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Synthesis and spectroscopic properties of cationic Ru(II) arene complexes $[Ru(\eta^6\text{-arene})(P)Cl(L)]^+$. ($P = PPh_3$, PEt_3, $MePPr^i_2$ and L = 4-cyanopyridine or 1,4-dicyanobenzene)

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Abstract

Reactions of $[Ru(\eta^6\text{-arene})(P)Cl_2]$ ($P = PPh_3$, PEt_3 or $MePPr^i_2$) with organonitriles 4-cyanopyridine or 1,4-dicyanobenzene (referred hereafter as CNPy or DCB) in methanol, in the presence of NH_4PF_6, gives the cationic arene complexes $[Ru(\eta^6\text{-arene})(P)Cl(L)]^+$ (L = CNPy or DCB). The reaction products have been characterized by physico-chemical methods viz., elemental analyses, IR, ^1H-, ^{13}C-, ^{31}P-NMR, electronic and FAB mass spectra. The spectral data of the complexes revealed the presence of a pendant nitrile group. These could behave as potential metallo-ligands and could find wide application in the syntheses of homo- or heterobimetallic mixed valence bridged complexes.

Keywords: Ruthenium arene complexes; 4-Cyanopyridine; 1,4-Dicyanobenzene; Metallo-ligands; Synthon

1. Introduction

Recently, considerable attention has been paid to the synthesis and characterization of homo- and hetero-polynuclear complexes owing to their potential use in photochemical molecular devices and as light sensitive probes in biological systems [1–3]. In this regard, organonitriles viz., 4-cyanopyridine (CNPy), 1,4-dicyanobenzene (DCB), 1,4-dicyano-*trans*-2-butene, 1,4-dicyanopiperazinedicarbonitrile, etc., have received special attention [4]. Interest in these ligands stems from the presence of the two donor sites, which raises the possibility of formation of mono- and binuclear complexes. Recently, we have shown that the reaction of dimeric chloro-bridged Ru(II) complexes $[\{Ru(\eta^6\text{-arene})CI_2\}_2]$ (η^6-arene = benzene, *p*-cymene or hexamethylbenzene) with CNPy, DCB or 1,4-piperazinedicarbonitrile, in dichloromethane, gives neutral mononuclear and binuclear complexes with the formulations $[Ru(\eta^6\text{-arene})Cl_2(L)]$ and $[\{Ru(\eta^6\text{-arene})Cl_2\}_2(\mu\text{-L})]$, whereas its reaction with dicyano *trans*-2-butene gives only binuclear complexes $[\{Ru(\eta^6\text{-arene})Cl_2\}_2(\mu\text{-DCBT})]$ [5]. Reactions of these organonitriles with closely related phosphine containing complexes $[Ru(\eta^6\text{-arene})Cl_2(L)]$ ($L = PPh_3$, $AsPh_3$, PMe_3 or $MeP(Pr^i)_2$] have not been studied. Because of our continuing interest in this area, we decided to carry out a detailed study of the reactivity of $[Ru(\eta^6\text{-arene})Cl_2(L)]$ ($L = PPh_3$, $AsPh_3$, PMe_3 or $MeP(Pr^i)_2$) with the organonitriles like CNPy and DCB. Our prime concern in undertaking this study was: (a) to investigate the stretching frequency of the nitrile group of the organonitrile when it is bound to electron rich metal centres in mononuclear and binuclear complexes; (b) to investigate how bridging affects the electronic and photophysical properties of the spectator ligand and (c) to investigate the effect on bonding properties of the second functional group remote from the coordinated site in the mononuclear complexes. In this paper we describe and discuss the spectral properties of the complexes resulting from the reactions of $[Ru(\eta^6\text{-arene})Cl_2(L)]$ with CNPy and DCB.

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2. Results and discussion

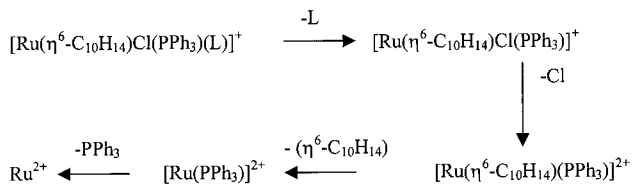
The phosphine containing arene complexes [Ru(η^6-arene)Cl_2(P)] (P = PPh_3, PEt_3 or $MePPr^i_2$) react with organonitriles, CNPy or DCB in the presence of NH_4PF_6 in methanol to from the mononuclear cationic arene complexes with the general formulation [Ru(η^6-arene)(P)Cl(L)]PF_6 (L = CNPy or DCB).

$$[Ru(\eta^6\text{-}C_6H_6)Cl_2(P)] + L \xrightarrow[NH_4PF_6]{MeOH} [Ru(\eta^6\text{-}C_6H_6)Cl(P)(L)]PF_6$$

Bright-yellow to orange cationic complexes are high melting, non-hygroscopic, air-stable, shiny crystalline solids. These are sparingly soluble in methanol, benzene, soluble in dichloromethane, chloroform, methanol, acetone, acetonitrile, dimethylformamide, dimethylsulfoxide and insoluble in petroleum ether and diethyl ether.

Analytical data of the complexes are consistent with our formulations. Conductance behavior of the complexes under study show that all these are ionic in nature and their conductances are in good agreement with those of similar electrolyte types under identical conditions.

Information about the composition of the complexes has also been obtained from fast atom bombardment spectroscopy. FAB mass spectra of the complexes (Fig. 1(a, b)) [Ru(η^6-$C_{10}H_{14}$)Cl(PPh_3)(CNPy)]PF_6 (**4**) and [Ru(η^6-$C_{10}H_{14}$)Cl(PPh_3)(DCB)]PF_6 (**11**) exhibit analogous fragmentation patterns. Molecular ion peaks appeared at m/z 637(Calc. 637) and m/z 661(Calc. 662), respectively, in the FAB mass spectra of these complexes corresponding to [Ru(η^6-$C_{10}H_{14}$)Cl(PPh_3)(CNPy)]$^+$ and [Ru(η^6-$C_{10}H_{14}$)(PPh_3)Cl(DCB)]$^+$. In step II, the coordinated organonitrile (CNPy or DCB) is given out to form [Ru(η^6-$C_{10}H_{14}$)Cl(PPh_3)]$^+$. It is evident from the presence of a peak at m/z 533 (Calc. 533). Step III of the fragmentation pattern involves loss of the chloro ligand to give dicationic species [Ru(η^6-$C_{10}H_{14}$)(PPh_3)]$^{2+}$, a corresponding peak is present at m/z 497 (Calc.497). In the next step, loss of the η^6-arene ligand takes place to form [Ru(PPh_3)]$^{2+}$, which is evident from the presence of a peak at m/z 363 (Calc. 363). This step suggested that Ru–P bond is stronger than the Ru–arene bond. Finally, the coordinated triphenylphosphine molecule is given out in phases. The overall fragmentation pattern may be given as:



The above fragmentation pattern conforms well to our formulation for these complexes. Further, the bonding mode in the complexes and their tentative structures have been deduced from following spectral studies (Fig. 2).

2.1. IR spectra

The ligand CNPy can bind a metal centre through its nitrile nitrogen, pyridine nitrogen or both the nitrogen atoms as in the bridged complexes. Coordination through the nitrile nitrogen is expected to lead a shift in the position of nitrile stretching frequency, while coordination through the pyridine ring nitrogen should lead to shifts in the position of pyridine ring vibrations (1543, 1493, 1410,1199, 1109, 1072 and 585 cm^{-1}) without a significant shift in the position of the nitrile stretching frequency ν(C≡N). The site of coordination of the ligand CNPy in the complexes have been elucidated from the shifts in the position of ν(C≡N) and pyridine ring vibrations.

IR spectra of complexes **1**–**7** under study exhibited strong vibrations around 2240 cm^{-1}, assignable to the

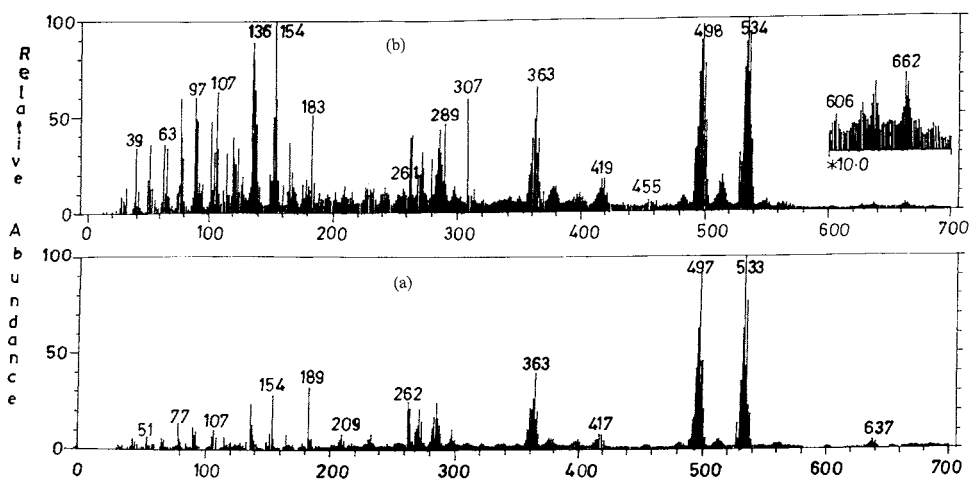


Fig. 1. FAB mass spectra of complexes **4a** and **11b**.

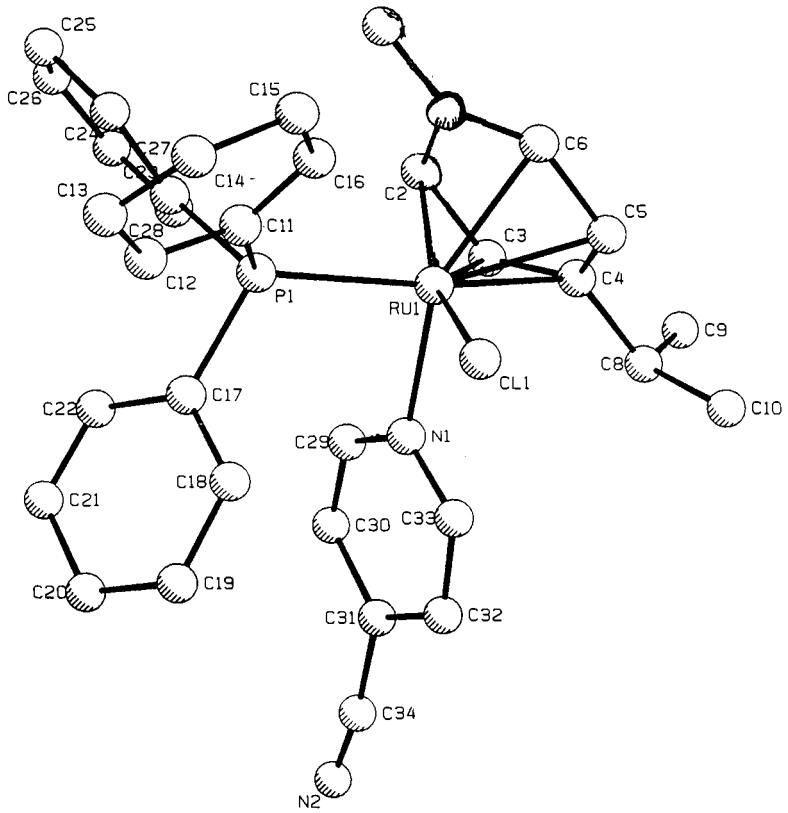


Fig. 2. A PLUTO representation of complex **4** based on 2000 reflections.

nitrile stretching frequency ν(C≡N). The position of the ν(C≡N) band in the complexes is essentially unaffected, implying non-coordination of the nitrile group. An insignificant change of (~ 3–5 cm^{-1}) in the position of the ν(C≡N) band could arise from resonance and electronic effects (π-back bonding) due to the linkage of CNPy with the metal centre. It is therefore presumed that the ligand binds with the metal centre through its pyridine ring nitrogen atom. This observation is consistent with earlier reports [6]. The bonding through the pyridine ring nitrogen is further supported by the shifts in the position of the bands having contribution from ν(C–C) and ν(C–N) of the pyridine molecule in the region 1600–1400 cm^{-1}, towards higher wave number side [6a, h,7].

The infrared spectra of free 1,4-dicyanobenzene molecules displays an intense sharp band at 2232 cm^{-1} corresponding to ν(C≡N) [4a]. IR spectra of the 1,4-dicyanobenzene complexes **8**–**14,** exhibited two sharp bands in the region ~ 2230 and ~ 2260 cm^{-1} assignable to ν(C≡N). The presence of two sharp bands in the nitrile frequency region suggested that only one of the nitrile groups of the DCB ligand is involved in coordination with the ruthenium(II) centre. The shift in the position of the band at 2232 cm^{-1} towards a higher wave number as compared with that in the free ligand reflects: (i) direct coordination of the metal ion Ru(II) to the nitrogen of the nitrile group and (ii) poor back-bonding from the Ru(II) centre. This observation is consistent with the conclusions drawn from ^{13}C-NMR spectral data of the complexes (vide infra).

The characteristic bands due to η^6-arene, coordinated phosphines PPh_3, PEt_3, $MePPr^i_2$ and the counter ion PF_6^- are also exhibited in the IR spectra of the respective complexes.

2.2. ^{1}H-NMR spectra

The ^{1}H-NMR spectral data along with their assignments are summarized with the selected data of the complexes. The ^{1}H-NMR spectra of the complexes $[Ru(\eta^6\text{-}C_6H_6)Cl(P)(CNPy)]^+$ with PPh_3, PEt_3, or $MePPr^i_2$ as co-ligands **1**–**3** showed sharp singlets (PPh_3, δ 5.99 ppm; PEt_3, 6.17 ppm; $MePPr^i_2$, 6.21 ppm) characteristic for the coordinated η^6-C_6H_6 ligand. The arene protons exhibited a downfield shift as compared with that in the precursor complex. Similar downfield shifts were observed for aromatic proton resonance of η^6-$C_{10}H_{14}$ and C_6Me_6 in their respective complexes $[Ru(\eta^6\text{-}C_{10}H_{14})Cl(P)(CNPy)]^+$ and $[Ru(\eta^6\text{-}C_6Me_6)Cl(PPh_3)(CNPy)]^+$ (**4**–**7**). The arene protons in all the complexes undergoes a downfield shift as compared with that in the $[\{Ru(\eta^6\text{-arene})Cl_2\}_2]$ (η^6-arene = benzene, *p*-cymene or hexamethylbenzene), and in the pre-

cursor complexes [Ru(η^6-arene)Cl_2(P)] or closely related complexes [Ru(η^6-arene)Cl_2(CNPy)] [5,8]. This observation is consistent with earlier reports. The shifting of the η^6-arene proton resonance towards the low-field side may result from the change of electron density on the metal due to bonding of the pyridine ring nitrogen with the Ru(II) centre. Furthermore, the nitrile group –CN, substituted in the *para* position of the pyridine ring pulls electron density away from the pyridine nucleus towards itself, which in turn affects electron density on the Ru(II) centre. It may consequently lead to a pull of more electron density from η^6-arene towards Ru(II), resulting in deshielding of the η^6-arene protons. α and β protons of the ligand CNPy resonated in the range δ 9.45–8.82 ppm and δ 7.93–7.71 ppm, respectively. In the majority of the complexes these exhibited upfield shift as compared with those in the free ligand [9a–c,10]. One may tentatively attribute these shifts to the π-backbonding from Ru(II) to the CNPy ligand.

The ^{1}H-NMR spectra of the [Ru(η^6-C_6H_6)Cl(P)(DCB)]$^+$ complexes **8**–**10** displayed sharp singlets (PPh_3; 6.14, PEt_3; 6.62, $MePPr^i_2$; 6.37) characteristic for coordinated η^6-C_6H_6 ligands. These, as well as proton resonance corresponding to η^6-arene in the complexes [Ru(η^6-$C_{10}H_{14}$)Cl(P)(DCB)]$^+$ and [Ru(η^6-C_6Me_6)(EPh_3)Cl(P)(DCB)]$^+$ (**11**–**14**), also exhibited downfield shift as compared with those in the arene complexes [Ru(η^6-$C_{10}H_{14}$)Cl_2}$_2$] and the precursor complexes [{Ru(η^6-arene)Cl_2(P)] [5,8]. It suggests that the CN moiety in DCB complexes affect the electronic environment of η^6-arene protons. The signals of the phenyl protons of the DCB resonated in the range δ 7.8–8.4 ppm. These also exhibited a downfield shifts as compared with those in the free ligand (δ 7.8 ppm) [4a].

Signals due to phosphine protons are found in their usual positions in the ^{1}H-NMR spectra of the respective complexes.

2.3. $^{13}C\{^1H\}$-NMR spectra

The ^{13}C-NMR spectral data of the complexes are consistent with the conclusions drawn from ^{1}H-NMR data. The η^6-C_6H_6 carbons in the complexes [Ru(η^6-C_6H_6)Cl(P)CNPy]$^+$ appeared at δ 90.93 (in PPh_3 complex), 93.21 (in PEt_3 complex) and 93.60 ppm in the $MePPr^i_2$ complex. It exhibited a downfield shift side as compared with precursor complexes [Ru(η^6-arene)Cl_2(P)]. The nitrile carbon (CN) of the CNPy ligand also displayed a downfield shift (PPh_3, δ 121.06 ppm; PEt_3, δ 119.6 ppm; $MePPr^i_2$, δ 120.2 ppm) in the complexes **1**–**3** as compared with those in the free ligand (δ 117.6 ppm). The α, β and γ carbons of CNPy resonated at δ 157.56, 128.6 and 126.77 ppm, respectively, in [Ru(η^6-C_6H_6)Cl(PPh_3)(CNPy)]$^+$ and at δ 150.72, 128.27 and 125.58 ppm in [Ru(η^6-C_6H_6)Cl(PEt_3)(CNPy)]$^+$. The ^{13}C-NMR spectra of complexes [Ru(η^6-$C_{10}H_{14}$)Cl(P)(CNPy)]$^+$ and [Ru(η^6-C_6Me_6)Cl(PPh_3)(CNPy)]$^+$ (**4**–**7**) followed the similar trends. The phosphine carbons in all these complexes resonated in their usual positions.

An interesting aspect of the ^{13}C-NMR spectra of the dicyanobenzene complexes [Ru(η^6-C_6H_6)Cl(P)(DCB)]$^+$ (**8**), [Ru(η^6-$C_{10}H_{14}$)Cl(P)(DCB)]$^+$ (**9**) are the presence of two resonance in the nitrile carbon region. ^{13}C-NMR spectra of all the complexes under study exhibited one resonance at δ 117.1 ppm characteristic of the uncoordinated nitrile carbon of the ligands, in addition to it another signal exhibiting an upfield shift is observable at around δ 115.74 ppm. The carbon at δ 115.7 ppm has assigned to coordinated C≡N carbon, while one at $\delta \sim 117$ ppm has been assigned to pendant C≡N group. It suggested that the dicyanobenzene molecule in these complexes is coordinated with the Ru(II) centre through one of its nitrile group. Although the shift is not very large, it may be that upon coordination of the nitrile nitrogen with the ruthenium, electron density on the carbon atom of the C≡N group is polarized towards the nitrogen atom. It results in deshielding of the carbon atom through the 'σ' bond, but the back donation of the electron density from the ruthenium to the π^* orbital of CN group more than compensates the deshielding effect, so that only a small amount of net shielding of the carbon nucleus occurs. This supports the back donation of π-electrons from ruthenium to the π^* orbitals of DCB. The carbon atoms (>C–CN) of the benzene ring of DCB underwent deshielding due to strong electron attracting inductive effect of CN group. This resonated at $\delta \sim 123$ ppm in these complexes compared with the values reported for the free ligand. The *ortho* and *meta* carbon atoms of the benzene ring appeared in the region characteristic for phenyl carbon resonances of other collegians present in the column in the region 120–136 ppm as multiplets.

2.4. ^{31}P-NMR spectra

The ^{31}P-NMR spectra of the complexes [Ru(η^6-C_6H_6)Cl(P)(CNPy)]$^+$ consisted of singlets (PPh_3, δ 37.47; PEt_3, 27.58; $MePP^ir_2$, 32.95 ppm) corresponding to coordinated phosphine ^{31}P nuclei. In the *p*-cymene complexes [Ru(η^6-$C_{10}H_{14}$)Cl(P)(CNPy)]$^+$ these are observable at δ 36.85; 30.00 and 24.06 ppm, respectively, corresponding to coordinated PPh_3, PEt_3 and $MePP^ir_2$ ligand. Similarly, all the DCB complexes under study exhibited sharp singlets. In all these complexes ^{31}P nuclei exhibited a downfield shift as compared with those in the free ligands. The deshielding may be caused by relatively less donation of electron density from the Ru(II) centre to phosphorous through back bonding, suggesting that the degree of dπ–pπ back bonding influences the chemical shift of the phosphorous atoms.

The ^{31}P nuclei of the counter ion PF_6^- resonated at $\delta \sim 103$ ppm in all these complexes in its septet pattern.

2.5. Electronic spectra

The interaction of filled $d\pi(t_2g)$ orbitals on Ru(II) with low lying π^* orbitals on the CNPy ligand should provide a metal-to-ligand charge transfer (MLCT) transition ($t_2g \rightarrow \pi^*$) in the electronic spectra of these complexes, with the transition energy of these bands varying with the nature of the ligands acting as π-acceptors. The presence of an electron withdrawing group (CN) in the *para* position of the pyridine molecule should decrease the energy of transition causing a red shift in the MLCT maxima, while an electron donating group should increase the transition energy [6a,b,7b,9].

The electronic spectra of 4-cyanopyridine complexes with the formulations $[Ru(\eta^6\text{-arene})Cl(P)(CNPy)]^+$ displayed bands ~ 450, ~ 330 and ~ 260–265 nm. The bands around 450 nm has been assigned to a MLCT transition [$t_2g(Ru(II) \rightarrow \pi^*(CNPy)$]. The λ_{max} and E_{max} values of this band is consistent with those of the pyridine bound CNPy complexes of Ru (II) [10a, b]. Further support for the bonding is provided by the fact that the aromatic nitrogen bonded complexes always absorb at a larger wavelength compared with nitrile (CN) bound complexes [6a,7b]. The bands around 350 nm are assigned to the MLCT transition arising from Ru (II) to π^* orbitals of the η^6-arene ligand. The possibility of these bands arising from other MLCT transitions may be ruled out since the likelihood of transitions appearing from Ru(II) to phosphines in the near UV region is obscured. The intra ligand $\pi \rightarrow \pi^*$ transitions are observed in the region 250–256 nm.

Electronic spectra of dicyanobenzene complexes with the formulations $[Ru(\eta^6\text{-arene})Cl(P)(DCB)]^+$ displayed bands in the region ~ 450, 340–360 and ~ 260 nm. The broad to medium intensity bands centred around 450 nm have been assigned to MLCT bands arising from drift of electron density from filled $Ru(II) \rightarrow d\pi(t_2g)$ orbitals to the low lying π^* orbitals of the –CN group of the DCB ligand. The position of this band is consistent with those in other nitrile complexes. The band around 450 nm did not show any solvatochromic effect in common organic solvents, indicating no change is the dipole moments of the molecule in the ground state and excited state. It further supported our charge transfer assignment. The band around 330 nm has been assigned to an MLCT transition [$Ru(II) \rightarrow \pi^*$ on the arene ring].

Analytical and spectral data of the complexes are in excellent agreement with our formulation of the complexes $[Ru(\eta^6\text{-arene})Cl(P)(L)]^+$, it suggested the presence of a pendant donor nitrile group. The presence of this group offers unique opportunity for behaving as metallo-ligand or as synthon in the synthesis of homo–hetero bimetallic mixed valence bridged complexes. An attempt was made to confirm the structure of one of the representative complex $[Ru(\eta^6\text{-}C_{10}H_{14})Cl(PPh_3)\text{-}(CNPy)]PF_6$ by single-crystal X-ray analysis. A single crystal of this complex showed decay after 2000 reflections. However, structure of the complex based on these 2000 reflections revealed the coordination of CNPy through the pyridine ring nitrogen and presence of a pendant donor nitrile group. Overall single crystal data is not worth publication.

3. Experimental

The chemicals used for the reaction were Analar or chemically pure grade. Solvents were dried prior to use. 4-Cyanopyridine, 1,4-dicyanobenzene, triphenylphosphine or triethylphosphine were used as received without further purification. The precursor complexes $[Ru(\eta^6\text{-arene})Cl_2(L)]$ and methyldiisopropylphoshine were prepared following the literature procedure [8]. The elemental analyses were performed by microanalytical division of RSIC, Central Drug Research Institute, Lucknow. IR spectra were recorded in Nujol mulls on Perkin–Elmer 577 and Perkin–Elmer 881 spectrophotometers. NMR spectra were recorded on a Varian unity 400 MHz or Varian Gemini 200 MHz or Bruker DRX 300 MHz instruments. The chemical shifts are given in ppm relative to tetramethylsilane (^1H, $^{13}C\{^1H\}$), 85% H_3PO_4 ($^{31}P\{^1H\}$). Electronic spectra were obtained on a Shimadzu UV-160 spectrophotometer. FAB mass spectra were recorded on a JEOL SX 102DA 6000 mass spectrometer using Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature (r.t.) with *m*-nitrobenzyl alcohol as the matrix.

3.1. Procedure

3.1.1. Preparation of $[Ru(\eta^6\text{-}C_6H_6)(PPh_3)Cl(CNPy)]PF_6$ (1)

A suspension of $[Ru(\eta^6\text{-}C_6H_6)Cl_2(PPh_3)]$ (512 mg, 1 mmol) and CNPy (104 mg, 1 mmol) in methanol (25 ml) was stirred for ~ 4.0 h at r.t. and filtered through Celite to remove any solid impurity. To the filtrate NH_4PF_6 (163 mg, 1 mmol) dissolved in methanol (10 ml) was added and left for slow crystallization. After 2–3 days a fine microcrystalline product separated out. It was filtered washed twice with methanol, diethyl ether and dried under vacuo. Yield 580 mg (80%). Anal. Calc. for $C_{30}H_{25}ClF_6N_2P_2Ru$: C, 49.62; H, 3.44; N, 3.85. Found; C, 49.50; H, 3.45; N, 3.82%. IR (Nujol) 2241 cm^{-1}, $\nu(C\equiv N)$; ^1H-NMR ($CDCl_3$, TMS, ppm); ^1H: δ 9.00 (d, 2H, 6.2 Hz, α*H*–CNPy); 7.70 (d, 2H, 6.4 Hz, β*H*-CNPy); 7.56–7.17 (br. m., 15H, PPh_3); 5.99 (sharp singlet, 6H, $\eta^6\text{-}C_6H_6$); $^{13}C\{^1H\}$: δ 157.56

(αC–CNPy); 135–128.8 (PPh_3); 128.611 (βC–CNPy); 126.77 (γC–CNPy); 121.063 (C≡N, CNPy); 90.95 (C_6H_6); $^{31}P\{^1H\}$: δ 37.47 (PPh_3), 103.32 (PF_6^-); UV–vis (acetone, λ_{max}, nm) 450, 330 and 265.

3.1.2. Preparation of $[Ru(\eta^6\text{-}C_6H_6)(PEt_3)Cl(CNPy)]PF_6$ (2)

It was prepared following the above procedure starting from $[Ru(\eta^6\text{-}C_6H_6)Cl_2(PEt_3)]$ with CNPy in methanol. Yield 60%. Anal. Calc. for $C_{18}H_{25}ClF_6N_2P_2Ru$: C, 37.14; H, 4.29; N, 4.81. Found: C, 37.10; H, 4.12; N, 4.65%. IR (Nujol) 2242 cm^{-1}, ν(C≡N); ^{1}H-NMR ($CDCl_3$, TMS, ppm); ^{1}H: δ 9.43 (d, 2H, 6.4 Hz, αH–CNPy); 7.96 (d, 2H, 6.8 Hz, βH–CNPy); 6.17 (sh. s., 6H, C_6H_6); 2.03 (m, 6H, CH_2, PEt_3), 1.08 (m, 9H, CH_3, PEt_3); $^{13}C\{^1H\}$: δ 150.72 (αC–CNPy); 128.27 (βC–CNPy); 125.58 (γC–CNPy); 119.6 (C≡N, CNPy); 93.21 (C_6H_6); 29.41 (CH_2 of PEt_3); 18.25 (CH_3 of PEt_3); $^{31}P\{^1H\}$: δ 27.58 (PEt_3), 103 (PF_6^-); UV–vis (acetone, λ_{max}, nm) 445, 300 and 240.

3.1.3. Preparation of $[Ru(\eta^6\text{-}C_6H_6)(MePPr^i_2)Cl(CNPy)]PF$ (3)

This complex was prepared from the reaction of $[Ru(\eta^6\text{-}C_6H_6)Cl_2(MePPr^i_2)]$ with CNPy in methanol. Yield 65%. Anal. Calc. for $C_{19}H_{27}ClF_6N_2P_2Ru$: C, 38.28; H, 4.53; N, 4.70. Found: C, 38.08; H, 4.58; N, 4.78%. IR (Nujol) 2245 cm^{-1}, ν(C≡N); ^{1}H-NMR ($CDCl_3$, TMS, ppm); ^{1}H: δ 9.45 (d, 2H, 6.8 Hz, αH–CNPy); 7.93 (d, 2H, 6.8 Hz, βH–CNPy); 6.21 (sh s, 6H, C_6H_6); 2.78 (m, $CH(CH_3)_2$); 2.48 ($CH(CH_3)_2$); 2.12 ($CH_3PPr^i_2$); $^{31}P\{^1H\}$: δ 32.95 ($MePPr^i_2$), 103.31 (PF_6^-); UV–vis (acetone, λ_{max}, nm) 435, 290, 260.

3.1.4. Preparation of $[Ru(\eta^6\text{-}C_{10}H_{14})(PPh_3)Cl(CNPy)]PF_6$ (4)

It was prepared following the above procedure starting from $[Ru(\eta^6\text{-}C_{10}H_{14})Cl_2(PPh_3)]$ with CNPy. Yield 80%. Anal. Calc. for $C_{34}H_{33}ClF_6N_2P_2Ru$: C, 52.20; H, 4.22; N, 3.58. Found: C, 51.86; H, 4.19; N, 3.51%. IR (Nujol) 2239 cm^{-1}, ν(C≡N); ^{1}H-NMR ($CDCl_3$, TMS, ppm); ^{1}H: δ 9.13 (d, 2H, 5.8 Hz, αH–CNPy); 7.71 (d, 2H, 6.6 Hz, βH–CNPy); 7.65–7.16 (br. m., 15H, $P(C_6H_5)_3$); 6.16, 6.41 (dd, 4H, 6.6 Hz, C_6H_4); 2.84 (sp., 1H, 2.4 Hz, $CHMe_2$), 1.96 (s, 3H, C–CH_3), 1.33 (d, 6H, 2.4 Hz, $CH(CH_3)_2$); $^{13}C\{^1H\}$: δ 158.38 (αC–CNPy); 135.14–129.35 ($P(C_6H_5)_3$), 128.00 (βC–CNPy); 124.35 (γC–CNPy); 120.68 (C≡N, CNPy); 106.06 (C–$CHMe_2$), 95.98 (C–CH_3); 88.22 and 89.15 (C_6H_4), 30.66 ($CHMe_2$), 21.47 ($CH(CH_3)_2$), 18.20 (C–CH_3); UV–vis (acetone, λ_{max}, nm) 456, 425, 260.

3.1.5. Preparation of $[Ru(\eta^6\text{-}C_{10}H_{14})(PEt_3)Cl(CNPy)]PF_6$ (5)

It was prepared following the above method starting from $[Ru(\eta^6\text{-}C_{10}H_{14})Cl_2(PEt_3)]$ with CNPy in methanol. Yield 78%. Anal. Calc. for $C_{22}H_{33}ClF_6N_2P_2Ru$: C, 41.41; H, 5.17; N, 4.39. Found: C, 41.21; H, 5.18; N, 4.40%. IR (Nujol) 2242 cm^{-1}, ν(C≡N); ^{1}H-NMR ($CDCl_3$, TMS, ppm); ^{1}H: δ 8.82 (d, 2H, 2.4 Hz, αH–CNPy); 7.84 (d, 2H, 2.4 Hz, βH-CNPy); 5.89–5.83 (dd, 4H, 2.8 Hz, C_6H_4); 2.65 (sp., 1H, 3.4 Hz, $CHMe_2$), 2.49 (m, CH_2 of PEt_3), 1.86 (s, 3H, C–CH_3), 1.36 (d, 6H, 2.6 Hz, $CH(CH_3)_2$); 1.18 (m, CH_3 of PEt_3); $^{13}C\{^1H\}$: δ 150.72 (αC–CNPy); 127.43 (βC–CNPy); 125.58 (γC–CNPy); 121.64 (C≡N, CNPy); 104.45 (C–$CHMe_2$); 95.39 (C–CH_3); 90.17–90.02 (C_6H_4); 30.76 ($CHMe_2$), 21.54 ($CH(CH_3)_2$); 18.132 (C–CH_3), 17.40 (CH_2 protons of PEt_3), 7.55 (CH_3 protons of PEt_3), $^{31}P\{^1H\}$: δ 30.00 (PEt_3), 103.32 (PF_6^-); UV–vis (acetone, λ_{max}, nm) 445, 320, 265.

3.1.6. Preparation of $[Ru(\eta^6\text{-}C_{10}H_{14})(MePPr^i_2)Cl(CNPy)]PF_6$ (6)

It was prepared following the above procedure starting from $[Ru(\eta^6\text{-}C_{10}H_{14})Cl_2(MePPr^i_2)]$ with CNPy in methanol. Yield 80%. Anal. Calc. for $C_{22}H_{33}ClF_6N_2P_2Ru$: C, 41.41; H, 5.17; N, 4.39. Found: C, 41.17; H, 5.12; N, 4.28%. IR (Nujol) 2224 cm^{-1}, ν(C≡N); ^{1}H-NMR ($CDCl_3$, TMS, ppm); ^{1}H: δ 8.82 (d, 2H, 4.4 Hz, αH–CNPy); 7.84 (d, 2H, 4.8 Hz, βH–CNPy); 6.00, 6.07 (dd, 4H, 5.6 Hz, C_6H_4); 2.70 (sp., 1H, 6.4 Hz, $CHMe_2$), 2.14 (s, 3H, C–CH_3), 2.04 (m, $CH(CH_3)_2$, $MePPr^i_2$); 1.28 (dd, 6.4 Hz, $CHCH_3$), 0.98 (m, $CH(CH_3)_2$ of $MePPr^i_2$; $^{31}P\{^1H\}$ (H_3PO_4): δ 24.06 ($MePPr^i_2$), 103.26 (PF_6^-).

3.1.7. Preparation of $[Ru(\eta^6\text{-}C_6Me_6)(PPh_3)Cl(CNPy)]PF_6$ (7)

This complex was prepared from the reaction of $[Ru(\eta^6\text{-}C_6Me_6)Cl_2(PPh_3)]$ with CNPy in methanol. Yield 70%. Anal. Calc. for $C_{36}H_{37}ClF_6N_2P_2Ru$: C, 53.36; H, 4.57; N, 3.45. Found: C, 53.48; H, 4.63; N, 3.50%. IR: (Nujol): 2238 cm^{-1}, ν(C≡N); ^{1}H-NMR ($CDCl_3$, TMS, ppm): 9.02 (d, 2H, 6.2 Hz, αH–CNPy); 7.82 (d, 2H, 6.2 Hz, βH– CNPy); 7.8–7.2 (br. m. $P(C_6H_5)_3$), 2.12 (s, $C_6(CH_3)_3$); $^{31}P\{^1H\}$: 38.6 (PPh_3), 103.25 (PF_6^-).

3.1.8. Preparation of $[Ru(\eta^6\text{-}C_6H_6)(PPh_3)Cl(DCB)]PF_6$ (8)

This complex was prepared from the reaction of $[Ru(\eta^6\text{-}C_6H_6)Cl_2(PPh_3)]$ with DCB in methanol. Yield 70%. Anal. Calc. for $C_{32}H_{25}ClF_6N_2P_2Ru$: C, 51.23; H, 3.33; N, 3.73. Found: C, 50.28; H, 3.25; N, 3.71%. IR (Nujol) 2268, 2230 cm^{-1}, ν(C≡N); ^{1}H-NMR ($CDCl_3$, TMS, ppm); ^{1}H: δ 8.06 (s, 4H, DCB); 7.8–7.2 (br. m., 15H), $P(C_6H_5)_3$), 6.148 (sh. s, 6H, η^6-C_6H_6); $^{31}P\{^1H\}$: δ 28.46 (PPh_3), 103.3 (PF_6^-).

3.1.9. Preparation of [Ru(η⁶-C_6H_6)(PEt_3)Cl(DCB)]PF_6 (9)

It was prepared following the above procedure starting from [Ru(η⁶-C_6H_6)Cl_2(PEt_3)] and DCB in methanol. Yield 68%. Anal. Calc. for $C_{20}H_{25}ClF_6N_2P_2Ru$: C, 39.63; H, 4.12; N, 4.62. Found: C, 39.71; H, 4.06; N, 4.59%. IR (Nujol) 2242, 2270 cm^{-1}, ν(C≡N); ^{1}H-NMR ($CDCl_3$, TMS, ppm); ^{1}H: δ 8.06 (s, 4*H*, DCB); 6.32 (sh. s., 6H, C_6H_6); 2.06 (6H, CH_2 protons of PEt_3); 1.03 (m, 9H, CH_3 protons of PEt_3); ^{13}C{^{1}H}: δ 133.18 (α*C*–C_6H_4); 128.28 (β*C*–C_6H_4); 117.51 (coordinated *C*≡N of DCB); 115.69 (uncoordinated *C*≡N of DCB); 93.79 (C_6H_6); 17.299 and 8.612 (carbons of PEt_3); ^{31}P{^{1}H}: δ 43.80 (PEt_3), 103.31 (PF_6^-); UV–vis (acetone, λ_{max}, nm) 435, 290, 240.

3.1.10. Preparation of [Ru(η⁶-C_6H_6)($MePPr^i_2$)Cl(DCB)]PF_6 (10)

It was prepared following the above procedure starting from [Ru(η⁶-C_6H_6)Cl_2($MePPr^i_2$)] and DCB in methanol. Yield 65%. Anal. Calc. for $C_{21}H_{27}ClF_6N_2P_2Ru$: C, 40.67; H, 4.35; N, 4.51. Found: C, 40.02; H, 4.31; N, 4.50%. IR (Nujol) 2240, 2272 cm^{-1}, ν(C≡N); ^{1}H-NMR ($CDCl_3$, TMS, ppm); ^{1}H: δ 8.8 (d, 2*H*, 6.0 Hz, DCB); 7.84 (d, 2*H*, 6.4 Hz, DCB); 6.37 (s., 6H, C_6H_6); 2.802 (m, 2H, 6.8 Hz, $CH(CH_3)_2$); 2.49 (d, 12H, 4 Hz, $CH(CH_3)_2$); 2.07(s, 3H, $CH_3PPr^i_2$); ^{31}P{^{1}H}: δ 43.80 ($MePPr^i_2$), 103.3 (PF_6^-); UV–vis (acetone, λ_{max}, nm) 445, 290, 239.

3.2. Preparation of [Ru(η⁶-$C_{10}H_{14}$)(PPh_3)Cl(DCB)]PF_6 (11)

It was prepared following the above procedure starting from [Ru(η⁶-C_6H_{14})Cl_2(PPh_3)] with DCB in methanol. Yield 80%. Anal. Calc. for $C_{36}H_{33}ClF_6N_2P_2Ru$: C, 53.63; H, 4.09; N, 3.47. Found: C, 53.59; H, 4.11; N, 3.41%. IR (Nujol) 2266 cm^{-1}, ν(C ≡ N); ^{1}H-NMR ($CDCl_3$, TMS, ppm); ^{1}H: δ 8.29 (d, 2H, 1.6 Hz, α*H*–DCB); 8.07 (d, 2H, 1.2 Hz, β*H*–DCB); 7.710–7.5 (br., m, PPh_3); 6.62–6.24 (dd, 4H, 3.4 Hz, C_6H_4); 2.33 (sp., 1H, 3.4 Hz, $CHMe_2$), 1.59 (s, 3H, C–CH_3), 1.09 (dd, 6H, 3.6 Hz, $CH(CH_3)_2$); ^{13}C{^{1}H}: δ 134.52–127.72 (*C* of DCB and PPh_3); 117.59 (*C*≡N coordinated DCB); (*C*≡N pendant DCB), 105.59 (*C*–$CHMe_2$), 96.22 (*C*–CH_3); 88.02 and 91.46 (C_6H_4), 30.16 ($CHMe_2$), 21.95 ($CH(CH_3)_2$), 18.70 (C–CH_3), ^{31}P{^{1}H} (H_3PO_4): δ 25.091 (PPh_3), 103.32 (PF_6^-); UV–vis (acetone, λ_{max}, nm) 430, 290, 239.

3.2.1. Preparation of [Ru(η⁶-$C_{10}H_{14}$)(PEt_3)Cl(DCB)]PF_6 (12)

It was prepared following the above procedure starting from [Ru(η⁶-$C_{10}H_{14}$)Cl_2(PEt_3)] with DCB in methanol. Yield (80%). Anal. Calc. for $C_{24}H_{33}ClF_6N_2P_2Ru$: C, 43.53; H, 4.98; N, 4.23. Found: C, 43.58; H, 4.92; N, 4.20%. IR (Nujol) 2240, 2266 cm^{-1}, ν(C≡N).

3.2.2. Preparation of [Ru(η⁶-$C_{10}H_{14}$)($MePPr^i_2$)Cl(DCB)]PF_6 (13)

It was prepared following the above procedure (a) starting from [Ru(η⁶-C_6H_{14})Cl_2($MePPr^i_2$)] with DCB in methanol. Yield 80%. Anal. Calc. for $C_{25}H_{35}ClF_6N_2P_2Ru$: C, 44.41; H, 5.18; N, 4.14. Found: C, 44.45; H, 5.09; N, 4.10%. IR (Nujol) 2239, 2270 cm^{-1}, ν(C≡N).

3.2.3. Preparation of [Ru(η⁶-C_6Me_6)(PPh_3)Cl(DCB)]PF_6 (14)

It was prepared following the above procedure (a) starting from [Ru(η⁶-C_6Me_6)Cl_2(PPh_3)] with DCB in methanol. Yield 80%. Anal. Calc. for $C_{38}H_{37}ClF_6N_2P_2Ru$: C, 54.70; H, 4.43; N, 3.35. Found: C, 44.45; H, 5.09; N, 4.10%. IR: (Nujol): 2245, 2260 cm^{-1}, ν(C≡N); ^{1}H-NMR (δ, ppm): 8.74 (d, 2H, 5.82 Hz, α*H*–DCB); 7.92 (d, 2H, 6.0 Hz, β*H*–DCB); 7.72–7.18 (br. m. $P(C_6H_5)_3$), 2.12 (s, $C_6(CH_3)_3$).

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