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Synthetic, spectral, electrochemical and structural aspects of some Ru(II) arene complexes with some novel bridging ligands

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Abstract

Reactions of chloro-bridged dimeric Ru(II) complexes $[\{Ru(\eta^6\text{-arene})Cl_2\}_2]$ with bridging ligands 1,4-dicyanamidobenzene, *N*,*N*′-dicyano 4-4′-diaminobiphenyl, 2,5-dichloro-1,4-dicyanamidobenzene and 2,5-dimethyl-1,4-dicyanamidobenzene (referred hereafter as $dcdH_2$, bpH_2, ddcl and dmcd) in dicloromethane at room temperature gave binuclear complexes with the general formulation $[\{Ru(\eta^6\text{-arene})Cl_2\}_2(\mu\text{-L})]$. However, reactions of these bridging ligands with the complexes $[Ru(\eta^6\text{-arene})(P)Cl_2](\eta^6\text{-arene} = \text{benzene or } p\text{-cymene}; P = PPh_3, PEt_3 \text{ or } MePPr^i_2)$ in methanol, in presence of NH_4PF_6, gave cationic arene complexes $[\{Ru(\eta^6\text{-arene})(P)Cl\}_2(L)]^{2+}$ ($L = dcdH_2$, bpH_2, dmcd or ddcl). 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 complexes under study are highly stable at room temperature. However, their solutions in coordinating solvents like acetonitrile or dimthylsulfoxide undergo substitution reactions to give substitutional products with the formulation $RuCl_2(sol)_4$. It has been confirmed by single crystal X-ray diffraction studies.

Keywords: Ruthenium arene complexes; 1,4-dicyanamidobenzene; *N*,*N*′-dicyano 4-4′-diaminobiphenyl; 2,5-dichloro-1,4-dicyanamidobenzene; 2,5-dimethyl-1,4-dicyanamidobenzene

1. Introduction

During the past couple of decades, much attention has been paid towards synthesis and characterization of polymetallic complexes, in which, the metal centers are coupled via a bridging ligands and possible application of such compounds as novel magnetic and solid state materials [1,1a,1b,1c,1d,1e,1f]. Recent studies have shown that the rate of electron transfer or the energy transfer in these systems depends, upon the electronic and structural properties of the bridging ligand. In this regard, coordination chemistry of a large number of ligands, which can provide pathway for metal-metal interaction viz. 1,4-dicyanamidobenzene, *N*,*N*′-dicyano-4-4′-diaminobiphenyl, 2,5-dichloro-1,4-dicyanamidobenzene and 2,5-dimethyl-1,4-dicyanamidobenzene have been explored [2,2a,2b]. Crutchley et al., have examined the metal–metal super exchange coupling of ruthenium ions in binuclear pentammine ruthenium complexes that incorporates bridging ligand $dicyd^{2-}$ (1,4-dicyanaminobenzene dianion) and its derivatives [3,3a,3b,3c,3d,3e]. They have shown that conproportionation constant of the mixed valence complexes $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{3+}$ are strongly sensitive to the donor properties of the solvent and solid state exchange mediating properties of the ligand $dicyd^{2-}$ and its derivatives are expected to be maximized when planarity is maintained. So far, only a little is known about the complexes in which two organometallic fragments are coupled by these ligands. Due to our continuing interest in this area and as a prelude [4a,4b,4c,4d,4e], towards our detailed investigation in the synthesis and characterization of the complexes in which, two equivalent metal centers are bridged by these ligands, we have carried out reactions of these ligands with arene ruthenium complexes $[\{Ru(\eta^6\text{-arene})Cl_2\}_2]$ (η^6-arene = benzene or *p*-cymene) and phosphine containing complexes $[Ru(\eta^6\text{-arene})Cl_2(L)]$ ($L = PPh_3$, PMe_3 or $MeP(Pr^i)_2$). In this paper we present spectroscopic and electrochemical properties of the complexes resulting from interaction

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of [{Ru(η^6-arene)Cl_2}$_2$] (η^6-arene = benzene, *p*-cymene) and phosphine containing complexes [Ru(η^6-arene)Cl_2(L)] (L = PPh_3, PMe_3 or $MeP(Pr^i)_2$) with 1,4-dicyanaminobenzene, *N*,*N*′-dicyano-4-4′-diaminobiphenyl, 2,5-dichloro-1,4-dicyanamidobenzene and 2,5-dimethyl-1,4-dicyanamidobenzene.

2. Experimental

The chemicals used for the reaction were Analar or chemically pure grade. Solvents were dried prior to use following literature procedures. The ligands 1,4-dicyanamidobenzene, *N*,*N*′-dicyano-4-4′-diaminobiphenyl, 2,5-dichloro-1,4-dicyanamidobenzene and 2,5-dimethyl-1,4-dicyanamidobenzene were prepared following the procedures described by Crutchley et al., [3a]. The precursor complexes [{Ru(η^6-arene)Cl_2}$_2$] and their derivatives [Ru(η^6-arene)Cl_2(L)] were prepared following the literature method [5,5a,5b]. The elemental analyses were performed by micro-analytical laboratory of the Regional Sophisticated Instrumentation Center, Central Drug Research Institute, Lucknow. IR spectra were recorded in Nujol mulls on a Perkin–Elmer 577 and Perkin–Elmer 881 spectrophotometer. NMR spectra were taken on Varian Unity 400 MHz or Varian Gemini 200 MHz instruments. The chemical shifts are given in ppm relative to Me_4Si (^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-NBA as the matrix.

2.1. Procedure

The complexes **1**–**5** were prepared following the general procedure (A) and the complexes **6**–**12** were prepared by the general procedure (B).

(A) In a typical reaction, a suspension of the chloro-bridged Ru(II) arene complexes [{Ru(η^6-arene)Cl_2}$_2$] (1.00 mmol) in CH_2Cl_2 (25 ml) were treated with the bridging ligands 1,4-dicyanamidobenzene, N,N′-dicyano-4-4′-diaminobiphenyl, 2,5-dichloro-1,4-dicyanamidobenzene and 2,5-dimethyl-1,4-dicyanamidobenzene. The resulting solutions were stirred at r.t. for 1 h. The precursor complexes slowly dissolved and color of the solution changed to bright yellow or yellow–orange and microcrystalline complexes separated. These were separated, washed several times with CH_2Cl_2, Et_2O and dried under vacuum.

(B) To a suspension of phosphine containing complexes [Ru(η^6-arene)Cl_2(L)] (2.0 mmol) in MeOH (25 ml), novel bridging ligands 11,4-dicyanamidobenzene, *N*,*N*′-dicyano-4-4′-diaminobiphenyl, 2,5-dichloro-1,4-dicyanamidobenzene and 2,5-dimethyl-1,4-dicyanamidobenzene (1.00 mmol) were added and the resulting solutions were stirred at r.t. for about 4 h. It was filtered through celite to remove any solid impurities. To the filtrate, saturated solution of NH_4PF_6 dissolved in 15 ml of MeOH was added, concentrated to dryness under reduced pressure. The yellow–orange solid mass thus obtained was extracted with CH_2Cl_2, filtered and the filtrate was layered with light petroleum. After 2–3 days, microcrystalline product separated out. These were filtered washed several times with MeOH, Et_2O and dried under vacuum.

3. Selected data of the complexes

3.1. [{Ru(η^6-$C_{10}H_{14}$)Cl_2}$_2$(μ-dcdH_2)] (1)

Yield; (654 mg, 85%); Anal. Calc. for $C_{28}Cl_4H_{34}N_4Ru_2$: C, 43.63; H, 4.41; Cl, 18.44; N, 7.27. Found: C, 43.30; H, 4.40; Cl, 18.36; N; 7.25%; IR (Nujol) 2284 cm^{-1}, ν(C≡N); ^{1}H-NMR (DMSO-d_6, TMS, δ ppm): δ 10.06 (s, dcdH_2), 6.94 (s, dcdH_2), 5.74–5.82 (AB pattern, C_6H_4, 64 Hz), 2.82 (septet, $CHMe_2$, 70 Hz), 2.06 (s, CH_3), 1.15 (d, $CHMe_2$), $^{13}C\{^1H\}$-NMR (DMSO-d_6) δ 133.52 (C–C_6H_4 dcdH_2), 116.38 (C, C≡N dcdH_2); 112.27 (C–C_6H_4 dcdH_2), 106.34 (C–$CHMe_2$), 100.05 (C–CH_3), 86.31 and 85.46 (C, C_6H_4), 29.92 (C–$CHMe_2$), 21.44 (C–$CHMe_2$), 17.80 (C–CH_3).

3.2. [{Ru(η^6-C_6H_6)Cl_2}$_2$(μ-dcdH_2)] (2)

Yield; (513 mg, 78%); Anal. Calc. for $C_{20}Cl_4H_{18}N_4Ru_2$: C, 36.47; H, 2.73; Cl, 21.58; N, 8.51. Found: C, 36.32; H, 2.64; Cl, 21.34; N, 8.48%. IR (Nujol) 2278 cm^{-1}, ν(C≡N); ^{1}H-NMR (DMSO-d_6, TMS, δ ppm): δ 10.08 (s, N–H dcdH_2), 7.35 (s, dcdH_2), 5.95 (s, C_6H_6); $^{13}C\{^1H\}$-NMR (DMSO-d_6) δ 133.52 (C–C_6H_4 dcdH_2), 116.37 (C, C≡N dcdH_2); 112.27 (C–C_6H_4, dcdH_2), 87.59 (C, C_6H_6).

3.3. [{Ru(η^6-$C_{10}H_{14}$)Cl_2}$_2$(μ-bpH_2)] (3)

Yield; (616 mg, 72%); Anal. Calc. for $C_{34}Cl_4H_{38}N_4Ru_2$: C, 48.22; H, 4.49; Cl, 16.58; N, 6.61. Found: C, 47.33; H, 4.61; Cl, 16.46; N, 6.76%. IR (Nujol) 2275 cm^{-1}, ^{1}H-NMR (DMSO-d_6, TMS, δ ppm): δ 10.05 (s, N–H of bpH_2), 7.62 (d, C_6H_4 of bpH_2, 8.6 Hz), 7.05 (d, C_6H_4 of bpH_2, 8.8 Hz), 5.74–5.82 (AB pattern, C_6H_4, 6.4 Hz), 2.81 (sep., $CHMe_2$, 7.0 Hz), 2.07 (s, CH_3), 1.15 (d, $CHMe_2$, 7.0 Hz), $^{13}C\{^1H\}$-NMR (DMSO-d_6): δ 137.68, 133.76 and 127.50 (C–C_6H_4 bpH_2), 115.40 (C, C≡N bpH_2); 111.95 (C–C_6H_4 bpH_2), 106.34 (C–$CHMe_2$), 100.03 (C–CH_3), 86.31 and 85.46

(C, C_6H_4), 29.92 (C–$CHMe_2$), 21.44 (C–$CHMe_2$), 17.80 (C–CH_3); UV (λ_{max}) 763, 423, 348, 295, 208 nm.

3.4. [{Ru(η^6-C_6H_6)Cl_2}$_2$(μ-bpH_2)] (4)

Yield; (585 mg, 80%); Anal. Calc. for $C_{26}Cl_4H_{22}N_4Ru_2$: C, 28.28; H, 2.90; N, 6.87. Found: C; 28.44, H; 2.94, N; 6.76%, IR (Nujol) 2268 cm^{-1}, ν(C≡N); ^{1}H-NMR (DMSO-d_6, TMS, δ ppm): δ 10.24(s, N–H of bpH_2), 7.62 (d, C_6H_4 of bpH_2, 8.6 Hz), 7.05 (d, C_6H_4 of bpH_2, 8.8 Hz), 6.12 (s, C_6H_6); ^{13}C{^{1}H}-NMR (DMSO-d_6); ^{13}C{^{1}H}-NMR (DMSO-d_6) δ 136.63, 133.56 and 127.48 (C–C_6H_4 bpH_2), 115.68 (C, C≡N bpH_2); 112.08 (C–C_6H_4 bpH_2, 90.62 (C, C_6H_6); UV (λ_{max}) 755, 415, 338, 290, 210 nm.

3.5. [{Ru(η^6-$C_{10}H_{14}$)Cl_2}$_2$(μ-ddCl)] (5)

Yield; (610 mg, 72%); Anal. Calc. for $C_{28}Cl_6H_{34}N_4Ru_2$: C, 39.85; H, 4.03; N, 6.64. Found: C; 39.68, H; 3.92, N; 6.56%, IR (Nujol) 2274 cm^{-1}, ν(C≡N), ^{1}H-NMR (DMSO-d_6, TMS, δ ppm): δ 9.82 (s, ddCl), 6.42 (s, ddCl), 5.64–5.42 (AB pattern, C_6H_4, 7 Hz), 2.92 (septet, $CHMe_2$,), 1.86 (s, CH_3), 1.36 (d, $CHMe_2$, 6.8 Hz), ^{13}C{^{1}H}-NMR (DMSO-d_6): δ 132–127 (C–C_6H_4), 119.22 (C, C≡N); 104.62 (C–$CHMe_2$), 101.03 (C–CH_3), 86.2 and 85.4 (C–C_6H_4), 31.2 (C–$CHMe_2$), 22.02 (C–$CHMe_2$), 18.21 (C–CH_3).

3.6. [{Ru(η^6-C_6H_6)Cl(PPh_3)}$_2$(μ-$dcdH_2$)](PF_6)$_2$ (6)

Yield (848 mg, 60%); Anal. Calc. for $C_{56}Cl_2F_{12}H_{48}N_4P_4Ru_2$: C, 47.96; H, 3.42; N, 3.99. Found: C; 47.56; H; 3.45, N; 4.05% IR (Nujol) 2283 cm^{-1}, ν(C≡N); ^{1}H-NMR (DMSO-d_6, TMS, δ ppm): δ 9.69 (s, N–H $dcdH_2$), 7.66–7.46 (br.m., aromatic protons of PPh_3); 6.82 (s, $dcdH_2$), 6.12 (s, C_6H_6); ^{13}C{^{1}H}-NMR (DMSO-d_6): δ 135.02 (C–C_6H_4 $dcdH_2$), 116.29 (C, C≡N $dcdH_2$); 112.27 (C–C_6H_4 $dcdH_2$), 87.59 (C, C_6H_6); ^{31}P{H}: 34.33 (P, PPh_3), 103.32 (P, PF_6).

3.7. [{Ru(η^6-C_6H_6)Cl(PEt_3)}$_2$(μ-$dcdH_2$)](PF_6)$_2$ (7)

Yield; (780 mg, 70%); Anal. Calc. for $C_{32}Cl_2F_{12}H_{48}N_4P_4Ru_2$: C, 34.50; H, 4.31; N, 5.03. Found: C, 34.54; H, 4.59, N; 5.26% IR (Nujol) 2256 cm^{-1}, ν(C≡N); ^{1}H-NMR (DMSO-d_6, TMS, δ ppm): δ 10.72(s, N–H $dcdH_2$); 6.82 (s, $dcdH_2$), 6.25 (s, C_6H_6), 2.03 (m,CH_2 of PEt_3), 1.18 (m, CH_3 of PEt_3); ^{13}C{^{1}H} δ 134.50 (C–C_6H_4 $dcdH_2$), 118.60(C, C≡N, $dcdH_2$); 112.27 (C–C_6H_4 $dcdH_2$), 87.32 (C, C_6H_6), 30.25 (C, CH_2 of PEt_3), 18.73 (C, CH_3 of PEt_3); ^{31}P{H}: 28.22(P, PEt_3), 103.32(P, PF_6).

3.8. [{Ru(η^6-C_6H_6)Cl(PMe^iPr_2)}$_2$(μ-$dcdH_2$)](PF_6)$_2$ (8)

Yield; (741 mg, 65%); Anal. Calc. for $C_{34}Cl_2F_{12}H_{52}N_4P_4Ru_2$: C, 35.75; H, 4.55; N, 4.90. Found: C, 35.86; H, 4.59, N; 5.06% IR (Nujol) 2266 cm^{-1}, ν(C≡N); ^{1}H-NMR (DMSO-d_6, TMS, δ ppm): δ 10.68(s, N–H $dcdH_2$); 6.79 (s, $dcdH_2$), 6.17 (s, C_6H_6), 2.77 (m, $CH(CH_3)_2$, 2.46 (m, $CH(CH_3)_2$, 2.18 (s, Me of PMe^iPr_2); ^{31}P{^{1}H}: 32.64 (P, PMe^iPr_2), 103.32 (P, PF_6); UV (λ_{max}) 748, 336, 301, 228 nm.

3.9. [{Ru(η^6-C_6H_6)Cl(PPh_3)}$_2$(μ-dmcd)](PF_6)$_2$ (9)

Yield (860 mg, 60%); Anal. Calc. for $C_{58}Cl_2F_{12}H_{52}N_4P_4Ru_2$: C, 48.63; H, 3.63; N, 3.91. Found: C, 48.42; H, 3.60, N, 3.84% IR (Nujol) 2250 cm^{-1}, ν(C≡N); ^{1}H-MR (DMSO-d_6, TMS, δ ppm): δ 9.19(s, N–H, dmcd); 6.64(br., $dcdH_2$), 5.96 (s, C_6H_6), 2.14(s, CH_3 of dmcd); ^{31}P{H}: 34.29(P, PEt_3), 103.29(P, PF_6).

3.10. [{Ru(η^6-C_6H_6)Cl(PPh_3)}$_2$(μ-ddCl)](PF_6)$_2$ (10)

Yield (848 mg, 55%); Anal. Calc. for $C_{56}Cl_4F_{12}H_{46}N_4P_4Ru_2$: C, 45.65; H, 3.12; N, 3.80. Found: C, 45.66; H, 3.04; N, 3.76% IR (Nujol) 2246 cm^{-1}, ν(C≡N); ^{1}H-NMR (DMSO-d_6, TMS, δ ppm): δ 10.08 (s, N–H ddCl); 7.22–7.86 (broad multiplet, aromatic protons of PPh_3), 6.46 (s, ddCl), 6.22 (s, C_6H_6); ^{13}C{^{1}H} δ 134.50–127 (C of PPh_3 and C_6H_4 ddCl), 116.60 (C, C≡N, $dcdH_2$).

3.11. [{Ru(η^6-$C_{10}H_{14}$)Cl(PPh_3)}$_2$(μ-$dcdH_2$)](PF_6)$_2$ (11)

Yield; (950 mg, 63%); Anal. Calc. for $C_{64}Cl_2F_{12}H_{64}N_4P_4Ru_2$: C, 50.76; H, 4.23; N, 3.70. Found: C, 50.77; H, 4.26; N, 3.68% IR (Nujol): 2272 cm^{-1}, ν(C≡N); ^{1}H-NMR (DMSO-d_6, TMS, δ ppm): δ 10.34 (s, $dcdH_2$), 7.22–7.68 (br.m, aromatic protons of PPh_3, 6.66 (s, $dcdH_2$), 5.64–5.96 (m, C_6H_4,), 2.96 (m, $CHMe_2$, 70 Hz), 2.06 (s, CH_3), 1.15 (d, $CHMe_2$), ^{13}C{^{1}H}-NMR (DMSO-d_6) δ 134.58–132.66 (C–C_6H_4 $dcdH_2$ + C PPh_3), 116.38 (C, C≡N $dcdH_2$); 113.06 (C–C_6H_4 $dcdH_2$), 104.34 (C–$CHMe_2$), 99.65 (C–CH_3), 88.32 and 86.46 (C, C_6H_4), 29.86 (C–$CHMe_2$), 21.44 (C–$CHMe_2$), 16.80 (C–CH_3); ^{31}P{H}: 38.36 (P, PPh_3), 103.46(P, PF_6).

3.12. [{Ru(η^6-$C_{10}H_{14}$)Cl(PPh_3)}$_2$(μ-bpH_2)](PF_6)$_2$ (12)

Yield; (875 mg, 85%); Anal. Calc. for $C_{70}Cl_2F_{12}H_{68}N_4P_4Ru_2$: C, 52.79; H, 4.27; N, 3.52. Found: C, 52.73; H, 4.80; N, 3.91% IR (Nujol) 2280 cm^{-1}, ^{1}H-NMR (DMSO-d_6, TMS, δ ppm): δ 10.55 (s, N–H of bpH_2), 7.82–7.05 (C_6H_4 of bpH_2 and aromatic protons of PPh_3), 5.64–5.86 (m, C_6H_4,), 2.81 (m, $CHMe_2$), 2.07 (s, CH_3), 1.15 (dd, $CHMe_2$), ^{13}C{^{1}H}-NMR (DMSO-d_6) δ

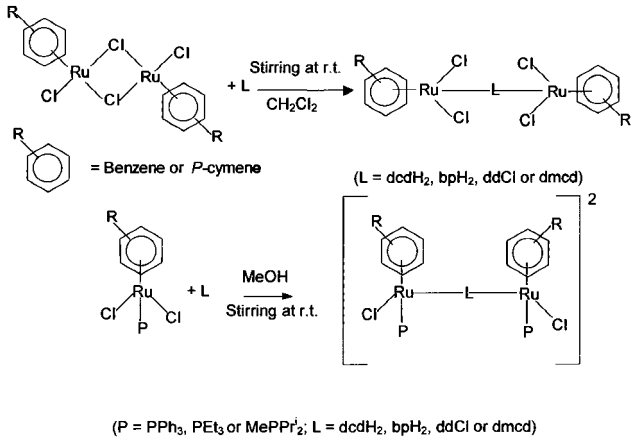
137.68–127.50 (C–C_6H_4 bpH_2 + C PPh_3), 115.40 (C, C≡N bpH_2); 112.94 (C–C_6H_4 bpH_2), 105.36 (C–$CHMe_2$), 100.33 (C–CH_3), 85.31 and 84.32 (C, C_6H_4), 30.24 (C–$CHMe_2$), 22.32 (C–$CHMe_2$), 18.86 (C–CH_3); $^{31}P\{H\}$: 38.36 (P, PPh_3) 107.22 (P, PF_6).

4. Results and discussion

Reaction of the Ru(II) arene complexes [{Ru(η^6-arene)Cl_2}$_2$] (η^6-arene = benzene or *p*-cymene with the bridging ligands 1,4-dicyanamidobenzene, *N*,*N*′-dicyano-4-4′-diaminobiphenyl, 2,5-dichloro-1,4-dicyanamidobenzene and 2,5-dimethyl-1,4-dicyanamidobenzene in dichloromethane at room temperature gave binuclear complexes in quantitative yield. However, reaction of the phosphine containing Ru(η^6-arene)Cl_2(P) (P = PPh_3, PEt_3 or $MePPr^i_2$) in presence of NH_4PF_6 with these ligands led in the formation of cationic complexes with the formulation [{Ru(η^6-arene)Cl(P)}$_2$(μ-L)]$(PF_6)_2$ (Scheme 1).

These are insoluble in methanol, ethanol, dichloromethane, carbon tetrachloride, benzene, diethyl ether and petroleum ether, partially soluble in acetone and soluble in co-ordinating solvents like acetonitrile, dimethylformamide and dimethylsulfoxide. The phosphine containing cationic complexes with the formulation [{Ru(η^6-arene)Cl(P)}$_2$(μ-L)]$(PF_6)_2$ are insoluble in hydrocarbon solvents partially soluble in methanol, ethanol; soluble in dichloromethane, carbon tetrachloride, acetone and co-ordinating solvents like acetonitrile, dimethylformamide and dimethylsulfoxide.

The elemental analyses of the complexes are in good agreement with their formulations. Conductance behavior of the complexes **6**–**12** showed that, these are ionic in nature and their conductances are consistent with those of similar electrolyte types under similar conditions. Presence of the peaks at *m*/*z* 699 and *m*/*z* 774 in the FAB mass spectra of the representative complexes **1** and **3** corresponding to [(η^6-$C_{10}H_{14}$)$RuCl_2$(μ-$dcdH_2$)-Ru(η^6-$C_{10}H_{14}$)]$^{2+}$ and [(η^6-$C_{10}H_{14}$)$RuCl_2$(μ-BPH_2)Ru-(η^6-$C_{10}H_{14}$)]$^{2+}$ respectively strongly suggested these to be binuclear complexes. More information about the structure and bonding in the complexes have been deduced from spectroscopic (IR, ^{1}H-, ^{13}C-, ^{31}P-NMR and electronic spectral) and electrochemical studies. The following spectroscopic and electrochemical data are consistent with the formulation of the complexes.



(P = PPh_3, PEt_3 or $MePPr^i_2$; L = $dcdH_2$, bpH_2, ddCl or dmcd)

Scheme 1.

Coordination of the bridging ligands under study with the metal center can occur via its amide or nitrile nitrogen atom depending upon nature of the metal center. In general, coordination with the transition metals occur via the nitrile nitrogen. The IR spectra of the complexes **1**–**12** displayed sharp bands in the nitrile stretching frequency region 2256–2284 cm^{-1} corresponding to cyanamide band *v*(NCN) [6,6a,6b,6c]. Interestingly, the nitrile stretching frequency band in all these complexes exhibited a positive shift as compared with that in the free cyanamide ligands. The positive shift in the position of *v*(C≡N) towards high wave number indicated end on co-ordination of the nitrile nitrogen with the Ru center [7]. The positive shift in the position of *v*(C≡N) in these complexes further illustrated that the cyanamide ligands are poorer π acid ligands than their nitrile analogue [8]. The position of *v*(C–N) at ~1010 cm^{-1}, in the IR spectra of the complexes remained practically unchanged. It implies that Ru coordination has no effect on N–C bond order, and further suggests non-involvement of amide lone pair in metal coordination [9]. The presence of only one sharp *v*(NCN) band in the IR spectra of the binuclear complexes further suggested that both the cyanamide groups of the bridging ligands be equivalently involved in coordination with the metal centers. The characteristic bands due to respective phosphines (PPh_3, PEt_3 or $MePPr^i_2$) and the counter ion PF_6^- were also present in the IR spectra of the respective complexes **6**–**12** at their usual positions.

The ^{1}H-NMR spectral data of the complexes alongwith their assignments are compiled with the selected data. The ^{1}H-NMR spectra of the complexes **1** and **3** showed sharp singlet at δ 5.95 and δ 6.02 ppm respectively, characteristic of the co-ordinated η^6-C_6H_6 ligand, along-with the proton resonances due to coordinated ligand $dcdH_2$ (δ 10.08 ppm, N–H, $dcdH_2$; δ 7.35 ppm, s, $dcdH_2$) in the complex **1** and bpH2 (δ 10.24 ppm, N–H, bpH_2; δ 7.62 ppm, d, bpH_2, 7.05 ppm, d, bpH_2) in the complex **3**. The ^{1}H-NMR spectra of the complexes demonstrated maintenance of the complex integrity. Further, the arene protons in these complexes exhibited a small downfield shift. Similarly, in the ^{1}H-NMR spectra of the other complex **2** and **4**–**12**, only a small (in some cases negligible) down-field shifts were observed in the position of the η^6-arene

proton resonance as compared to that in the precursor complexes [{Ru(η⁶-arene)Cl_2}$_2$] or [Ru(η⁶-arene)Cl_2(P)] (P = PPh_3, PEt_3 or $MePPr^i_2$) [4,10]. The shifts in the position of η⁶-arene proton resonance towards low field side may result from the changes in local electron density on the metal center ruthenium due to its coordination with nitrile nitrogen atom of the cyanamide ligand. Only a small or negligible shift in the position of the η⁶-arene proton resonance shows, that the –N(H)–C≡N moiety does not affect much the electronic environment of the arene protons. The aromatic protons of the ligand $dcdH_2$ or bpH_2 resonated, at almost the same position, as in the free ligand. This shows that, the coordination of these ligands with the Ru(η⁶-arene)Cl_2 moiety has no significant effect on the chemical shifts of the phenyl and amine protons. Thus the ^{1}H-NMR spectral data are consistent with the conclusions drawn from IR spectral studies. Resonances due to the phosphine protons were present at their usual position in the ^{1}H-NMR spectra of the respective complexes **6**–**12**.

The ^{13}C{^{1}H}-NMR spectral data are compiled with the selected data of the complexes. They are consistent with the conclusions drawn from ^{1}H-NMR data. The arene carbons in the complexes **1** and **3** [{Ru(η⁶-arene)Cl_2}$_2$] (μ-L)] (L = $dcdH_2$ or bpH_2) resonated at δ 87.59 and 90.62 ppm respectively. It exhibited a small downfield shift as compared to that in the precursor complex [{Ru(η⁶-C_6H_6)Cl_2}$_2$]. Similarly, the η⁶-arene carbons in the ^{13}C{^{1}H}-NMR spectra of the other complex **2** and **4**–**12** also exhibited a downfield shift. It may result from coordination of Ru(II) through nitrile nitrogen atom. Along with the arene carbons, the ligand carbons resonated in their characteristic region. The resonance in the region δ 115–119 ppm in the ^{13}C-NMR spectrum of the complexes has been assigned to nitrile C atom by analogy with the resonance of the organonitriles [11]. The phosphine carbons in the ^{13}C{^{1}H}-NMR spectra of the complexes **6**–**12** resonated at their usual positions.

The ^{31}P-NMR spectra of the phosphine containing dinuclear complexes **6**–**12** exhibited single sharp signals (**6**, δ 34.33; **7**, δ 28.22; **8**, δ 34.64; **9**, δ 34.29; **11**, δ 38.36 and **12**, δ 38.36 ppm) corresponding to phosphine ^{31}P nuclei. In all these complexes the ^{31}P nuclei exhibited a down field shift as compared to that in the free phosphines and the respective precursor complexes [Ru(η⁶-arene)Cl_2(P)] (P = PPh_3, PEt_3 or $MePPr^i_2$). The deshielding of the phosphorus may be caused by relatively less donation of electron density from the Ru(II) center through back bonding. This suggests that the degree of dπ–pπ back bonding influence the chemical shift of the phosphorus nuclei. The ^{31}P nuclei of the counter ion PF_6^- in these complexes resonated at $\delta \sim$ 103 ppm in its characteristic septet pattern.

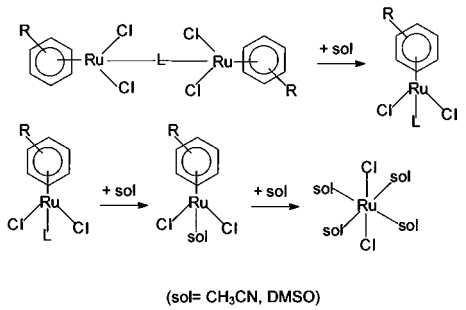
Electronic spectral data alongwith their assignments for the binuclear complexes are compiled with the selected data of the complexes. In the electronic spectra of these complexes, intense π–π* transitions are exhibited in the UV region and ligand to metal charge transfer bands in the visible region. The same general trend is observable in the electronic spectra of all the complexes. For example, the electronic spectra of the representative complex **3** displayed bands in the region ~750, 420, 308 and 208 and 210 nm. The bands in the visible region at 750 and 420 nm have been assigned to LMCT transitions. The bands around 335, 310 and 208 nm has been assigned to phenyl ring π–π* transitions. It is consistent with the other reports [12].

The cyclic voltammograms were recorded as described elsewhere. The plots of peak current vs. square root of the scan rate are linear indicating that diffusion limiting processes occur at the electrode. The CV scan [{Ru(η⁶-C_6H_6)Cl(PPh_3)}$_2$(μ-ddCl)](PF_6)$_2$ exhibits an irreversible anodic wave at E_{pa} −0.933 and cathodic peak at E_{pc} −0.400 and +1.233 V vs. Ag/AgCl (in acetonitrile at a scan rate of 100 mV s^{-1}). Analogous $PMe(Pr^i)_2$ complex [{Ru(η⁶-C_6H_6)Cl($PMe(Pr^i)_2$}$_2$(μ-ddCl)](PF_6)$_2$ exhibits waves in the same region. The wave at E_{pa} −0.933 V may arise due to reduction of –NCN group of the ruthenium center. But, in the case of PEt_3 and dichloro complex [{Ru(η⁶-$C_{10}H_{14}$)Cl_2}$_2$(μ-bpH_2)] it is observed at −0.84 V (vs. Ag/AgCl), it is unlikely that the reduction wave is originating from $Ru^{II} \rightarrow Ru^{I}$ process and hence it corresponds to coordinating ligands. The oxidation wave originates from $Ru^{III} \rightarrow Ru^{II}$ process.

The above analytical and spectral data support well the formulation of these complexes and these are highly stable in solid state. However, it was observed that their solutions are stable only for a couple of hours at room temperature in coordinating solvents like acetonitrile and dimethyl sulphoxide. Solutions of these complexes turned bright yellow form orange–red after 10–12 h. It was further found, that after 36–40 h, they completely decomposed to well known complexes with the formulation $RuCl_2(sol)_4$ (sol = CH_3CN or DMSO).

It was further confirmed by single crystal X-ray analysis. Due to poor solubility of these in solvents like dichloromethane, methanol, acetone we were trying to grow single crystals from CH_3CN–diethyl ether. After 2–3 days we could get diffraction quality crystals in quantitative yield. Surprisingly, the analytical and spectral data corresponded to $RuCl_2(CH_3CN)_4$ instead of those of **1**–**4**. Single crystal X-ray analysis further confirmed the formation of to $RuCl_2(CH_3CN)_4$. Since the single crystal data matched well to the one reported only recently by Hockless et al., [13] these are not being reported here.

Interestingly, the complex $RuCl_2(CH_3CN)_4$ is a member of an extended substitutional series with the general formulation $[Ru^{II}Cl_{6-n}(CH_3CN)_n]^{n-4}$ Or $[Ru^{III}Cl_{6-n}$-



Scheme 2.

$(CH_3CN)_n]^{n-3}$, It has been prepared along with other routes by photolysis of an chloro-bridged Ru(II) arene complex $[RuCl_2(\eta^6\text{-}o\text{-}^nBu_2C_6H_4)\}_2]$ ($\eta^6\text{-}o\text{-}^nBu_2C_6H_4$ = *o*-di-*n*-butylbenzene) in low or poor yield [14a–d]. At our hands the complex has indirectly been obtained just by substitution of a coordinated arene and bridging ligand at room temperature in excellent yield. It appears, that, in the coordinating solvents the binuclear complexes $[(\eta^6\text{-arene})RuCl_2(\mu\text{-L})RuCl_2(\eta^6\text{-arene})]$ dissociated to give mononuclear complexes $[(\eta^6\text{-areneRuCl}_2)(L)]$. The monomer subsequently looses the bridging ligand to form solvated species $[(\eta^6\text{-arene})Cl_2Ru(sol)]$. The latter species slowly reacts with solvent to form the final product and arene is given out. The overall reaction sequence may be given as follows (Scheme 2).

Since the complexes $RuCl_2(sol)_4$ find wide applications as precursors for many reactions, this route may offer convenient single stage synthesis of these complexes in large scale.

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