A New Route for Synthesis of $[(\eta^5\text{-}C_5H_5)L_2Ru(\mu\text{-}CN)RuL'_2(\eta^5\text{-}C_5H_5)]^+X^-$ (L, L′ = PPh_3, $AsPh_3$ or $SbPh_3$; L_2, L'_2 = $PPh_2CH_2CH_2PPh_2$ or $PPh_2CH_2PPh_2$; X^- = BF_4^-, PF_6^- or BPh_4^-) Using 1,3,5-Triazine

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Abstract

$[(\eta^5\text{-}C_5H_5)L_2Ru(\mu\text{-}CN)RuL'_2(\eta^5\text{-}C_5H_5)]^+X^-$ (L, L′ = PPh_3, $AsPh_3$ or $SbPh_3$; L_2, L'_2 = dppe or dppm; X^- = BF_4, PF_6, BPh_4) have been synthesised by a novel and an unusual one pot reaction of $[Ru(\eta^5\text{-}C_5H_5)L_2X]$ (L = PPh_3, $AsPh_3$ or $SbPh_3$; L_2 = dppe or dppm; X = Cl, Br, H) with 1,3,5-triazine.

Introduction

Most of the properties of the aromatic, resonance stabilised 1,3,5-triazine, highly unstable in the presence of a base like H_2O, ROH or NH_3 are determined by the difference in the electron density on N and C atoms of the ring [1–8]. Its dissociation into HCN is highly improbable under the usual experimental conditions [1, 3]. The nucleophilicity of the nitrogen atoms could be utilised to provide a general route to synthesise trinuclear triazine bridged complexes by interaction with the metal complexes. When the reactions are carried out in OH containing solvents, a competitive hydrolysis reaction of 1,3,5-triazine may lead to formation of either a formato or/and formamidino complexes [3]. Under ordinary reaction conditions, cyano- or/and cyano-bridged bimetallic complexes are highly unexpected. In this communication we wish to report the first example where the triazine molecule has been completely dissociated. As a result of this 'dissociation' a novel and unusual one pot synthesis of $[(\eta^5\text{-}C_5H_5)L_2Ru(\mu\text{-}CN)RuL_2(\eta^5\text{-}C_5H_5)]^+X^-$ (L, L′ = PPh_3, $AsPh_3$ or $SbPh_3$; L_2, L'_2 = dppe or dppm; X^- = PF_6^-, BF_4^-, BPh_4^-) by the interaction of $[Ru(\eta^5\text{-}C_5H_5)L_2X]$ (L = PPh_3, $AsPh_3$ or $SbPh_3$; L_2 = dppe or dppm; X = Cl, Br or H) with 1,3,5-triazine in methanol has been developed which is reported here. Similar reactions were also carried out using $[Ru(bipy)_2Cl_2]$ where formation of the formamidino complexes of ruthenium has been suggested. These reactions have also been carried out in other –OH containing solvents.

The following example is representative of the reactions carried out. To a suspension of $[Ru(\eta^5\text{-}C_5H_5)L_2X]$ (L = PPh_3, $AsPh_3$ or $SbPh_3$; L_2 = dppe or dppm; X = Cl, Br or H) (0.13 mmol) in methanol (30 ml) was added the salt of a suitable anion ($NaBF_4$, NH_4PF_6 or $NaBPh_4$) (0.25 mmol) and 1,3,5-triazine (0.40 mmol). It was stirred for a couple of minutes and the subsequent mixture was heated to reflux for about 15 h. Initially the colour of the solution changed to deep red which finally faded to orange or a light yellowish orange colour and all the suspended material went into solution. The clear refluxed solution was concentrated on a water-bath whereupon bright yellow shining crystal separated out. (In some cases the yellow crystals were separated out from the solution during refluxing period. In those cases the solution was not concentrated.) The crystals were separated by centrifugation, washed several times with methanol, ether and dried in vacuum (yield, *c.* 60%). They analysed for $[(\eta^5\text{-}C_5H_5)L_2Ru(\mu\text{-}CN)RuL'_2(\eta^5\text{-}C_5H_5)]^+X^-$ (L, L′ = PPh_3, $AsPh_3$ or $SbPh_3$, $L_2L'_2$ = dppe or dppm; X^- = PF_6^-, BF_4^- or BPh_4^-) (Table 1).

The final crystalline products were confirmed by various physicochemical techniques (microanalysis, melting point (m.p.), mixed m.p., IR, ^1H, ^{31}P, ^{13}C NMR, electronic spectra, X-ray powder pattern) and compared with those of the authentic samples obtained from literature methods [9, 10]. These were further confirmed by carrying out reactions described in the literature [10].

Our initial experiments of the interaction of 1,3,5-triazine with other systems like $[Ru(bipy)_2X_2]$ (X = Cl) in alcohols suggested that the former gets initially hydrolysed with the formation of either buff or red coloured formato or formamidino complexes. These have been separated and analysed. We therefore speculate that the red coloured complex formed initially during the reaction is the formamido complex of $[Ru(\eta^5\text{-}C_5H_5)L_2]^+$ (L = PPh_3, $AsPh_3$ or $SbPh_3$; L_2 = dppe or dppm) coordinated as monodentate. The latter on refluxing dissociates

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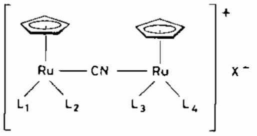
TABLE 1. Characterisation data of the complexes



Ligands[a]				Anion X^-	Colour, (melting point (°C)) Yield (%)	IR (cm^{-1})	η^5-C_5H_5 ^1H NMR		Analyses: found (calc.)			$^{31}P\{^1H\}$NMR	
L_1	L_2	L_3	L_4				1[c]	2[d]	C	H	N		
P	P	P	P	PF_6	Y[b], (178–180) 60	2080	4.19	4.05	63.8 (64.2)	4.22 (4.51)	0.87 (0.9)	47.3	41.6
P	P	P	P	BF_4	Y, (148) 56	2060	4.18	4.06	67.3 (67.5)	4.8 (4.7)	1.12 (0.93)	47.4	41.5
P	P	P	P	BPh_4	Y, (152) 61	2085	4.18	4.05	74.1 (74.4)	5.6 (5.2)	0.79 (0.81)	47.6	41.6
A	P	A	P	PF_6	Y, (175 59	2080	4.19	4.06	60.1 (60.7)	4.5 (4.27)	0.90 (0.85)	46.9	40.8
A	P	A	P	BF_4	Y, (153) 58	2080	4.18	4.05	62.6 (63.75)	4.7 (4.4)	1.21 (0.88)	47.0	40.6
A	P	A	P	BPh_4	Y, (155) 62	2090	4.20	4.07	71.0 (70.8)	4.7 (4.96)	0.72 (0.77)	46.8	40.7
A	A	A	A	PF_6	Y, (172–175) 60	2090	4.20	4.08	58.0 (57.6)	4.12 (4.05)	0.88 (0.81)		
A	A	A	A	BF_4	Y, (152) 58	2070	4.18	4.06	60.1 (60.4)	4.51 (4.2)	1.1 (0.8)		
A	A	A	A	BPh_4	Y, (149) 61	2080	4.18	4.07	67.9 (67.5)	4.3 (4.73)	0.69 (0.73)		
Sb	Sb	Sb	Sb	PF_6	Y, (176) 60	2085	4.36 4.22	4.10 4.08	52.8 (52.0)	3.7 (3.65)	0.78 (0.73)		
Sb	Sb	Sb	Sb	BF_4	Y, (157) 59	2070	4.33 4.21	4.09 3.9	54.1 (54.3)	3.51 (3.76)	1.2 (0.75)		
Sb	Sb	Sb	Sb	BPh_4	Y, (160) 61	2085	4.35 4.22	4.09 4.0	61.2 (61.5)	4.6 (4.3)	0.70 (0.67)		
dppe		dppe		PF_6	Y, >235 60	2110	4.35	4.17	57.2 (58.2)	4.53 (4.45)	1.16 (1.1)	82.1	79.7
dppe		dppe		BF_4	Y, (220) 60	2100	4.36	4.15	60.3 (60.9)	4.3 (4.67)	1.18 (1.12)	82.3	79.8
dppe		dppe		BPh_4	Y, (224) 58	2090	4.35	4.16	70.2 (70.9)	5.6 (5.29)	1.01 (0.95)	82.2	79.7
dppm		dppm		PF_6	Y, (172–175) 61	2090	4.30	4.16	57.1 (57.6)	4.6 (4.24)	1.2 (1.1)	81.8	78.1
dppm		dppm		BF_4	Y, (168) 57	2100	4.32	4.15	60.9 (60.3)	4.7 (4.45)	1.19 (1.15)	81.6	78.3
dppm		dppm		BPh_4	Y, (159) 60	2100	4.30	4.17	71.0 (70.6)	5.2 (5.1)	0.90 (0.96)	81.7	78.2

[a] P = PPh_3, A = $AsPh_3$, Sb = $SbPh_3$, dppe = 1,2-bis(diphenylphosphino)ethane, dppm = bis(diphenylphosphino)methane. [b] Y = yellow. [c] 1, Cp linked with Ru–CN–. [d] 2, Cp linked with Ru–NC–.

releasing one mole of NH_3 and the resulting product subsequently interacts with another mole of $[Ru(\eta^5\text{-}C_5H_5)L_2]^+$ forming a more stable CN bridged complex. The work on this and other reactions is under progress.

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