

Syntheses and characterization of cyano-bridged homo and hetero bimetallic complexes containing η^5 and η^6 -cyclic hydrocarbons

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Abstract

The reactions of $[(\text{ind})\text{Ru}(\text{PPh}_3)_2\text{CN}]$ ($\text{ind} = \eta^5\text{-C}_9\text{H}_7$) (**1**) and $[\text{CpRu}(\text{PPh}_3)_2\text{CN}]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) (**2**) with $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{bipy})\text{Cl}]\text{Cl}$ ($\text{bipy} = 2,2'\text{-bipyridine}$) (**3**) in the presence of $\text{AgNO}_3/\text{NH}_4\text{BF}_4$ in methanol, respectively, yielded dicationic cyano-bridged complexes of the type $[(\text{ind})(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Ru}(\text{bipy})(\eta^6\text{-}p\text{-cymene})](\text{BF}_4)_2$ (**4**) and $[\text{Cp}(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Ru}(\text{bipy})(\eta^6\text{-}p\text{-cymene})](\text{BF}_4)_2$ (**5**). The reaction of $[\text{CpRu}(\text{PPh}_3)_2\text{CN}]$ (**2**), $[\text{CpOs}(\text{PPh}_3)_2\text{CN}]$ (**6**) and $[\text{CpRu}(\text{dppe})\text{CN}]$ (**7**) with the corresponding halide complexes and $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$ formed the monocationic cyano-bridge complexes $[\text{Cp}(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Os}(\text{PPh}_3)_2\text{Cp}](\text{BF}_4)$ (**8**), $[\text{Cp}(\text{PPh}_3)_2\text{Os}(\mu\text{-CN})\text{Ru}(\text{PPh}_3)_2\text{Cp}](\text{BF}_4)$ (**9**) and $[\text{Cp}(\text{dppe})\text{Ru}(\mu\text{-CN})\text{Os}(\text{PPh}_3)_2\text{Cp}](\text{BF}_4)$ (**10**) along with the neutral complexes $[\text{Cp}(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}_2]$ (**11**), $[\text{Cp}(\text{PPh}_3)_2\text{Os}(\mu\text{-CN})\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}_2]$ (**12**), and $[\text{Cp}(\text{dppe})\text{Ru}(\mu\text{-CN})\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}_2]$ (**13**). These complexes were characterized by FT IR, ^1H NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and the molecular structures of complexes **4**, **8** and **11** were solved by X-ray diffraction studies.

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1. Introduction

Cyanide has been used frequently as a ligand to bridge two metal centers and such complexes have interesting magnetic properties [1]. Cyano-bridged, dinuclear transition metal complexes have seen application in the areas of electron delocalization and charge transfer studies [2]. Baird et al. [3a] have successfully demon-

strated the nucleophilic character of the terminal nitrogen of the cyano ligand of the M-CN fragment to afford cationic complexes of the type M-CN-M^+ or isonitrile complexes $\text{M}^+\text{-CNR}$ by reacting such metal complexes with alkyl halides (RX). This synthetic strategy has been often utilized to provide a general route to synthesize cationic dinuclear cyano-bridged complexes. In continuation of our previous work on some cyano-bridged complexes [3b,3c], we would like to describe here the synthesis of cyano-bridged complexes (dicationic, cationic and neutral) formed from the reaction between the appropriate $[\text{M}]-\text{CN}$ and $[\text{M}]-\text{X}$ fragments.

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2. Experimental

All chemicals were obtained from commercial sources. Infrared spectra were recorded as KBr pellets using a Perkin-Elmer model-983 spectrophotometer. ^1H NMR spectra were recorded on a Bruker ACF 300 spectrometer and referenced to external TMS. $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts were recorded relative to H_3PO_4 (85%). Elemental analyses were performed by the Regional Sophisticated Instrumentation Centre, NEHU, Shillong. $[\text{CpOs}(\text{PPh}_3)_2\text{CN}]$ [4], $[(\text{ind})\text{Ru}(\text{PPh}_3)_2\text{CN}]$ [5], $[\text{CpRu}(\text{PPh}_3)_2\text{CN}]$ [6], $[\text{CpRu}(\text{dppe})\text{CN}]$ [7] and $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$ [8] were prepared according to the literature procedures.

3. Preparation of the complexes

3.1. Preparation of $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{bipy})\text{Cl}]\text{Cl}$ (**3**)

A suspension of $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$ (0.1 g, 0.163 mmol) and 2,2'-bipyridine (0.063 g, 0.407 mmol) in methanol (15 ml) was stirred at room temperature for 1 h. Methanol was removed on a rotary evaporator and the residue was extracted with acetone. Subsequent concentration and addition of excess hexane afforded the orange-red microcrystalline compound.

3.2. Preparation of $[(L)(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Ru}(\text{bipy})-(\eta^6\text{-}p\text{-cymene})](\text{BF}_4)_2$ [$L = \text{ind}$ (**4**), $L = \text{Cp}$ (**5**)]

A suspension of $[(L)\text{Ru}(\text{PPh}_3)_2\text{CN}]$ (1.22 mol), $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{bipy})\text{Cl}]\text{Cl}$ (1.22 mmol), AgNO_3 (2.44 mmol) and NH_4BF_4 (3.66 mmol) in distilled acetone (25 ml) was refluxed for 2 h. The resulting solution was filtered and concentrated to ~ 5 ml. Addition of excess hexane to this solution gave the yellow microcrystalline compounds.

3.3. Preparation of $[\text{Cp}(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Os}(\text{PPh}_3)_2\text{-Cp}]\text{BF}_4$ (**8**), $[\text{Cp}(\text{PPh}_3)_2\text{Os}(\mu\text{-CN})\text{Ru}(\text{PPh}_3)_2\text{Cp}]\text{-BF}_4$ (**9**) and $[\text{Cp}(\text{dppe})\text{Ru}(\mu\text{-CN})\text{Os}(\text{PPh}_3)_2\text{Cp}]\text{BF}_4$ (**10**)

A suspension of equimolar amounts of the cyano-complexes and the corresponding halide complexes and a slight excess of NH_4BF_4 in distilled methanol (20 ml) was refluxed for 3 h (1 h for **8**). The color of the solution changed to greenish yellow. The solvent was removed on a rotary evaporator and the residue was extracted with dichloromethane, whereupon the white insoluble material was filtered off. The solution was concentrated to ~ 5 ml and addition of excess hexane gave the compounds **8** and **9** as a light green and as a pale yellow orange crystalline solid, respectively.

3.4. Preparation of $[\text{Cp}(L)_2\text{M}(\mu\text{-CN})\text{Ru}(\text{Cl}_2)(\eta^6\text{-}p\text{-cymene})]$ ($M = \text{Ru}$, $L = \text{PPh}_3$ (**11**), $M = \text{Os}$, $L = \text{PPh}_3$ (**12**); $M = \text{Ru}$ (**13**), $L_2 = \text{dppe}$)

A suspension of equimolar amounts of $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{Cl}_2)]_2$ and the cyano-complexes (**2**, **6**, **7**) in methanol was refluxed for 2 h. Removal of the solvent in vacuo afforded the desired complexes as orange-red crystalline powder.

4. Structure analysis and refinement

X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). In the case of complex **4**, Enraf Nonius Cad-4 was employed. Indexing was performed from a series of twelve 0.5° rotation images with exposures of 30 s. Rotation images were processed using crystal clear [9], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values, which were then passed on to the crystal structure [9] program package for further processing and structure solution on a Dell Pentium III computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using the REQAB program [10]. The structure was solved by direct methods (SIR97) [11]. Refinement was performed by a full-matrix least squares method based on F^2 using SHELXL 97 [12]. All reflections used during refinement (F^2 's that were experimentally negative were replaced by $F^2 = 0$). Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined using a "riding" model. Refinement converged at a final value of $R_1 = 0.0363$, 0.0384 and 0.0935 for the complexes **11**, **8**, and **4**, and at values of $wR_2 = 0.1145$, 0.0948 and 0.2553 for complexes **11**, **8** and **4**, respectively (for unique data F^2).

Table 2 listed the cell information, data collection parameters and refinement data. Figs. 1–3 are ORTEP [13] representations of complexes **4**, **8** and **11**, respectively. Selected bond lengths and angles are given in Tables 3–5 for the complexes **4**, **8** and **11**, respectively.

5. Results and discussion

5.1. Dicationic complexes

Treatment of the cyano-complexes (**1**, **2**) with the halo complex (**3**) in refluxing conditions in the presence of AgNO_3 (as a halide scavenger) after work up, afforded the dicationic complexes, $[(\text{ind})(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Ru}(\text{bipy})(\eta^6\text{-}p\text{-cymene})]^{2+}$ (**4**) ($\text{ind} = \eta^5\text{-C}_9\text{H}_7$) and $[\text{Cp}(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Ru}(\text{bipy})(\eta^6\text{-}p\text{-cymene})]^{2+}$ (**5**) ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$). These two complexes were isolated as tetrafluoroborate salts (Scheme 1).

These two new dimetallic cations **4** and **5** exhibit medium intensity IR bands assignable to $\nu_{(\text{C}=\text{N})}$ at 2085 and 2075 cm^{-1} which are slightly shifted toward higher energies as compared to the parent mononuclear cyano-complexes (**1**) [$\nu_{(\text{C}=\text{N})}$ 2065 cm^{-1}] and (**2**) [$\nu_{(\text{C}=\text{N})}$ 2070 cm^{-1}]. The high energy shift of ν_{CN} band on coordination to second metal maybe explained [14] in terms of removal of electron density from the lowest filled CN $\sigma^*(s)$ orbital on the coordinating nitrogen of the cyanide group. Moreover, upon 'bridge' formation, there is a simple mechanical constraint on the CN motion imposed by the presence of the second metal center which

shifts ν_{CN} to a higher frequency [15]. This shift to higher frequency upon bridging has also been explained on the basis of force field arguments [16]. Very strong broadbands assignable to $\nu_{(\text{BF})}$ of BF_4 are observed at 1080 cm^{-1} for both the complexes beside other absorption bands characteristic of triphenyl-phosphines.

The complexes were also characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The NMR data are presented in Table 1. The proton NMR spectra of these complexes exhibit characteristic peaks for all functional groups. The ^{31}P NMR spectra of these complexes exhibit only one singlet suggesting that the both the P atoms

Table 1
Spectroscopic data of the complexes

Complexes	(CN)	^1H NMR (ppm)	$^{31}\text{P}\{^1\text{H}\}$ NMR (ppm)
4	2085	9.84 (d, 1H, 6), 8.63 (d, 1H, 9), 8.14 (t, 1H, 6), 7.82 (t, 1H, 6), 7.45–6.59 (m, 34H), 6.28 (d, 1H, 6), 5.96 (d, 1H, 6), 5.75 (m, 2H), 4.67 (t, 1H, 2), 4.07 (d, 2H, 2), 2.21 (sept, 1H), 0.83 (d, 6H, 9)	49.39 (s)
5	2075	9.45 (d, 2H, 6), 8.44 (t, 2H, 6), 8.20 (t, 2H, 6), 8.05 (d, 2H, 6), 7.88–6.79 (m, 30H), 6.20 (d, 1H, 6), 6.09 (d, 1H, 9), 6.02 (d, 1H, 6), 5.81 (d, 1H, 9), 4.38 (s, 5H), 2.4 (sept, 1H), 2.1 (s, 3H), 1.08 (d, 6H, 9)	50.42 (s)
8	2077	7.25–7.00 (m, 60H), 4.25 (s, 5H), 4.23 (s, 5H)	48.56 (s), 0.50 (s)
9	2069	7.25–7.00 (m, 60H), 4.32 (s, 5H), 4.10 (s, 5H)	42.94 (s), 2.00 (s)
10	2080	7.77–6.85 (m, 40H), 4.7 (s, 5H), 3.79 (s, 5H), 2.93–2.71 (m, 4H)	82.63 (s), 0.50 (s)
11	2110	7.35–7.17 (m, 30H), 5.49 (d, 1H, 6), 5.35 (d, 1H, 3), 5.24 (d, 1H, 6), 5.04 (d, 1H, 6), 4.40 (s, 5H), 2.90 (sept, 1H), 2.18 (s, 3H), 1.23 (d, 6H, 9)	49.32 (s)
12	2105	7.35–7.17 (m, 30H), 5.42 (d, 1H, 6), 5.33 (d, 1H, 3), 5.16 (d, 1H, 6), 5.12 (d, 1H, 6), 4.52 (s, 5H), 2.82 (sept, 1H), 2.00 (s, 3H), 0.98 (d, 6H)	1.32 (s)
13	2103	7.41–7.11 (m, 20H), 4.65 (s, 5H), 2.89–2.71 (m, 4H), 6.12 (d, 2H, 6), 6.07 (d, 2H, 6), 4.23 (s, 5H), 2.93–2.71 (m, 4H), 2.4 (sept, 1H), 2.21 (s, 3H), 1.02 (d, 6H, 9)	83.4 (s)

Table 2
Summary of structure determination of compounds **11**, **8** and **4**

	$\text{C}_{52}\text{H}_{51}\text{Cl}_2\text{NP}_2\text{Ru}_2$	$\text{C}_{83}\text{BH}_{70}\text{NP}_4\text{F}_4\text{OsRu}$	$\text{C}_{66}\text{H}_{59}\text{B}_2\text{F}_8\text{N}_3\text{P}_2\text{Ru}_2$
Empirical formula	$\text{C}_{52}\text{H}_{51}\text{Cl}_2\text{NP}_2\text{Ru}_2$	$\text{C}_{83}\text{BH}_{70}\text{NP}_4\text{F}_4\text{OsRu}$	$\text{C}_{66}\text{H}_{59}\text{B}_2\text{F}_8\text{N}_3\text{P}_2\text{Ru}_2$
Formula weight	1022.9	1583.36	1331.86
Temperature (K)	120(2)	143(2)	293(2)
Wavelength (Å)	0.71073	0.71069	1.54178
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$P2_1/c$
<i>Unit cell dimensions</i>			
a (Å)	25.485(5)	25.510(4)	13.9100(10)
b (Å)	20.779(4)	13.863(2)	23.0670(10)
c (Å)	20.931(4)	20.050(3)	19.7260(10)
β (°)	124.913(2)	93.430(3)	108.46
Volume (Å ³)	9089(3)	7078(2)	6003.6(6)
Z	4	4	4
D_{calc} (Mg/m ³)	1.495	1.486	1.474
$F(0\ 0\ 0)$	4160	3184	2704
Crystal size	0.40 × 0.29 × 0.18	0.46 × 0.20 × 0.10	0.1 × 0.2 × 0.4
θ range for data collection (°)	1.38–28.29	5.02–54.96	3.04–70.83
Limiting indices	$-33 \leq h \leq 33$, $-26 \leq k \leq 26$, $-27 \leq l \leq 26$	$-31 \leq h \leq 30$, $-12 \leq k \leq 17$, $-25 \leq l \leq 18$	$0 \leq h \leq 16$, $0 \leq k \leq 8$, $-23 \leq l \leq 22$
Reflections collected/unique	50,186/10,540 [$R_{\text{int}} = 0.0238$]	22,729/7619 [$R_{\text{int}} = 0.0315$]	10,787/10,787 [$R_{\text{int}} = 0.0000$]
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	10,540/0/532	7619/0/406	10,787/9/732
Goodness-of-fit on F^2	1.073	1.089	0.757
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0363$, $wR_2 = 0.1145$	$R_1 = 0.0384$, $wR_2 = 0.0948$	$R_1 = 0.0935$, $wR_2 = 0.2553$
R indices (all data)	$R_1 = 0.0399$, $wR_2 = 0.1188$	$R_1 = 0.0505$, $wR_2 = 0.0987$	$R_1 = 0.1038$, $wR_2 = 0.2693$
Largest difference peak and hole	3.670 and -0.453	+2.183 and -0.591	1.475 and -2.809

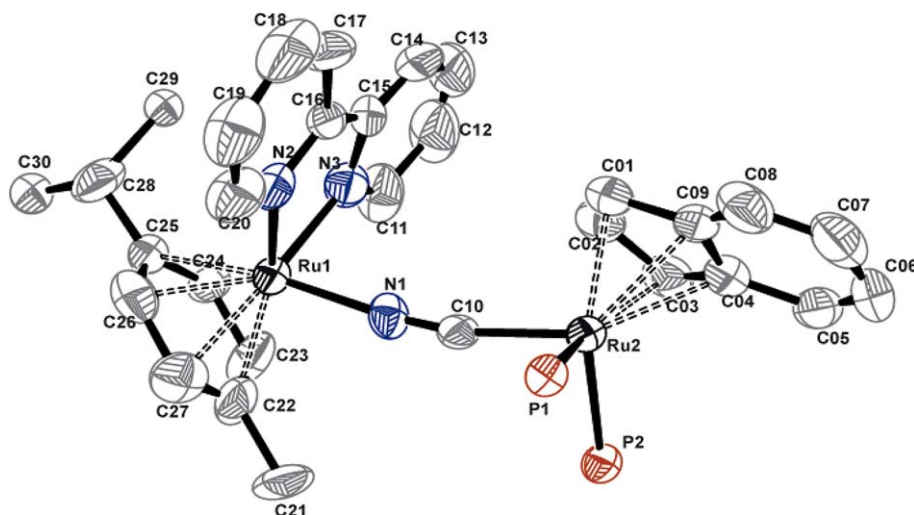


Fig. 1. Thermal ellipsoid (drawn at the 30% probability level) plot of $[(\text{ind})(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Ru}(\text{bipy})(\eta^6\text{-}p\text{-cymene})]^{2+}$ (**4**) with BF_4^- group, phenyl groups of PPh_3 and hydrogens omitted for clarity.

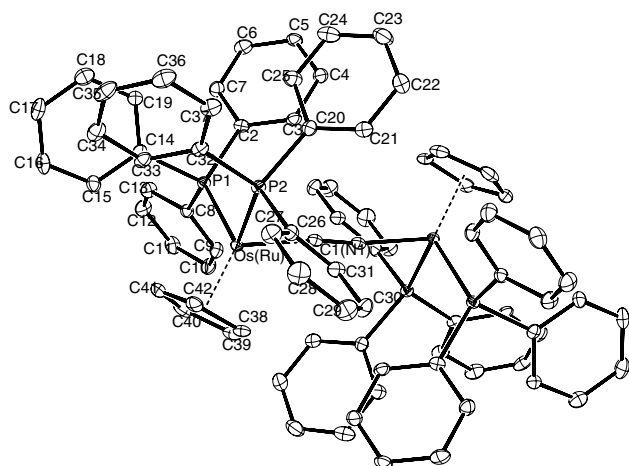


Fig. 2. ORTEP drawing of the $[\text{Cp}(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Os}(\text{PPh}_3)_2\text{Cp}]\text{BF}_4$ (**8**) with 30% probability thermal ellipsoids. BF_4^- anion and hydrogens omitted for clarity.

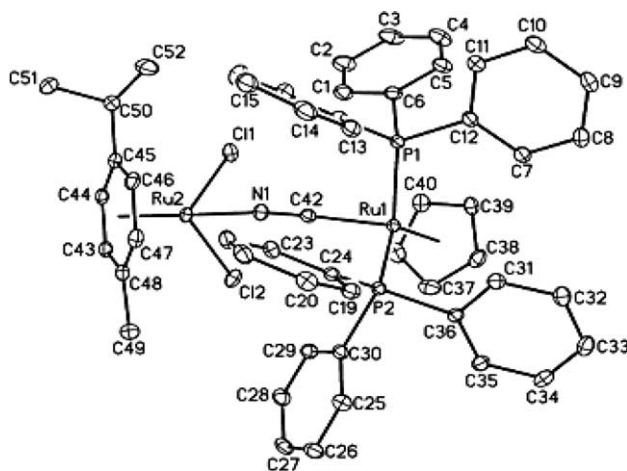


Fig. 3. Thermal ellipsoid (drawn at the 30% probability level) plot of $[\text{Cp}(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]\text{BF}_4$ (**11**) with BF_4^- anion and all the hydrogens being omitted for clarity.

Table 3

Selected bond lengths (Å) and bond angles (°) for the complex $[(\text{ind})(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Ru}(\text{bipy})(\eta^6\text{-}p\text{-cymene})](\text{BF}_4)_2$ (**4**) (estimated standard deviations are shown in parenthesis)

Bond lengths			
Ru(1)–N(1)	2.055(12)	Ru(1)–N(2)	2.165(16)
Ru(1)–N(3)	2.071(13)	Ru(1)–C(22)	2.17(2)
Ru(1)–C(23)	2.21(2)	Ru(1)–C(24)	2.130(17)
Ru(1)–C(25)	2.177(13)	Ru(1)–C(26)	2.143(17)
Ru(1)–C(27)	2.21(2)	Ru(2)–C(10)	1.957(13)
Ru(2)–P(1)	2.341(4)	Ru(2)–P(2)	2.362(3)
Ru(2)–C(01)	2.201(15)	Ru(2)–C(02)	2.170(15)
Ru(2)–C(03)	2.218(16)	Ru(2)–C(04)	2.367(15)
Ru(2)–C(09)	2.441(15)	C(10)–N(1)	1.111(17)
Bond angles			
N(1)–Ru(1)–N(3)	83.5(5)	N(1)–Ru(1)–N(2)	83.5(5)
N(3)–Ru(1)–N(2)	79.0(6)	Ru(1)–N(1)–C(10)	170.3(12)
N(1)–C(10)–Ru(2)	168.0(11)	C(10)–Ru(2)–P(1)	85.7(4)

Table 4

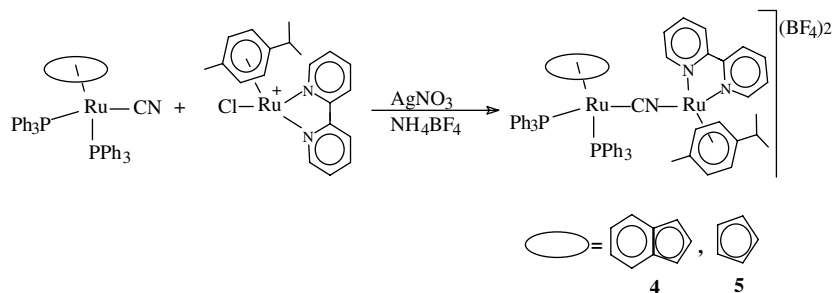
Selected bond lengths (Å) and bond angles (°) for the complex $[\text{Cp}(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Os}(\text{PPh}_3)_2\text{Cp}]\text{BF}_4$ (**8**) (estimated standard deviations are shown in parenthesis)

Bond lengths			
Os(Ru)–P2	2.3328(9)	Os(Ru)–C1(N1)	2.058(3)
C1(N1)–C1(N1)*	1.139(6)	Os(Ru)–P1	2.3327(9)
Bond angles			
C1–Os(Ru)–P2	89.73(9)	C1(N1)*–C1(N1)–Os(Ru)	172.1(4)
C1–Os(Ru)–P1	95.70(8)		

Table 5

Selected bond lengths (Å) and bond angles (°) for the complex $[\text{Cp}(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]\text{BF}_4$ (**11**) (estimated standard deviations are shown in parenthesis)

Bond lengths					
Ru(1)–C(42)	1.975(3)	Ru(1)–P(1)	2.2976(8)	Ru(1)–P(2)	2.2973(8)
Ru(2)–N(1)	2.048(3)	C(42)–N(1)	1.153(4)	Ru(2)–Cl(1)	2.4230(9)
Ru(2)–Cl(2)	2.4235(9)				
Bond angles					
Ru(1)–C(42)–N(1)	169.7(3)	P(1)–Ru(1)–P(2)	102.55(3)		
P(1)–Ru(1)–C(42)	88.77(9)	P(2)–Ru(1)–C(42)	91.52(9)		
Ru(2)–N(1)–C(42)	168.7(3)	N(1)–Ru(2)–Cl(1)	84.68(8)		
N(1)–Ru(2)–Cl(2)	85.02(8)	Cl(1)–Ru(2)–Cl(2)	88.03(3)		



Scheme 1.

of the triphenylphosphine ligands are in similar chemical environments.

It is worth mentioning that in a compound such as $[(\eta^6\text{-arene})\text{Ru}(\text{N},\text{N}')\text{Cl}]^+$, the arene (specifically *p*-cymene) ligand tended to be very labile during attempts to substitute the chloride ligand and often resulted in the displacement of the arene from the coordination sphere. Even though some arene-ruthenium(II) complexes containing tripodal nitrogen donor ligands have been synthesized [17], to our knowledge, complexes **4** and **5** offer the only examples of complexes having an $[(\eta^6\text{-arene})\text{Ru}]$ fragment, where the other available coordination sites are occupied by bipyridine and a nitrogen donor ligand.

5.2. X-ray structure of $[(\text{ind})(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Ru}(\text{bipy})(\eta^6\text{-}p\text{-cymene})][\text{BF}_4]_2$ (**4**)

Crystals suitable for an X-ray structure analysis were obtained via slow diffusion of hexane into a concen-

trated acetone solution of the compound. An ORTEP [13] representation is shown in Fig. 1 and a summary of X-ray structure determination is given in Table 2. Because of the poor quality of the data obtained from the complex $[(\text{ind})(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Ru}(\text{bipy})(\eta^6\text{-}p\text{-cymene})](\text{BF}_4)_2$ (**5**), discussion of the geometrical data will be only for the sake of comparison. The disposition of the bridging cyano ligand is such that the four atoms Ru(1), N(1), C(10), and Ru(2) are almost collinear with an angle of 170.3° at nitrogen and 168° at carbon. The Ru(1)–N(1) bond length of $2.055(12)$ Å is slightly shorter than the value of 2.15 Å noted in $[\text{Cp}(\text{dppe})\text{Ru}(\mu\text{-CN})\text{Ru}(\text{PPh}_3)_2\text{Cp}]^+$ [3] and the value of 2.165 Å noted in typical ruthenium N-donor systems like $[(\eta^4\text{-C}_8\text{H}_{12})\text{RuCl}_2(\text{CO})(\text{NCM}_2)]$ [18]. This supports the charge distribution $\text{Ru}^+-\text{N}\equiv\text{C}-\text{Ru}$ with the positive charge being localized on the metal bearing nitrogen. The C–N bond length of $1.111(17)$ Å is also slightly shorter than the value of $1.14(2)$ Å noted in $[\text{Cp}(\text{dppe})-$

$\text{Ru}(\mu\text{-CN})\text{Ru}(\text{PPh}_3)_2\text{Cp}]^+$. The $\text{Ru}(2)\text{-C}(10)$ bond length of 1.957(13) Å is also shorter than the Ru-C bond length of 2.03 Å found in $[\text{Cp}(\text{dppe})\text{Ru}(\mu\text{-CN})\text{-Ru}(\text{PPh}_3)_2\text{Cp}]^+$ [3], being closer to the values found in ruthenium-isonitrile complexes like $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\text{-}(\text{CNC}_6\text{H}_4\text{Me-}p)] \cdot \text{EtOH}$ (1.94 Å) [19] and $[\text{RuI}_2(\text{CO})(\text{PPh}_3)\{\text{CH}(\text{NMe})\text{C}_6\text{H}_4\text{Me-}p\}(\text{CNBu}^t)]$ (1.998 Å) [20].

5.3. Mono-cationic complexes

Reactions of the cyanide complexes **2**, **6** and **7** with the corresponding halo-complexes were also investigated, offering an example of heterobimetallic cyano-bridged species (Scheme 2). In comparison with those of **4** and **5**, the stretching frequency of the bridging cyano-ligand in these complexes **8–10** differs very little from those of the parent cyano-complex (shifted to a higher wave number by around 5 cm^{-1}). Here, the CN stretching frequency may not be the ideal gauge to determine whether coordination has taken place since the absorption of the bridging cyano group is generally in a higher region than in these complexes. The ^1H NMR spectrum clearly indicates the presence of the cyclopentadienyl ligands in all the complexes. In the case of complex **8**, however, the two Cp peaks are closely spaced and appear almost like a doublet for which an unambiguous assignment could not be made. The ^{31}P NMR spectra of these complexes show two singlets, one at the high field region assigned to the resonance of the P atoms attached to osmium metal (Table 1).

5.4. X-ray structure of $[\text{Cp}(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Os}(\text{PPh}_3)_2\text{Cp}]\text{BF}_4$ (**8**)

Crystals suitable for an X-ray structure analysis were obtained via slow diffusion of hexane into a concentrated dichloromethane solution of the compound. The ORTEP representation of complex (**8**) is shown in Fig. 2 and a summary of the X-ray structure determination is given in Table 2. The molecule lies on a crystallographic center of symmetry; the midpoint of the C1–N1 bond is on the center at 1/4, 1/4, 1/2. This serves to completely disorder the Os and Ru atoms and the C1 and

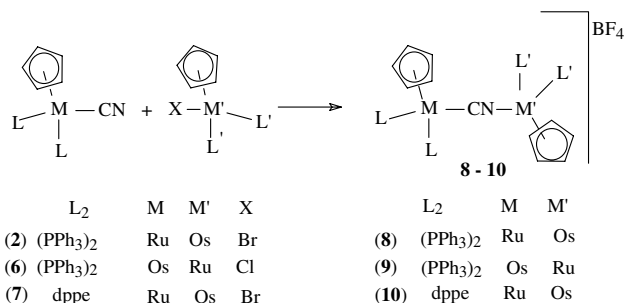
N1 atoms so that it is not possible to differentiate the Ru atom from the Os atom or the N1 atom from the C1 atom. In addition, the BF_4 ion is disordered over at least three areas and could not be reliably modeled. The C1(N1)–C1(N1)* bond length of 1.139(6) Å in (**8**) is close to the value of 1.14(2) Å observed in $[\text{Cp}(\text{dppe})\text{Ru}(\mu\text{-CN})\text{Ru}(\text{PPh}_3)_2\text{Cp}]^+$, being longer than that of **5**.

5.5. Neutral complexes

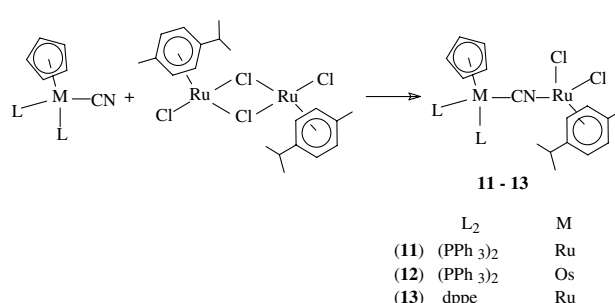
It is well known that the complex $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$ is a versatile starting material for synthetic manipulations. The chloride bridges may be easily cleaved to give a mono-nuclear compound or else the $p\text{-cymene}$ ligand may be replaced under forcing conditions. Thus, the reaction of the cyano-complexes **2**, **6** and **7** with $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$ afforded neutral bimetallic cyano-bridged complexes (Scheme 3) as anticipated.

Infrared spectroscopy affords an ideal gauge to determine whether the coordination of the second metal has taken place or not. The infrared spectra of the complexes **11**, **12** and **13** exhibit strong bands assignable to $\nu_{(\text{C}=\text{N})}$ at 2110, 2105 and 2103 cm^{-1} , respectively. The stretching frequency of the cyanide band is shifted by about 30 cm^{-1} , quite a significant shift when compared to that observed in the previous cationic complexes. It is apparent that the chloride ligands participate to enhance donation of the electron lone pairs from both the atoms in the CN moiety towards the ruthenium metal center, which are in fact anti-bonding with respect to C=N bond. Hence the $\nu_{(\text{C}=\text{N})}$ frequency increases with increasing donation of these lone pairs [14].

The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectral data are given in Table 1. The proton NMR spectra of these complexes exhibit a strong resonance for Cp protons at around 4.5 ppm, while the $p\text{-cymene}$ resonance appears in the usual range as a doublet, singlet and septet for the isopropyl methyl groups, methyl group and proton of isopropyl group, respectively. The ^{31}P NMR spectrum exhibits a sharp singlet for the triphenylphosphine phosphorus atoms.



Scheme 2.



Scheme 3.

5.6. X-ray structure of $[Cp(PPh_3)_2Ru(\mu-CN)RuCl_2(\eta^6-p\text{-cymene})]BF_4$ (**11**)

Crystals suitable for X-ray structure analysis were obtained via slow diffusion of diethylether into a concentrated methanol solution of the compound. The ORTEP representation is shown in Fig. 3 and a summary of the X-ray structure determination given in Table 2. The disposition of the bridging cyano-ligand is such that the four atoms Ru(1), C(42), N(1) and Ru(2) are almost collinear with an angle of 169.7° at the carbon and of 168.7° at the nitrogen; these angles are quite similar to those for the complex **5**. The Ru(2)–Cl(1) and Ru(2)–Cl(2) bond distances of 2.4290(9) and 2.4290(9) Å, respectively, are also essentially similar and quite comparable with those of other neutral *p*-cymene ruthenium complexes [21]. The Ru(1)–P(1) and Ru(1)–P(2) bond lengths are again more or less similar, being 2.2976(8) and 2.2973(8) Å, respectively, but slightly shorter than those found in $[CpRu(PPh_3)_2Cl]$ [22].

The CN bond length in the dicationic, cationic and neutral complexes **4**, **8** and **11**, respectively, lies in the order $4 < 8 < 11$, being 1.111(17), 1.139(6) and 1.153(4) Å, respectively. The $\nu_{(C=N)}$ frequency increases with increasing donation of anti-bonding electron pair from both atoms of the CN group (see Table 1).

6. Supplementary material

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre (CCDC) at CCDC No. **257427** for complex **11**, **257428** for complex **8** and **257429** for complex **4**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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