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REACTIONS OF [RuCp(EPh$_3$)$_2$Cl] {E = P, As, Sb} WITH Ni(II) COMPLEXES OF N-CYANODITHIOCARBIMATE ANIONS BEARING PENDANT DONOR GROUPS

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ABSTRACT

Reactions of planar $[Ni(cdc)_2]^{2-}$ and $[(PPh_3)_2Ni(cdc)]$ bearing pendant donor groups have been carried out with $[RuCp(EPh_3)_2Cl]$ (E = P, As, Sb). The reaction products have been characterized using various physico-chemical techniques, elemental analyses, magnetic measurements, melting points, IR, UV-vis, ^1H and ^{13}C NMR spectroscopy.

INTRODUCTION

The planar N-cyanodithiocarbimate anion in Fig. 1 (hereafter referred as cdc^{2-}) having three potential binding sites promises useful applications in synthesizing cis-sulfur ligated cdc^{2-} bridged di/polynuclear metallic complexes[1-7].

However, since it can exist in dithiol-dithionate resonating forms providing an extended π system and thus assisting charge delocalization, one of its many interesting features, which is potentially relevant to electron transfer processes, also concerns the synthesis of μ-cdc^{2-} bridged mixed valence dinuclear complexes. Despite the wide range of its anionic complexes available in the literature[8-10], their functional significance is attributed to the presence of uncoordinated CN as pendant group in almost all cis-sulfur ligated monomers. These complexes, therefore, represent a unique opportunity of behaving as metallo-ligands and as synthons for the development of hetero multimetal systems resulting from the interaction between metal centres and the remote cyanide nitrogen. Within this framework, as a prelude to detailed investigations of metallo ligand systems, we have chosen for the present study to examine the reactivity of anionic $[Ni(cdc)_2]^{2-}$ complexes with $[RuCp(EPh_3)_2Cl]$ which dissociates into $[RuCp(EPh_3)_2]^+$ in polar solvents like methanol. Besides the possibility of Ru-N bond formation, another alternative possibility of the latter cation behaving as unreactive discrete cationic species balancing the anionic charges on the precursor Ni(II) complexes also exists. The present report focuses on the results of this preliminary study.

RESULTS AND DISCUSSION

All the newly prepared complexes showed a negative test for chloride ion indicating $[RuCp(EPh_3)_2]^+$ as one of the reactive species.

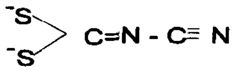


Fig. 1

The chloride replacement reactions of [RuCp(EPh$_3$)$_2$Cl] with one equivalent of [Ni(cdc)$_2$]$^{2-}$ or [(PPh$_3$)$_2$Ni(cdc)] gave orange-brown complexes for which microanalytical data were consistent with the formulation K$^+$[RuCp(EPh$_3$)$_2$]$^+$[Ni(cdc)$_2$]$^{2-}$.½H$_2$O and [RuCp(EPh$_3$)$_2$]-[Ni(cdc)(PPh$_3$)$_2$]$^+$Y$^-$ (Y$^-$ = PF$_6$, BPh$_4$, BF$_4$).

$$[\mathrm{Ni(cdc)_2}]^{2-}+[\mathrm{RuCp(EPh_3)_2Cl}] \xrightarrow[\text{Refluxing}]{\text{Methanol}} [\mathrm{RuCp(EPh_3)_2Ni(cdc)_2}]^-.\ \tfrac{1}{2}\mathrm{H_2O} + \mathrm{Cl^-}$$

$$[\mathrm{(PPh_3)_2Ni(cdc)}]+[\mathrm{RuCp(EPh_3)_2Cl}]+\mathrm{Y^-} \xrightarrow[\text{Refluxing}]{\text{Methanol+Acetone (1:1)}} [\mathrm{RuCp(EPh_3)_2Ni(cdc)(PPh_3)_2}]^+\mathrm{Y^-}+\mathrm{Cl^-}$$

(Where Y$^-$ = PF$_6$, BPh$_4$ or BF$_4$)

These have been identified by spectral (IR, ^{1}H, ^{13}C NMR, electronic) and other relevant data presented in Table I. These form high melting, air-stable, non-hygroscopic, microcrystalline solids, slightly soluble in acetone, CH$_3$OH and benzene. They are soluble in halogenated solvents and insoluble in ether and petroleum ether.

All the synthesized complexes exhibited diamagnetic behaviour. The monoanionic nature of K[RuCp(EPh$_3$)$_2$Ni(cdc)$_2$] . ½H$_2$O and the monocationic nature of [RuCp(EPh$_3$)$_2$Ni(cdc)(PPh$_3$)$_2$]PF$_6$ has been tested by cationic and anionic resins, respectively, in which the species are absorbed.

Table I
Analytical Data of the Complexes

S.No.	Complexes	Yield %	Colour (M.P.)	C	H	N	S	Major IR Bands	^1H Bands	λ_{Max} (nm)
1.	$K[(N_2C_2S_2)Ni(\mu\text{-}S_2C_2N_2)RuCp(PPh_3)_2].\frac{1}{2}H_2O$ $C_{44}H_{35}KN_4NiP_2RuS_4.\frac{1}{2}H_2O$	80	O 190°C	53.1 (52.83)	3.5 (3.42)	5.52 (5.49)	12.8 (12.52)	2320	4.7 7.5	337 445
2.	$K[(N_2C_2S_2)Ni(\mu\text{-}S_2C_2N_2)RuCp(AsPh_3)_2].\frac{1}{2}H_2O$ $As_2C_{44}H_{35}KN_4NiRuS_4.\frac{1}{2}H_2O$	72	OB 185°C	49.1 (48.79)	3.2 (3.12)	5.32 (3.06)	11.62 (11.53)	2315	4.5 7.7	345 440
3.	$K[(N_2C_2S_2)Ni(\mu\text{-}S_2C_2N_2)RuCp(SbPh_3)_2].\frac{1}{2}H_2O$ $C_{44}H_{35}KN_4NiRuS_4Sb_2.\frac{1}{2}H_2O$	70	O 192°C	44.6 (45.00)	2.92 (2.85)	4.71 (4.66)	11.1 (10.65)	2322	4.5 7.5	345 460
4.	$K[(N_2C_2S_2)Ni(\mu\text{-}S_2C_2N_2)RuCp(PPh_3)(AsPh_3)].\frac{1}{2}H_2O$ $AsC_{44}H_{35}KN_4NiPRuS_4.\frac{1}{2}H_2O$	70	OB 205°C	51.2 (50.8)	3.4 (3.22)	5.27 (5.26)	12.4 (12.01)	2310	5.1 7.8	330 440
5.	$K[(N_2C_2S_2)Ni(\mu\text{-}S_2C_2N_2)RuCp(PPh_3)(SbPh_3)].\frac{1}{2}H_2O$ $C_{44}H_{35}KN_4NiPRuS_4Sb.\frac{1}{2}H_2O$	72	B 189°C	47.9 (48.62)	3.9 (3.08)	5.2 (5.04)	11.7 (11.5)	2315	5.0 7.8	335 448
6.	$[(PPh_3)_2Ni(\mu\text{-}S_2C_2N_2)RuCp(PPh_3)_2][BF_4]$ $BC_{74}F_4H_{60}N_2NiP_4RuS_2$	65	OB 204°C	64.6 (6.32)	4.33 (4.34)	1.89 (1.91)	2.17 (2.14)	2270	4.45	360 440
7.	$[(PPh_3)_2Ni(\mu\text{-}S_2C_2N_2)RuCp(PPh_3)_2][BPh_4]$ $BC_{98}H_{80}N_2NiP_4RuS_2$	65	YB 210°C	55.8 (55.54)	3.79 (3.77)	1.64 (1.64)	1.93 (1.83)	2275	4.5	350 440
8.	$[(PPh_3)_2Ni(\mu\text{-}S_2C_2N_2)RuCp(PPh_3)_2][ClO_4]$ $C_{74}ClH_{60}N_2NiO_4P_4RuS_2$	68	OB 206°C	64.1 (63.75)	4.4 (4.30)	1.92 (1.88)	2.32 (2.1)	2260	4.6	360 430

9.	$[(PPh_3)_2Ni(\mu\text{-}S_2C_2N_2)RuCp(PPh_3)_2][PF_6]$	65	B	61.7	4.2	1.92	2.2	2255	4.35	355
	$C_{74}F_6H_{60}N_2NiP_4RuS_2$		205°C	(61.5)	(4.15)	(1.81)	(2.05)			446
10.	$[(PPh_3)_2Ni(\mu\text{-}S_2C_2N_2)RuCp(AsPh_3)_2][BF_4]$	60	OB	61.7	4.3	1.9	2.3	2260	4.6	365
	$As_2BC_{74}F_4H_{60}N_2NiP_2RuS_2$		210°C	60.76	(4.10)	(1.79)	(2.03)			
11.	$[(PPh_3)_2Ni(\mu\text{-}S_2C_2N_2)RuCp(AsPh_3)_2][BPh_4]$	64	B	53.2	3.65	1.67	1.85	2340	4.5	360
	$As_2BC_{98}H_{80}N_2NiP_2RuS_2$		205°C	(52.87)	(3.56)	(1.56)	(1.74)			448
12.	$[(PPh_3)_2Ni(\mu\text{-}S_2C_2N_2)RuCp(AsPh_3)_2][ClO_4]$	70	YB	59.7	4.2	1.97	2.32	2310	4.6	355
	$As_2C_{74}ClH_{60}N_2NiO_4P_2RuS_2$		208°C	(60.22)	(4.09)	(1.77)	(2.01)			456
13.	$[(PPh_3)_2Ni(\mu\text{-}S_2C_2N_2)RuCp(AsPh_3)_2][PF_6]$	65	YB	59.2	3.8	1.86	2.1	2320	4.6	350
	$As_2C_{74}F_6H_{60}N_2NiP_2RuS_2$		204°C	(58.23)	(3.96)	(1.72)	(1.95)			460
14.	$[(PPh_3)_2Ni(\mu\text{-}S_2C_2N_2)RuCp(SbPh_3)_2][BF_4]$	65	B	56.9	4.1	1.8	2.1	2325	4.4	345
	$BC_{74}F_4H_{60}N_2NiP_2RuS_2Sb_2$		195°C	(57.31)	(3.90)	(1.69)	(1.91)			458
15.	$[(PPh_3)_2Ni(\mu\text{-}S_2C_2N_2)RuCp(SbPh_3)_2][BPh_4]$	63	YO	50.7	3.45	1.7	1.9	2315	4.4	348
	$BC_{98}H_{60}N_2NiP_2RuSb_2$		206°C	(50.23)	(3.41)	(1.48)	(1.66)			440
16.	$[(PPh_3)_2Ni(\mu\text{-}S_2C_2N_2)RuCp(SbPh_3)_2][ClO_4]$	64	OB	57.0	3.9	1.8	1.95	2335	4.6	345
	$C_{74}ClH_{66}N_2NiO_4P_2RuSb_2$		205°C	(56.83)	(3.86)	(1.67)	(1.90)			445
17.	$[(PPh_3)_2Ni(\mu\text{-}S_2C_2N_2)RuCp(SbPh_3)_2][PF_6]$	64	OB	55.1	3.86	1.75	2.05	2330	4.5	340
	$C_{74}F_6H_{60}N_2NiP_2RuS_2Sb_2$		208°C	(55.05)	(3.74)	(1.76)	(1.84)			456

O = Orange, YO = Yellow Orange, B = Brown, YB = Yellow Brown, OB = Orange Brown

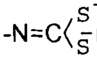
There could be four modes of reactions of $[Ni(cdc)_2]^{2-}$ or $[Ni(PPh_3)_2(cdc)]$ yielding complexes with structures A, B, C or D in Fig. 2.

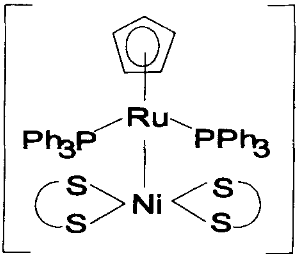
Similar structures could be drawn for $[Ni(cdc)(PPh_3)_2\text{-}RuCp(EPh_3)_2]^+$ also.

The diamagnetic nature of the complexes eliminates structure [A] which should exhibit paramagnetic behaviour. Presumably, the formation of the square pyramidal product [A] in which the species $[RuCp(EPh_3)_2]^+$ acts as a fifth coordinated ligand to the Ni^{2+} ion is inhibited because of the repulsion between the two positively charged species viz. Ni^{2+} and $[RuCp(EPh_3)_2]^+$ ions. The IR and the NMR spectral data of the complexes have been found to some extent useful in distinguishing the preferred structure [C] over [B] and [D].

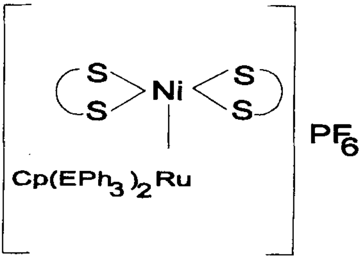
Infrared Spectra

The ligand cdc^{2-} exists in the following two resonating forms with predominant contribution from [E][1,5,11] in Fig. 3.

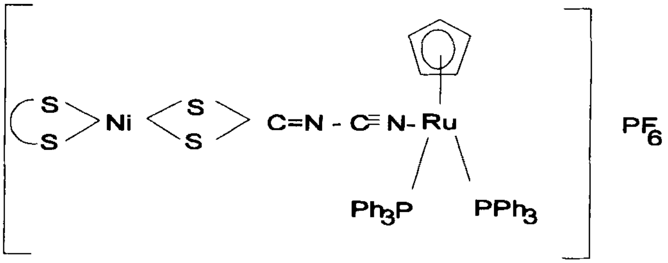
With a number of divalent metal ions complexes of the types $[M(cdc)_2)]^{2-}$ and $[M(PPh_3)_2(cdc)]$ have been isolated[11]. They exhibit bands in their IR spectra in the region 2160-2180 cm^{-1} assigned to ν (C ≡N) and in the region 700-1600 cm^{-1} due to normal modes of vibrations of the  $-N{=}C\langle^{S^{-}}_{S}$ moiety.[2,5,11,17-20]. Thus, $[Ni(cdc)_2]^{2-}$ displays bands at 2185 cm^{-1}, [ν(C≡N)], 1425 cm^{-1}, 1040-1028 cm^{-1}, 970 cm^{-1} due to normal modes having contributions from ν(C=N), ν(C--N), ν(C=S)[2,5,11,17-20] [with the 970 cm^{-1} band having a major contribution from ν(C=S)]. The characteristic bands in the spectra of all the isolated complexes are



[A]



[B]

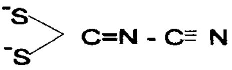


[C]

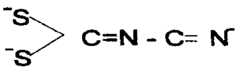
$[RuCp(EPh_3)_2]^+K^+[Ni(cdc)_2]^{2-}$

[D]

Fig. 2. Proposed Structures of the Complexes



[E]



[F]

Fig. 3. Resonating forms of the ligand cdc^{2-}

displayed in the same range. In structures [B] and [C] of the complexes $[RuCp(EPh_3)_2\ Ni(cdc)_2]^-$ one of the cdc^{2-} ligand molecules (coordinated with $[RuCp(EPh_3)_2]^+$) is infrared-spectroscopically different from the other cdc^{2-} molecule. It will result in splitting of most of the IR bands assigned to cdc^{2-} into two. The positions of one of the split bands ought to be almost the same as those found in the spectrum of $[Ni(cdc)_2]^{2-}$. In the spectra of all the synthesized complexes most of the cdc^{2-} bands are split and the positions of one of the two split bands coincides with those displayed by the $[Ni(cdc)]^{2-}$ spectrum; those of the second ones exhibited shifts (*Fig. 4*). *This observation confirms the possibility of the complexes* having structures [B] or [C] and is contrary to the one expected for the formation of addition compounds having the structure [D].

Generally, coordination to the nitrogen end of the cyano group raises the frequency of the ν(C≡N) band and this blue-shift suggests lack of π back bonding from the metal end to the CN group.[21,22] The appearance of a band at 2320 cm^{-1} assigned to the coordinated C=N stretching mode with its corresponding blue-shift of about 120 cm^{-1} with respect to that for uncoordinated ν(C≡N) is consistent with the formation of a C=N bonded complex (structure [C]). An increase of about 120 cm^{-1} in the frequency of the ν(C≡N) band is rather unexpected if one presumes bonding of ruthenium through $-CS_2$ sulfur (structure [B]). In addition, a weak band at 2195 cm^{-1} confirms the presence of an uncoordinated CN group in these complexes.

The shifts in the position of the bands observed in the range 700-1600 cm^{-1} are irregular, supposedly because of extensive mixing of various $-N=C\langle^{S^-}_{S}$-vibrational modes, exhibited in this range. However, the

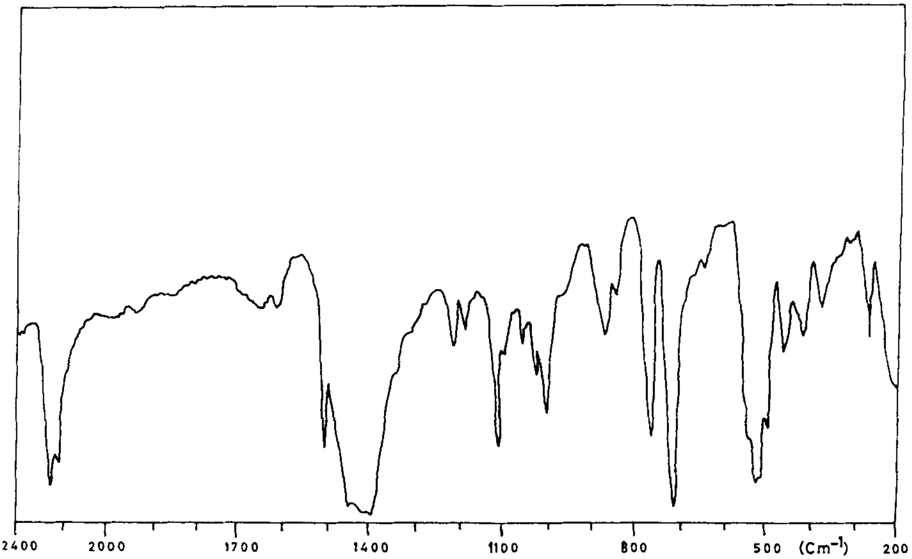


Fig. 4. IR Spectrum of K[(S$_2$C$_2$N$_2$) Ni (μ-S$_2$C$_2$N$_2$)RuCp(PPh$_3$)$_2$] (KBr)

shifts in the band positions given below, tentatively favour structure [C] over structure [D], because (a) the frequency of the band at 970 cm^{-1} arising from major contributions from C=S and (C-N) is increased to about 1000 cm^{-1} and (b) the frequency of the band at 1425 cm^{-1} assigned to ν (C=N) is lowered to 1385 cm^{-1}.

The cdc^{2-} bands in the spectra of the complexes [PPh$_3$)$_2$Ni(cdc)RuCp(EPh$_3$)$_2$]$^+$ exhibit no splitting as expected. However, the shift (~35 cm^{-1}) in the position of ν(C≡N) (~2220 cm^{-1}) in the complexes is lowered with respect to those obtained in [Ni(cdc)$_2$RuCp(EPh$_3$)$_2$]$^-$, possibly because of the presence of two π acid (PPh$_3$) ligand molecules bonded to the Ni^{2+} ion. In addition, analogous to the latter complexes, a blue-shift (~ +20 cm^{-1}) in the band position at 970

cm^{-1} and a red-shift (~ -25 cm^{-1}) in that of ν(C=N) at 1425 cm^{-1} support the ruthenium/NC interaction.

The bands due to the counter anions, PF_6, BF_4 and BPh_4, have been observed at their usual positions in their spectra.

^{1}HNMR Spectra

^{1}HNMR spectra (Fig. 5) of the complexes exhibit a singlet in the region δ 4.5 - 4.7 ppm for Cp protons, in addition to a complex pattern of phenyl proton signals of PPh_3 or its analogues between δ 6.8 ppm and 8.0 ppm. The singlet of the cyclopentadienyl protons around δ 4.6 ppm in these compounds is shifted towards low field (deshielding). The shift of Cp protons in these compounds relative to the starting chloro complex (δ 4.1)[16] indicates interaction of $[Ni(cdc)]^{2-}$ or $[Ni(PPh_3)_2cdc]$ with $[RuCp(EPh_3)_2]^+$ and a decrease of the electron density on the ruthenium center in the complex. Possibly, back bonding from the CN moiety to Ru(π) is absent in the complexes.

^{13}C NMR Spectra

The complexes $[Ni(cdc)_2RuCp(EPh_3)_2]^-$ exhibit a fairly well resolved ^{13}C NMR spectrum. The signal at δ 83.1 ppm is assigned to η^5-C_5H_5 carbons and the multiplet in the region of δ 128-136 ppm to phenyl carbons in EPh_3.

Other complexes exhibited poorly resolved ^{13}C spectra because of their poor solubility in the solvents.

Electronic Spectra

The colour of the complexes is orange brown. The positions of the maxima of the complexes are given in Table 1. The major spectral features

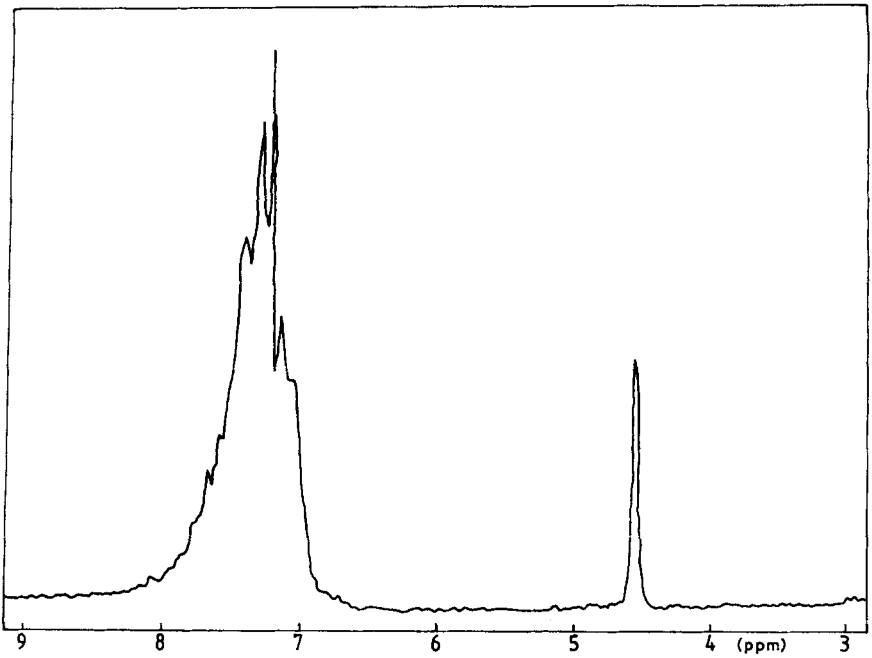


Fig. 5. ^{1}H NMR Spectrum of K[(S$_2$C$_2$N$_2$) Ni (μ-S$_2$C$_2$N$_2$) RuCp(PPh$_3$)$_2$] (CDCl$_3$)

of the other complexes are virtually similar. Furthermore, except for a couple of bands below 400 nm, the band positions of the complexes almost coincide with those present in the spectrum of $[Ni(cdc)_2]^{2-}$ indicating invariant ligand field symmetry in (square planar) $[Ni(cdc)_2]^{2-}$ and $[Ni(cdc)_2RuCp(EPh_3)_2]^+$ ions.[11] This is in conformity with the inference of magnetic data. The extra band at 369 nm may be assigned to the M-Cp charge transfer transition. However one ought to observe a weak intraligand cdc^{2-} band also around 400 nm, not displayed in the spectra of the complexes. Therefore, a possibility of a potential merging of the two bands giving an overall broad band around 369 nm exists.

CONCLUSION

Although the study reported here is somewhat incomplete with respect to the interpretation of electronic and NMR spectra, it is clear that the described compound results from mainly σ type of interaction of $RuCp(EPh_3)_2]^+$ and the pendant -N-C=N group of $[Ni(cdc)_2)]^{2-}$ with practically no back-bonding of T_2g Ru(II) and the π orbitals of C=N. Although from the available data the extent of interaction between the moieties could not be assessed, a weak bond between CN and Ru^{2+} is preferred over a stronger one.

EXPERIMENTAL

All the common chemicals were of Analar grade and were used as such without further purification. Synthetic reactions were carried out under an atmosphere of pure dry nitrogen. Solvents were dried and distilled under a blanket of deoxygenated nitrogen.

Starting materials were synthesized and purified according to the reported methods[11,16]. Melting points of the complexes were taken on a Fischer John's melting point apparatus. IR spectra were collected in KBr discs on a Perkin-Elmer-580 and Shimadzu-420 spectrophotometers. Shimadzu UV-160 and JEOL FX90 Q spectrophotometers were used to acquire the electronic and NMR spectral data of the complexes. Elemental analyses were performed by the Microanalytical Center of the Central Drug Research Institute, Lucknow.

Synthesis

The general procedure used for the synthesis of the complexes are as follows.

Preparation of K[(N$_2$C$_2$S$_2$)Ni(μ-S$_2$C$_2$N$_2$)RuCp(EPh$_3$)$_2$] . ½H$_2$O

In a typical reaction 0.150 g (0.65 mmol) of [Ni(cdc)$_2$)]$^{2-}$ in methanol (25 mL) was added dropwise to a stirred refluxing solution of [RuCp(EPh$_3$)$_2$Cl] (0.753 g, 1 mmol) in methanol (25 mL). A brownish microcrystalline compound immediately separated out. The suspension was cooled to room temperature. The brown compound was isolated by centrifugation, washed several times successively with methanol and ether. Recrystillyzation from CH$_2$Cl$_2$/petroleum ether yielded a pure complex which was dried *in vacuo* (yield 0.392 g, 80%).

Preparation of [(PPh$_3$)$_2$Ni(μ-S$_2$C$_2$N$_2$)RuCp(PPh$_3$)$_2$] PF$_6$

To a slurry of [Ni(PPh$_3$)$_2$(S$_2$C$_2$N$_2$)] (0.150 g, 0.214 mmol) in acetone/methanol 1:1 mixture (25 mL) was added a 25 mL solution of [RuCp(PPh$_3$)$_2$Cl (0.158 g, 0.217 mmol) in methanol (25 mL). The mixture was heated to reflux. After about 4 hours all the suspended material had dissolved to give a brown solution, which was cooled to room temperature. It was filtered to remove any undissolved solid impurities. The filtrate was evaporated to near dryness *in vacuo* and the solid mass was extracted with benzene. To the benzene extract (20 mL) ammonium hexaflourophosphate (ca. 0.160 g, 1.0 mmol) dissolved in methanol (25 mL) was added and the mixed solution was left for slow crystallization. The brown crystals thus obtained were separated by filtration, washed with methanol and diethyl either. It was dried *under vacuo* (yield 0.217 g, 65%).

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