H), 6.4–7.5 (m, 68 H, for Ph group)	96, 109, 127–136	52 (PPh ₃)
= Cp, Ar' = indenyl; = PPh ₃ , L ₂ = dppe (9)	2073, 840	2.4–2.8 (m, 4H), 3.7 (s, 5H), 4.5 (d, 2H, $J_{\text{H}} = 1.8$ Hz), 4.89 (t, 1H, $J_{\text{H}} = 1.8$ Hz), 6.7–7.4 (m, 54H, Ph group)	19, 64, 85.2, 91, 111, 124–137	47 (PPh ₃), 83.0 (dppe)
= Ar' = indenyl; ' = PPh ₃ , L ₂ = dppe (10)	2066, 840	2.5–2.9 (m, 4H), 4.7 (d, 2H, $J_{\text{H}} = 2.1$ Hz), 5.1 (t, 1H, $J_{\text{H}} = 2.5$ Hz), 6.7–7.4 (m, Ph, 58 H)	19, 70, 91, 94, 111, 124–133	53.2 (PPh ₃) 85.3 (dppe)
= indenyl, Ar' = Cp; = dppe, L' = PPh ₃ (11)	2065, 839	2.38–2.8 (m, 4H), 3.6 (s, Cp), 4.8 (d, 2H, $J_{\text{H}} = 2.5$), 4.96 (t, 1H, $J_{\text{H}} = 2.0$), 6.6–7.3 (m, Ph, 54H)	19.47, 28.1, 69.5, 82.7, 109.7, 124–137	41.6 (Cp) 84 (dppe)
₂ (³ / ₂ -CN– (<i>p</i> -cymene)) (12)	2112	1.24 (d, 6H, $J_{\text{H}} = 6$ Hz), 2.16 (s, Me) 2.9 (sept, 1H, isopropyl), 4.4 (s, 5H, Cp) 5.03 (d, 2H, ring protons of cymene, $J_{\text{H}} = 6$ Hz) 5.23 (d, 2H, ring protons of cymene, $J_{\text{H}} = 6$ Hz), 7.3–7.6 (m, Ph)		49.3

KBr discs, ^b CDCl₃; ^c ¹³C NMR signal of the bridging cyano group was not observed

due to PF_6^- counter ion are observed as a septet around δ 137 ppm in the ^{31}P { 1H } NMR spectra of these complexes. In the ^{13}C NMR spectra signals due to carbons of Cp, indenyl and phenyl groups of phosphines are also observed in the range of 90, 70, 111 and 127–138 ppm respectively (table 1).

4. Conclusions

Complexes **7–12** were isolated successfully by reacting cyanide complexes **1–3** with chloride complexes **4–6** in methanol. The reactivity of cyanide complexes with mild electrophiles viz. solvated cations indicates the strong electron donor capability of cyanide group in cyanide complexes. On the basis of spectral data, the molecular formula proposed for these complexes is: $[(Ar)_2Ru-CN-Ru(Ar')L'_2]PF_6$.

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